Quantum and Statistical Physics I

Tom Cohen, Jacob Cigliano, Hersh Kumar

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1 Formalism and Notation

1.1 Dimensional Analysis

This course uses units of $\hbar = k_B = c = 1$. Fixing units like this greatly simplifies calculations, but in order to actually compare theory to experiment, we need to replace our units afterwards. At first it seems like there is no unique way to do this — after all, if $\hbar = 1$, then I can always multiply by $\hbar$, $\hbar^2$, $\hbar^3$, etc. But we always fix our units in such a way that this is not an issue. In the SI system, there are 7 fundamental dimensionful units. We can set ratios of these units equal to whatever we choose. In practice, we make the 3 identifications above, as these are the ratios that will show up throughout the course. Making these identifications corresponds to redefining one of our fundamental units in terms of the others. But the remaining dimensionality must still add up. It is easiest to see this in terms of an example.

First, let's recall the units of each of the ratios we have normalized. The square bracket tells us that we are looking at the units of a number:

$$[\hbar] = [\text{angular momentum}] = \frac{(\text{mass})(\text{length})^2}{(\text{time})} = \frac{kg\,\ell^2}{s} \tag{1.1}$$

$$[k_B] = \frac{kg\,\ell^2}{s^2 K} \tag{1.2}$$

$$[c] = [\text{speed}] = \frac{\ell}{s} \tag{1.3}$$

Clearly the Boltzmann constant k_B is the odd one out. Since it includes a factor of temperature (K for Kelvin) in the denominator, it's best to just remember that it multiplies with temperature T to produce units of energy:

$$[k_B T] = \frac{kg\,\ell^2}{s^2} = (\text{mass})(\text{velocity})^2 = [\text{Energy}]$$

Let's move onto the example. Later in the course, we will derive the critical density

$$n_c = \frac{\xi\left(\frac{3}{2}\right)}{(2\pi)^{3/2}}\,(mT)^{3/2}$$

Can we replace the proper dimensionful constants in this term, even without seeing the derivation? The prefactor is dimensionless, so the only dimensionful terms are m (mass) and T (temperature). Try it yourself, knowing that density has dimensions of $[1/V] = 1/\ell^3$.

Okay, let's do it. We want to correct the units of mT from $kg\,K$ to $1/\ell^2$. When I raise this to 3/2 we will retrieve the proper units of $1/\ell^3$. First, we always want to get rid of the temperature first, so we put in a k_B:

$$[mk_B T] = \text{mass} \times \text{Energy}$$

Recall from undergraduate quantum that energy can be written $p^2/2m$, or (momentum)^2/mass. Thus

$$[mk_BT] = (\text{momentum})^2$$

Also recall that angular momentum is has units of length × momentum. Therefore

$$\left[\frac{mk_BT}{\hbar^2}\right] = \frac{1}{\ell^2}$$

We have found the proper conversion, and our final formula for the critical density is

$$n_c = \frac{\xi\left(\frac{3}{2}\right)}{(2\pi)^{3/2}}\left(\frac{mk_BT}{\hbar^2}\right)^{3/2}$$

As mentioned above, we have found the right answer without knowing anything about the derivation. This should be the first way you check your answers to homeworks and exams. If you can't get a dimensional equality by replacing some missing constants, something is wrong.

1.2 Vectors, Bases, and Operators

For a more in depth review of linear algebra and Dirac notation, see the first chapter of Sakurai's Modern Quantum Mechanics.

Let us consider the analogy of an arbitrary vector in 3D classical mechanics, for example velocity. The actual vector, pointing from one point to another, is physical & exists no matter how I describe it. However, the components of this vector depend on our choice of coordinate system/basis. Therefore we will use whatever coordinate system simplifies things.

Quantum mechanics is analogous. We have $|\psi\rangle$, a vector in an abstract complex vector space that gives the state of a system (this space is known as the Hilbert space of the system). We can always choose a convenient basis to describe its "components". $|\psi\rangle$ is known as a "ket" vector. The space of kets has the usual properties of a vector space:

- For every ket $|\psi\rangle$ there is a dual "bra" vector $\langle\psi|$.
- If $|\Phi\rangle = a\,|\phi\rangle$, then $\langle\Phi| = \langle\phi|\,a^*$, where the $*$ denotes complex conjugation.
- **Inner Products:** $\langle\alpha|\beta\rangle$ is an inner product. It is a bra-ket (bracket). The properties of an inner product are as follows:
  (1) $\langle\alpha|\beta\rangle^* = \langle\beta|\alpha\rangle$
  (2) $\langle\alpha|\alpha\rangle \in \mathbb{R}$
  (3) $\langle a\alpha|\beta\rangle = a\,\langle\alpha|\beta\rangle$. We can use this and (1) to show that $\langle\alpha|a\beta\rangle = a^*\,\langle\alpha|\beta\rangle$.
  (4) $\langle\alpha|\alpha\rangle \geq 0$. If $\langle\alpha|\alpha\rangle \neq 0$ then we can normalize $|\alpha\rangle$ by taking $|\tilde{\alpha}\rangle = \frac{|\alpha\rangle}{\sqrt{\langle\alpha||\alpha\rangle}}$ so that $\langle\tilde{\alpha}|\tilde{\alpha}\rangle = 1$.

In quantum mechanics the state of a system $|\psi\rangle$ is normalized: $\langle\psi|\psi\rangle = 1$. This is connected to the probability interpretation of quantum mechanics.

We introduce a complete, orthonormal basis, chosen for convenience. Our basis states are given by kets $|i\rangle$, with dual bras $\langle i|$. Orthonormality tells us that $\langle i|j\rangle = \delta_{ij}$, where δ_{ij} is the Kronecker delta. Completeness means that our basis vectors satisfy the aptly named "completeness relation",

$|\alpha\rangle = \sum_j c_j |j\rangle$. Orthonormality makes our basis easy to work with, specifically when taking inner products. For example,

$$\langle\alpha|\alpha\rangle = \sum_{i,j} \langle i| c_i^* c_j |j\rangle = \sum_{i,j} c_i^* c_j \delta_{ij} = \sum_i |c_i|^2$$

Completeness ensures that every ket in our space can be "decomposed" into the sum of basis kets. This introduces a representation of every ket in a complex vector space, with components given by the c_j. We can use these properties to represent the identity matrix in a useful way:

$$\sum_i |i\rangle \langle i|\alpha\rangle = \sum_{i,j} |i\rangle \langle i|j\rangle c_j = \sum_{i,j} |i\rangle \delta_{ij} c_j = \sum_i c_i |i\rangle = |\alpha\rangle$$

That is,

$$\mathbf{1} = \sum_i |i\rangle \langle i|$$

You can think of this operator as taking a vector α and giving its basis representation $\sum_j c_j |j\rangle$, by projecting onto the individual basis elements and summing.

This identity operator allows us to work with general operators in a much easier manner, and illustrates one of the most important techniques in this course: inserting a 1. Consider any operator A. Then

$$A = \mathbf{1}A\mathbf{1} = \sum_{i,j} |i\rangle \langle i|A|j\rangle \langle j| = \sum_{i,j} |i\rangle A_{ij} \langle j|$$

The complex numbers $A_{ij} = \langle i|A|j\rangle$ are called the matrix elements of A. They tell us the action of A on an arbitrary state vector, just from its action on the basis $|i\rangle$. Since quantum mechanics is almost entirely about the action of linear operators on states in our Hilbert space, this is an incredibly important decomposition. We can compute explicitly that

$$|\beta\rangle = A|\alpha\rangle = \sum_{i,j,k} |i\rangle A_{ij} \langle j|c_k|k\rangle = \sum_{i,j,k} A_{ij} c_k |i\rangle \delta_{jk} = \sum_i \left(\sum_j A_{ij} c_j\right) |i\rangle = \sum_i b_i |i\rangle \tag{1.4}$$

Where $b_i = \sum_j A_{ij} c_j$. From this, one can see that linear operators behave the same way as matrices in linear algebra. This provides the intuition behind why $A_{ij} = \langle i|A|j\rangle$ is known as a matrix element.

This analogy carries over to operator multiplication. Suppose that A, B are operators such that $C = AB$. Then

$$C_{ij} = \langle i|C|j\rangle = \langle i|AB|j\rangle = \langle i|A\mathbf{1}B|j\rangle = \sum_k \langle i|A|k\rangle \langle k|B|j\rangle = \sum_k A_{ik} B_{kj} \tag{1.5}$$

which is the usual definition of matrix multiplication from linear algebra.

The Hermitian adjoint $A^\dagger$ of an operator A is defined to act the same way on a bra that A acts on a ket:

$$A|\alpha\rangle = |\beta\rangle \quad \leftrightarrow \quad \langle\beta| = \langle\alpha| A^\dagger \tag{1.6}$$

From this, we can find a matrix definition of the Hermitian adjoint. If we let $A|j\rangle = |\beta\rangle$, then we can rewrite the matrix element A_{ij}:

$$A_{ij} = \langle i|A|j\rangle = \langle i|\beta\rangle$$

$$A_{ij}^{*} = \langle i|A|j\rangle^{*} = \langle i|\beta\rangle^{*} = \langle \beta|i\rangle = \langle j|\, A^{\dagger}\, |i\rangle = A_{ji}^{\dagger}$$

Therefore as a matrix, $A^{\dagger}$ is the complex conjugate transpose of A. It is easy to show that $(AB)^{\dagger} = B^{\dagger}A^{\dagger}$.

Projection operators are another important type of operator. We call O_p a projection operator if $O_p^2 = O_p$.[1] For example, let $O_p = |i\rangle\langle i| + |j\rangle\langle j|$. Then

$$\begin{aligned} O_p^2 &= (|i\rangle\langle i| + |j\rangle\langle j|)(|i\rangle\langle i| + |j\rangle\langle j|) && (1.7)\\ &= |i\rangle\langle i|i\rangle\langle i| + |i\rangle \cancelto{0}{\langle i|j\rangle} \langle j| + |j\rangle \cancelto{0}{\langle j|i\rangle} \langle i| + |j\rangle\langle j|j\rangle\langle j| && (1.8)\\ &= O_p && (1.9) \end{aligned}$$

Note that we use the orthonormality condition of our basis, $\langle i|j\rangle = \delta_{ij}$.

1.3 Tensor Product Spaces

In quantum mechanics, the state space of a composite system is built from the Hilbert spaces of its subsystems. If system A has Hilbert space $\mathcal{H}_A$ and system B has Hilbert space $\mathcal{H}_B$, then the joint system is described by the tensor product space

$$\mathcal{H}_{AB} = \mathcal{H}_A \otimes \mathcal{H}_B.$$

A basis for $\mathcal{H}_{AB}$ is given by tensor products of basis vectors: if $\{|a_i\rangle\}$ is an orthonormal basis of $\mathcal{H}_A$ and $\{|b_j\rangle\}$ is an orthonormal basis of $\mathcal{H}_B$, then

$$\{|a_i\rangle \otimes |b_j\rangle\}_{i,j}$$

forms an orthonormal basis of $\mathcal{H}_{AB}$. States of the joint system are linear combinations of such product states.

Tensor product structure distinguishes between *product states*, $|\psi_A\rangle \otimes |\psi_B\rangle$, and more general *entangled states*, which cannot be written as a simple product. Entanglement is a uniquely quantum feature with no classical analog, and it arises naturally from this construction.

Operators on the full system act on $\mathcal{H}_{AB}$ and can be written as linear combinations of tensor products of operators on the subsystems. For operators $A : \mathcal{H}_A \to \mathcal{H}_A$ and $B : \mathcal{H}_B \to \mathcal{H}_B$, their tensor product $A \otimes B$ acts on product states by

$$(A \otimes B)\big(\,|\psi_A\rangle \otimes |\psi_B\rangle\,\big) = (A\,|\psi_A\rangle) \otimes (B\,|\psi_B\rangle)$$

To describe an operator acting only on subsystem A, one takes $A \otimes I_B$, where I_B is the identity on $\mathcal{H}_B$. Similarly, an operator on subsystem B is written $I_A \otimes B$. For example, a Hamiltonian of the form

$$H = H_A \otimes I_B + I_A \otimes H_B$$

describes two noninteracting subsystems, while terms such as $V_{AB} = \sum_{\alpha} A_{\alpha} \otimes B_{\alpha}$ encode interactions between them.

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[1] This property is known as *idempotence*.

1.4 Density Matrices

As we have seen, the state of a quantum system is usually represented by a normalized vector $|\psi\rangle$ in a Hilbert space $\mathcal{H}$. This description is complete for *pure states*, but it is insufficient to describe statistical ensembles of quantum states or systems entangled with an environment. That is, how can we mathematically distinguish between actual superposition and a statistical mixture of states? For this purpose, the *density matrix* formalism is introduced.

Given a statistical ensemble of pure states $\{|\psi_i\rangle, p_i\}$, where $|\psi_i\rangle \in \mathcal{H}$ and p_i are classical probabilities with $\sum_i p_i = 1$, the density operator is defined as

$$\hat{\rho} = \sum_i p_i \, |\psi_i\rangle \langle\psi_i| \, . \tag{1.10}$$

If the system is in a single pure state $|\psi\rangle$, then

$$\hat{\rho} = |\psi\rangle \langle\psi| \, , \tag{1.11}$$

which satisfies $\hat{\rho}^2 = \hat{\rho}$ and $\mathrm{Tr}(\hat{\rho}^2) = 1$. In contrast, for a mixed state one has $\mathrm{Tr}(\hat{\rho}^2) < 1$ (Since each $p_i < 1$, $p_i^2 < p_i$ and $\sum_i p_i^2 < \sum_i p_i$).

The density operator $\hat{\rho}$ has the following properties:

1. Hermiticity: $\hat{\rho}^\dagger = \hat{\rho}$.
2. Positivity: $\langle\phi| \hat{\rho} |\phi\rangle \geq 0$ for all $|\phi\rangle \in \mathcal{H}$.
3. Normalization: $\mathrm{Tr}(\hat{\rho}) = 1$.

For an observable represented by a Hermitian operator A, the expectation value in the state ρ is

$$\langle A\rangle = \langle\psi|A|\psi\rangle = \mathrm{Tr}[\hat{\rho}A] \tag{1.12}$$

This generalizes the usual pure-state expression $\langle A\rangle = \langle\psi| A |\psi\rangle$.

For a bipartite system $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$, the state of subsystem A is obtained by the *partial trace* over subsystem B:

$$\hat{\rho}_A = \mathrm{Tr}_B(\hat{\rho}_{AB}) \tag{1.13}$$

This allows the study of subsystems entangled with larger environments.

The density matrix for a system with Hamiltonian $\hat{H}$ evolves according to the von Neumann equation:

$$\frac{d\hat{\rho}}{dt} = -i[\hat{H}, \hat{\rho}] \tag{1.14}$$

which is the analog of the Schrödinger equation for mixed states[2].

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[2] In the presence of dissipation or decoherence (or more generally, any coupling of the system to an environment), the evolution is more generally described by the Lindblad master equation.

2 Quantum Mechanics

2.1 Hermitian Operators

An operator H is Hermitian if $H^\dagger = H$. In quantum mechanics, all physical observables are associated with Hermitian operators due to several nice properties they have. The first is that the diagonal matrix elements of a Hermitian operator H are real:

$$\langle i|H|i\rangle = \langle i|H^\dagger|i\rangle^* = \langle i|H|i\rangle^* \tag{2.1}$$

In order for this equality to hold, $\langle i|H|i\rangle$ must be a real number. The general matrix elements of H satisfy $H_{ij}^* = H_{ji}$. The eigenvalues of a Hermitian matrix H are real, which we can show by first using the definition of an eigenvalue/eigenvector pair, and then applying the bra of the eigenvector from the left on both sides of the relation:

$$H|\psi_j\rangle = h_j|\psi_j\rangle \quad \Longrightarrow \quad \langle\psi_j|H|\psi_j\rangle = \langle\psi_j|h_j|\psi_j\rangle = h_j\langle\psi_j|\psi_j\rangle = h_j \tag{2.2}$$

And thus h_j must be real.

Finally, eigenvectors of H that have distinct eigenvalues are orthogonal. To show this, consider the matrix element $\langle\psi_j|H|\psi_i\rangle$, where both $|\psi_i\rangle$ and $|\psi_j\rangle$ are eigenvectors of H, with eigenvalues h_i and h_j respectively. If we first apply H to $|\psi_i\rangle$, we are left with:

$$\langle\psi_j|H|\psi_i\rangle = \langle\psi_j|h_i|\psi_i\rangle = h_i\langle\psi_j|\psi_i\rangle \tag{2.3}$$

If we instead apply H onto the bra $\langle\psi_j|$, we are left with:

$$\langle\psi_j|H|\psi_i\rangle = \langle\psi_j|h_j|\psi_i\rangle = h_j\langle\psi_j|\psi_i\rangle \tag{2.4}$$

The only way for both of these conditions to be true, under the assumption that the eigenvalues are distinct, $h_i \neq h_j$, is that $\langle\psi_j|\psi_i\rangle = 0$, the eigenvectors are orthogonal.

We can use this property to always construct an orthonormal basis out of eigenstates of a Hermitian operator. If degeneracies exist, we can use Gram-Schmidt in the space of degenerate states to orthogonalize them.

2.2 Unitary Operators

An operator is unitary if $U^\dagger U = UU^\dagger = \mathbf{1}$, or equivalently, $U^\dagger = U^{-1}$. Let us quickly discuss the important properties of unitary matrices. The first is that unitary operators preserve the norm of a vector. That is, if $|\beta\rangle = U|\alpha\rangle$, then $\langle\beta|\beta\rangle = \langle\alpha|U^\dagger U|\alpha\rangle = \langle\alpha|\alpha\rangle$. In the language of quantum mechanics, unitary operators map from physical states to other physical states, for reasons that will become more clear when we discuss measurement. Unitary operators also allow us to convert orthonormal bases to other orthonormal bases. Suppose we have an orthonormal basis spanned by vectors $\{|i\rangle, |j\rangle, \dots\}$. If we apply a unitary operator U to each of these vectors:

$$|i'\rangle = U|i\rangle \tag{2.5}$$
$$|j'\rangle = U|j\rangle \tag{2.6}$$
$$\vdots \tag{2.7}$$

Then the vectors $\{|i'\rangle, |j'\rangle, \dots\}$ form an orthonormal basis:

$$\langle i'|j'\rangle = \langle i|U^\dagger U|j\rangle \tag{2.8}$$
$$= \langle i|j\rangle \tag{2.9}$$
$$= \delta_{ij} \tag{2.10}$$

Finally, the eigenvalues of unitary operators are pure phases (have norm 1). Suppose we have a unitary U with eigenvector $|j\rangle$ and associated eigenvalue u_j, so $U|j\rangle = u_j|j\rangle$. Now looking at the orthonormality condition for $|j\rangle$:

$$1 = \langle j|j\rangle \tag{2.11}$$
$$= \langle j|U^\dagger U|j\rangle \tag{2.12}$$
$$= \langle j|u_j^* u_j|j\rangle \tag{2.13}$$
$$= u_j^* u_j \tag{2.14}$$

From this, we have that $u_j = e^{i\theta_j}$. We can also think of unitary operators as two different types of transformations, active and passive transformations. Active transformations transform states, while passive transformations leave states alone and transform operators.

- Active: $|i'\rangle = U|i\rangle$
- Passive: $\langle j'|A|i'\rangle = \langle j|U^\dagger AU|i\rangle = \langle j|A'|i\rangle$

Unitary transformations can be used to move a system into an eigenbasis: $AU|i'\rangle = A|i\rangle = a_i|i\rangle$. Clearly then $U^\dagger AU$ is diagonal: $\langle j'|U^\dagger AU|i\rangle = \langle j|A|i\rangle = a_i\langle j|i\rangle = a_i\delta_{ij}$.

2.3 Measurement

The state of the system is given by a normalized ket $|\psi\rangle$. Each physical quantity is associated with a Hermitian operator. Let us consider some operator A. We can choose an orthonormal eigenbasis in which A is diagonal:

$$A = \sum_i a_i|i\rangle\langle i| \tag{2.15}$$
$$= a_i P_i \tag{2.16}$$

Where we define the projector onto state $|i\rangle$, $P_i = |i\rangle\langle i|$.

The **Born Rule** states that if one measures A, after the measurement the system will be in one of the eigenstates of A. The probability of being in the eigenstate $|i\rangle$ is

$$\begin{aligned} \text{Prob}_i &= \langle\psi|P_i|\psi\rangle && (2.17)\\ &= \langle\psi|i\rangle\langle i|\psi\rangle && (2.18)\\ &= |\langle i|\psi\rangle|^2 && (2.19)\end{aligned}$$

The value of the quantity measured in that state is a_i, the associated eigenvalue of $|i\rangle$. The average value of A over numerous measurements, or the expectation value, is denoted by $\langle A\rangle$ and is defined as follows:

$$\langle A\rangle = \sum_i \text{Prob}_i\, a_i = \langle\psi|\sum_i a_i\,|i\rangle\langle i|\psi\rangle = \langle\psi|A|\psi\rangle \tag{2.20}$$

because A is diagonal in our choice of basis. But $\langle A\rangle = \langle\psi|A|\psi\rangle$ should not depend on using the basis in which A is diagonal, so the result holds in general.

We can also compute the expectation value using the decomposition of a state. Given a state $|\psi\rangle = \sum_i c_i\,|i\rangle$:

$$\begin{aligned} \langle A\rangle &= \sum_{i,j} c_j^*\,\langle j|A|i\rangle\, c_i && (2.21)\\ &= \sum_{i,j} c_j^* A_{ji} c_i && (2.22)\end{aligned}$$

Or equivalently, by defining a projection onto our state, $P_\psi = |\psi\rangle\langle\psi|$, we can leverage the definition of the expectation value in the density matrix formalism:

$$\begin{aligned} \langle A\rangle &= \text{Tr}\,[P_\psi A] && (2.23)\\ &= \sum_i \langle i|P_\psi A|i\rangle && (2.24)\\ &= \sum_{i,j} \langle i|P_\psi|j\rangle\langle j|A|i\rangle && (2.25)\\ &= \sum_{i,j} \langle i|\psi\rangle\langle\psi|j\rangle\langle j|A|i\rangle && (2.26)\\ &= \sum_{i,j} c_i c_j^* A_{ji} && (2.27)\end{aligned}$$

2.4 Commutators

The commutator of two operators A and B is denoted by $[A,B]$, and is defined as:

$$[A,B] = AB - BA \tag{2.28}$$

Similarly, we define the anticommutator of two operators as $\{A,B\}$:

$$\{A,B\} = AB + BA \tag{2.29}$$

From the definition of the commutator, we can state some easily proven identities:

- $[A, B] = -[B, A]$
- $[A, BC] = [A, B]C + B[A, C]$
- $[AB, C] = A[B, C] + [A, C]B$
- $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

The last identity is known as the Jacobi Identity. The key aspect of quantum mechanics is that commutators of important operators are nonzero, the canonical examples being position and momentum.

Two observables A and B are said to be compatible if they can be measured at the same time. In essence, this means that operators share eigenvalues. Let us consider the situation when they do not. Measuring A projects the state onto an eigenstate of A. Measuring B now projects the state onto an eigenstate of B. But this has destroyed the information about which eigenstate of A the system was in. To see what restrictions this places on A and B, we will first make our claim and then demonstrate how this allows simultaneous measurement.

Claim: If A and B are compatible then $[A, B] = 0$. Simultaneous eigenvalues means that there is an eigenbasis of states[1] $\{|i\rangle\}$ for which

$$A\,|i\rangle = a_i\,|i\rangle \qquad\qquad B\,|i\rangle = b_i\,|i\rangle$$

Given this shared eigenbasis, we can compute the action of B and then A:

$$\begin{aligned} AB\,|i\rangle &= Ab_i\,|i\rangle && (2.30)\\ &= b_i a_i\,|i\rangle && (2.31) \end{aligned}$$

Similarly, we can look at the action of A and then B:

$$\begin{aligned} BA\,|i\rangle &= Ba_i\,|i\rangle && (2.32)\\ &= a_i b_i\,|i\rangle && (2.33) \end{aligned}$$

Since these are the same, it must then be true that $AB - BA = 0$, and thus $[A, B]\,|i\rangle = 0$.

If $|\psi\rangle$ is not in an eigenstate of A then there is some uncertainty when we measure. How do we quantify this uncertainty? The standard statistical quantity is the variance, σ^2:

$$\begin{aligned} \sigma_A^2 &= \langle A^2\rangle - \langle A\rangle^2 && (2.34)\\ &= \langle (A - \langle A\rangle)^2\rangle && (2.35) \end{aligned}$$

If we are in an eigenstate of A, $A\,|i\rangle = a_i\,|i\rangle$, we can see that the variance is zero:

$$\begin{aligned} \sigma_A^2 &= \langle A^2\rangle - \langle A\rangle^2 && (2.36)\\ &= \langle i|A^2|i\rangle - \langle i|A|i\rangle^2 && (2.37)\\ &= a_i^2 - a_i^2 && (2.38)\\ &= 0 && (2.39) \end{aligned}$$

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[1] It is not always as simple as this, when either A or B have degenerate eigenvalues, things get more complicated, and the best you can aim for is block-diagonalization.

If A and B are incompatible, i.e. $[A, B] \neq 0$, then there is a generalized uncertainty relation bounding $\sigma_A^2 \sigma_B^2$ from below:

$$\sigma_A^2 \sigma_B^2 \geq \frac{1}{4} \left| \langle [A, B] \rangle \right|^2 \tag{2.40}$$

The derivation of this relation depends on the Cauchy-Schwarz inequality:

$$\langle \alpha | \alpha \rangle \langle \beta | \beta \rangle \geq \left| \langle \alpha | \beta \rangle \right|^2 \tag{2.41}$$

If we choose the following definitions of $|\alpha\rangle$ and $|\beta\rangle$:

$$|\alpha\rangle = (A - \langle \psi | A | \psi \rangle) |\psi\rangle \tag{2.42}$$

$$|\beta\rangle = (B - \langle \psi | B | \psi \rangle) |\psi\rangle \tag{2.43}$$

and apply the Cauchy-Schwarz inequality, we obtain the generalized uncertainty principle, Equation 2.40

If $[A, B] = i$, which is the case for $\hat{x}$ and $\hat{p}$, then we recover the famous Heisenberg Uncertainty Principle[2]:

$$\sigma_A^2 \sigma_B^2 \geq \frac{1}{4} \tag{2.44}$$

One cannot simultaneously measure both A and B with small uncertainty.

2.5 Two-Level Systems

Let us now consider the simplest quantum system, a 2-level system. This system has a basis of 2 states - $|\uparrow\rangle$ and $|\downarrow\rangle$, or $|a\rangle$ and $|b\rangle$, or $|0\rangle$ and $|1\rangle$. Some examples of two-level systems are a spin-$\frac{1}{2}$ system, or an occupied/unoccupied state, or a qubit in a quantum computer. Despite being physically different these are all mathematically the same.

In this system, we can write down 4 linearly independent Hermitian matrices, that will serve as a basis for Hermitian operators in the Hilbert space:

$$\mathbf{1} = |\uparrow\rangle \langle\uparrow| + |\downarrow\rangle \langle\downarrow| \tag{2.45}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{2.46}$$

$$\hat{\sigma}_x = |\uparrow\rangle \langle\downarrow| + |\downarrow\rangle \langle\uparrow| \tag{2.47}$$

$$= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{2.48}$$

$$\hat{\sigma}_y = -i |\uparrow\rangle \langle\downarrow| + i |\downarrow\rangle \langle\uparrow| \tag{2.49}$$

$$= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \tag{2.50}$$

$$\hat{\sigma}_z = |\uparrow\rangle \langle\uparrow| - |\downarrow\rangle \langle\downarrow| \tag{2.51}$$

$$= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{2.52}$$

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[2] Note that we are using natural units!

These matrices, known as the Pauli matrices, are traceless, Hermitian and involutory (hence unitary), and satisfy the (anti)commutation relations

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k, \qquad \{\sigma_i, \sigma_j\} = 2\delta_{ij}\mathbf{1} \tag{2.53}$$

Where ϵ_{ijk} is the Levi-Civita symbol. We can reproduce the standard angular momentum commutation relations by defining the spin operators $S_i = \sigma_i/2$. It is often useful to think of these matrices as a Cartesian vector.

$$\boldsymbol{n} \cdot \boldsymbol{\sigma} = n_i\sigma_i, \qquad ||\boldsymbol{n}|| = 1 \tag{2.54}$$

We can also write the most general operator in the Hilbert space as a linear combination of these 4 basis operators:

$$H = h_1\mathbf{1} + h_x\hat{\sigma}_x + h_y\hat{\sigma}_y + h_z\hat{\sigma}_z \tag{2.55}$$

Where $h_1, h_x, h_y, h_z \in \mathbb{C}$. Writing this in a more compact form:

$$H = h_1\mathbf{1} + \boldsymbol{h} \cdot \boldsymbol{\sigma} \tag{2.56}$$

Which we can write as a matrix:

$$H = \begin{bmatrix} h_1 + h_z & h_x + h_y \\ h_x - ih_y & h_1 - h_z \end{bmatrix} \tag{2.57}$$

Suppose we want to find the eigenvalues of this general operator. To do this, we can compute the trace and the determinant:

$$\mathrm{Tr}[H] = 2h_1 \tag{2.58}$$

$$\det H = h_1^2 - (h_x^2 + h_y^2 + h_z^2) \tag{2.59}$$

From these, we can write down the characteristic equation:

$$\lambda^2 - 2h_1\lambda + (h_1^2 - \boldsymbol{h}^2) = 0 \tag{2.60}$$

From this, we find that $\lambda = h_1 \pm |\boldsymbol{h}|$.

Now let us look at the link between the Pauli matrices and 3-dimensional rotations. Consider the following operator:

$$R(\phi) = \cos(\phi)\hat{\sigma}_x + \sin(\phi)\hat{\sigma}_y \tag{2.61}$$

$$= \begin{bmatrix} 0 & e^{-i\phi} \\ e^{i\phi} & 0 \end{bmatrix} \tag{2.62}$$

We can write down the most general unitary operator on our 2-level system:

$$U(\delta, \theta, \hat{n}) = e^{i\delta}e^{i\frac{\theta}{2}\hat{n}\cdot\boldsymbol{\sigma}} \tag{2.63}$$

$$= e^{i\delta}e^{i\frac{\theta}{2}(n_x\sigma_x + n_y\sigma_y + n_z\sigma_z)} \tag{2.64}$$

Note that the parameter δ here is just a phase, so really we can consider this operator to be parameterized by 3 variables, one that specifies the angle of the rotation, θ, and two independent variables that specify the axis, $\hat{n}$. We can also write this in terms of sines and cosines:

$$U(\delta, \theta, \hat{n}) = e^{i\delta}\left(\cos\left(\frac{\theta}{2}\right) + i\hat{n} \cdot \boldsymbol{\sigma} \sin\left(\frac{\theta}{2}\right)\right) \tag{2.65}$$

2.6 Continuous Variables

Let's now move into a continuous domain. We will start with systems corresponding to motion in one spatial dimension. Consider the operator $\hat{x}$ and consider an eigenstate of $\hat{x}$ with eigenvalue x':

$$\hat{x}\,|x'\rangle = x'\,|x'\rangle \tag{2.66}$$

How is the state $|x'\rangle$ normalized? For operators with discrete eigenvalues, we had that the overlap between any two eigenstates was a Kronecker delta:

$$\langle\alpha|\beta\rangle = \delta_{\alpha\beta} \tag{2.67}$$

The continuous analogue of this relation is to use the delta function:

$$\langle x''|x'\rangle = \delta(x' - x'').$$

Note that this means that the state cannot be normalized to unity: $\langle x'|x'\rangle = \delta(0) = \infty$.

We can construct the unit operator analogously to the discrete construction, by changing the sum over the discrete projectors to an integral over the projectors:

$$\mathbf{1} = \sum_n |n\rangle\langle n| = \int \mathrm{d}x'\ |x'\rangle\langle x'|$$

We can quickly demonstrate that this still behaves the way we expect the identity operator to behave:

$$\hat{\mathbf{1}}\,|x''\rangle = \int \mathrm{d}x'\ |x'\rangle\langle x'|x''\rangle \tag{2.68}$$

$$= \int \mathrm{d}x'\ |x'\rangle\,\delta(x' - x'') \tag{2.69}$$

$$= |x''\rangle \tag{2.70}$$

As expected, the operator leaves the original state unchanged.

Suppose we take the state $|\psi\rangle$, and insert the identity operator before it:

$$|\psi\rangle = \int \mathrm{d}x\ |x\rangle\,\underbrace{\langle x|\psi\rangle}_{\psi(x)} \tag{2.71}$$

We see that our spatial wavefunction $\psi(x)$ is equivalent to $\langle x|\psi\rangle$.

We can now make a table of the analogies between discrete and continuous systems:

Discrete Eigenvalues	Continuous Eigenvalues
$\hat{A}\,|j\rangle = a_j\,|j\rangle$	$\hat{x}\,|x'\rangle = x'\,|x'\rangle$
$\langle\psi_j|\psi_k\rangle = \delta_{jk}$	$\langle x'|x''\rangle = \delta(x'' - x')$
$\sum_k$	$\int \mathrm{d}x$
$|\psi\rangle = \sum_k c_k\,|k\rangle$	$|\psi\rangle = \int \mathrm{d}x\,\psi(x)\,|x\rangle$
$c_k = \langle k|\psi\rangle$	$\psi(x) = \langle x|\psi\rangle$
$\mathbf{1} = \sum_k |k\rangle\langle k|$	$\mathbf{1} = \int \mathrm{d}x\ |x\rangle\langle x|$

Figure 2.1: Analogies between discrete and continuous systems in quantum mechanics.

What about momentum? De Broglie realized that a state of good momentum has wavelength $\frac{2\pi}{p}$, or wave number $k = p$ (in units with $\hbar = 1$). Therefore

$$\langle x|p\rangle = Ce^{ipx}$$

The constant C is fixed by our normalization condition:

$$\begin{aligned}
\langle p'|p''\rangle &= \delta(p'' - p') && (2.72)\\
&= \langle p'|\hat{\mathbf{1}}|p''\rangle && (2.73)\\
&= \int \mathrm{d}x \, \langle p'|x\rangle \langle x|p''\rangle && (2.74)\\
&= C^2 \int \mathrm{d}x \, e^{-ip'x} e^{ip''x} && (2.75)\\
&= C^2 \int \mathrm{d}x \, e^{i(p''-p')x} && (2.76)\\
&= C^2 2\pi\delta(p'' - p') && (2.77)\\
& && (2.78)
\end{aligned}$$

From this, we can extract that $C = \frac{1}{\sqrt{2\pi}}$, which gives us that:

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi}} e^{ipx} \tag{2.79}$$

The momentum space wave function can be found in the same way we found the position space wavefunction, in Eqn. 2.71:

$$\begin{aligned}
|\psi\rangle &= \int \mathrm{d}p' \, |p'\rangle \langle p'|\psi\rangle \\
&= \int \mathrm{d}p' \, |p'\rangle \, \phi(p') && (2.80)
\end{aligned}$$

We can invert this equation to isolate $\phi(p)$:

$$\phi(p) = \int \mathrm{d}p' \, \phi(p') \, \underbrace{\langle p|p'\rangle}_{\delta(p-p')} \tag{2.81}$$

Let's see if we can connect the momentum and position space wavefunctions:

$$\begin{aligned}
|\psi\rangle &= \int \mathrm{d}p \, \phi(p) \, |p\rangle && (2.82)\\
&= \int \mathrm{d}p \, \phi(p) \Big(\int \mathrm{d}x \, |x\rangle \langle x| \Big) \, |p\rangle && (2.83)\\
&= \int \mathrm{d}p \, \phi(p) \int \mathrm{d}x \, |x\rangle \langle x|p\rangle && (2.84)\\
&= \int \mathrm{d}x \left(\frac{1}{\sqrt{2\pi}} \int \mathrm{d}p \, e^{ipx} \phi(p) \right) |x\rangle && (2.85)
\end{aligned}$$

In the final step, we insert Eqn. 2.79. We can now utilize Eqn. 2.71, Which gives us two relations:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int \mathrm{d}p \, e^{ipx} \phi(p) \tag{2.86}$$

$$\phi(p) = \frac{1}{\sqrt{2\pi}} \int \mathrm{d}x \, e^{-ipx} \psi(x) \tag{2.87}$$

You might recognize these as the Fourier and inverse Fourier transforms of our momentum and spatial wavefunctions.

Note that if $\langle\psi|\psi\rangle = 1$, then

$$\int \mathrm{d}x \, \psi^*(x)\psi(x) = \int \mathrm{d}p \, \phi^*(p)\phi(p) = 1 \tag{2.88}$$

We can easily prove this identity by inserting identities:

$$\begin{aligned} \langle\psi|\psi\rangle &= \langle\psi| \left(\int \mathrm{d}x \; |x\rangle \langle x| \right) |\psi\rangle && (2.89) \\ &= \int \mathrm{d}x \; \langle\psi|x\rangle \langle x|\psi\rangle && (2.90) \\ &= \int \mathrm{d}x \, \psi^*(x)\psi(x) && (2.91) \end{aligned}$$

and similarly for p, by inserting the identity in the momentum eigenbasis.

We can very quickly discuss the matrix elements of the position operator:

$$\begin{aligned} \langle x|\hat{x}|x'\rangle &= x' \langle x|x'\rangle && (2.92) \\ &= x'\delta(x - x') && (2.93) \end{aligned}$$

We see that the matrix elements of $\hat{x}$ are delta functions.

Let us now show that $\hat{p}$ is the generator of infinitesimal translations, that is:

$$e^{i\hat{p}x_0} |x'\rangle = |x' - x_0\rangle \tag{2.94}$$

To prove this, we can start from the left side of the relation, and use our go-to technique, inserting the identity twice:

$$\begin{aligned} e^{i\hat{p}x_0} |x'\rangle &= \left(\int \mathrm{d}x'' \; |x''\rangle \langle x''| \right) e^{i\hat{p}x_0} \left(\int \mathrm{d}p' \; |p'\rangle \langle p'| \right) |x'\rangle && (2.95) \\ &= \iint \mathrm{d}x'' \, \mathrm{d}p' \; |x''\rangle \langle x''|e^{i\hat{p}x_0}|p''\rangle \langle p''|x'\rangle && (2.96) \\ &= \iint \mathrm{d}x'' \, \mathrm{d}p' \; |x''\rangle \, e^{ip''x_0} \langle x''|p''\rangle \left(\frac{1}{\sqrt{2\pi}} e^{-ip''x'} \right) && (2.97) \\ &= \iint \mathrm{d}x'' \, \mathrm{d}p'' \, |x''\rangle \left(\frac{1}{\sqrt{2\pi}} e^{ip''x_0} e^{ix''p''} \right) \left(\frac{1}{\sqrt{2\pi}} e^{-ip''x'} \right) && (2.98) \\ &= \frac{1}{2\pi} \iint \mathrm{d}x'' \, \mathrm{d}p'' \, |x''\rangle \, e^{ip''(x_0 + x'' - x')} && (2.99) \\ &= \int \mathrm{d}x'' \, \delta(x_0 + x'' - x') \, |x''\rangle && (2.100) \end{aligned}$$

$$= |x' - x_0\rangle \tag{2.101}$$

In the third line, we have used the fact that $\langle p''|x'\rangle = \frac{1}{\sqrt{2\pi}} e^{-ip''x'}$, and the fact that $e^{i\hat{p}x_0}\,|p''\rangle = e^{ip''x_0}$. We have shown that $e^{i\hat{p}x_0}$ generates translations by x_0. What does $e^{-i\hat{p}x_0}\hat{x}e^{i\hat{p}x_0}$ do?

$$\begin{aligned}
\langle x'|\, e^{-i\hat{p}x_0}\hat{x}e^{i\hat{p}x_0}\,|x''\rangle &= |x' - x_0\rangle\,\hat{x}\,\langle x'' - x_0| \qquad (2.102)\\
&= (x'' - x_0)\delta((x' - x_0) - (x'' - x_0)) \qquad (2.103)\\
&= (x'' - x_0)\delta(x' - x'') \qquad (2.104)\\
&= \langle x'|\,\hat{x} - x_0\,|x''\rangle \qquad (2.105)
\end{aligned}$$

This holds for all x', x'', ergo, we have shown that $e^{-i\hat{p}x_0}\hat{x}e^{i\hat{p}x_0} = \hat{x} - x_0$. Let us expand the exponential of the momentum operator in a power series:

$$\begin{aligned}
e^{-i\hat{p}x_0}\hat{x}e^{i\hat{p}x_0} &= \left(\mathbf{1} - i\hat{p}x_0 - \frac{1}{2}\hat{p}^2x_0^2 + \ldots\right)\hat{x}\left(\mathbf{1} - i\hat{p}x_0 - \frac{1}{2}\hat{p}^2x_0^2 + \ldots\right) \qquad (2.106)\\
&= \hat{x} + x_0 i(\hat{x}\hat{p} - \hat{p}\hat{x}) - \frac{x_0^2}{2}(\hat{p}^2\hat{x} - 2\hat{p}\hat{x}\hat{p} + \hat{x}\hat{p}^2) + \ldots \qquad (2.107)\\
&= \hat{x} + x_0 i\,[\hat{x}, \hat{p}] - \frac{x_0^2}{2}\,[\hat{p}, [\hat{p}, \hat{x}]] + \ldots \qquad (2.108)
\end{aligned}$$

Now matching this expansion to the exact value, $\hat{x} - x_0$:

$$\hat{x} - x_0 = \hat{x} + x_0 i[\hat{x}, \hat{p}] - \frac{x_0^2}{2}\,[\hat{p}, [\hat{p}, \hat{x}]] + \ldots \tag{2.109}$$

From this, we can see that $i[\hat{x}, \hat{p}] = -1$, and $[\hat{p}, [\hat{x}, \hat{p}]] = 0$. The only way that both of these can be true is if $[\hat{x}, \hat{p}] = i$. This is the famous canonical commutation relation that follows directly from the de Broglie hypothesis.

Now let us see if we can find an explicit operator for $\hat{p}$. To do this, we will look at matrix elements of the momentum operator. Consider the matrix element $\langle x''|\hat{p}|x'\rangle$:

$$\begin{aligned}
\langle x''|\, e^{i\hat{p}x_0}\,|x'\rangle &= \langle x''|x' - x_0\rangle \qquad (2.110)\\
&= \delta(x'' - (x' - x_0)) \qquad (2.111)\\
& \qquad (2.112)
\end{aligned}$$

Now let us expand this delta function as a Taylor series:

$$\delta(x'' - (x' - x_0)) = \delta(x'' - x') + \delta'(x'' - x')x_0 + \frac{1}{2}\delta''(x' - x'')x_0^2 + \cdots \tag{2.113}$$

Now let us also Taylor expand the original matrix element, and equate the two series:

$$\langle x''|\mathbf{1} + i\hat{p}x_0 - \frac{1}{2}\hat{p}^2x_0^2 + \ldots|x'\rangle = \delta(x'' - x') + \delta'(x'' - x')x_0 + \frac{1}{2}\delta''(x' - x'')x_0^2 + \cdots \tag{2.114}$$

Looking at this equation term by term, based on the order of x_0:

$$\begin{aligned}
\langle x''|x'\rangle &= \delta(x'' - x') \qquad (2.115)\\
i\,\langle x''|\hat{p}|x'\rangle &= \delta'(x'' - x') \qquad (2.116)\\
-\frac{1}{2}\,\langle x''|\hat{p}^2|x'\rangle &= \frac{1}{2}\delta''(x' - x'') \qquad (2.117)
\end{aligned}$$

The first of these relations (2.115) is something we already knew, it's the orthonormality condition. Looking at the second equation (2.116), we can write out the derivative of the delta function:

$$\langle x''|\hat{p}|x'\rangle = -i\frac{\partial}{\partial x''}\delta(x''-x') \tag{2.118}$$

$$= -i\frac{\partial}{\partial x''}\langle x''|x'\rangle \tag{2.119}$$

$$= i\frac{\partial}{\partial x'}\langle x''|x'\rangle \tag{2.120}$$

Thus we have shown that:

$$\langle x''|\hat{p}|x'\rangle = \left\langle -i\frac{\partial}{\partial x''}x'' \middle| x' \right\rangle \tag{2.121}$$

$$= \left\langle x'' \middle| i\frac{\partial}{\partial x'} \middle| x' \right\rangle \tag{2.122}$$

We can now look at $\langle x|\hat{p}|\psi\rangle$ to arrive at a familiar result:

$$\langle x|\hat{p}|\psi\rangle = -i\frac{\partial}{\partial x}\langle x|\psi\rangle \tag{2.123}$$

$$= -i\frac{\partial}{\partial x}\psi(x) \tag{2.124}$$

Returning to the order x_0^2 term, (2.117), we have that

$$\langle x''|\hat{p}^2|x'\rangle = -\delta''(x'-x'') \tag{2.125}$$

$$= -\frac{\partial^2}{\partial x'^2}\langle x''|x'\rangle \tag{2.126}$$

$$= \frac{\partial^2}{\partial x''^2}\langle x''|x'\rangle \tag{2.127}$$

2.7 Quantum Dynamics

The key insight for dynamics of a system is that at all times, $\langle\psi(t)|\psi(t)\rangle = 1$. From this, we infer that the infinitesimal generator of time translations is Hermitian. This operator is the Hamiltonian.

Suppose we have $|\psi(t_0)\rangle$, and we want to find $|\psi(t)\rangle$. We claim that there must be some unitary operator U that evolves the system through time:

$$|\psi(t)\rangle = \hat{U}(t,t_0)\,|\psi(t_0)\rangle \tag{2.128}$$

This operator is the time evolution operator. We know that the state stays normalized, since unitary operators are norm preserving:

$$\langle\psi(t_0)|U^\dagger U|\psi(t_0)\rangle = \langle\psi(t)|\psi(t)\rangle \tag{2.129}$$

$$= 1 \tag{2.130}$$

To understand what $\hat{U}$ is, we will begin by stating our solution.

Claim

$$\frac{d\hat{U}(t,t_0)}{dt}U^\dagger(t,t_0) = -iH \tag{2.131}$$

Where H is some Hermitian operator.

To prove our claim, let us first note that

$$\frac{d}{dt}\left(\hat{U}^\dagger(t)\hat{U}(t)\right) = 0 \tag{2.132}$$

since the argument to the derivative is the identity operator, and is time-independent. We can now apply the product rule to the left side, and then rearrange terms:

$$\frac{d}{dt}[\hat{U}^\dagger]\hat{U}(t) + \frac{d}{dt}[\hat{U}]\hat{U}^\dagger = 0 \tag{2.133}$$

$$\frac{d}{dt}[\hat{U}^\dagger]\hat{U}(t) = -\frac{d}{dt}[\hat{U}]\hat{U}^\dagger \tag{2.134}$$

$$\tag{2.135}$$

If we take the Hermitian adjoint of both sides, we will note that $\frac{d}{dt}[\hat{U}]\hat{U}^\dagger$ is anti-Hermitian (the adjoint picks up a minus sign). This means that if we multiply by i, what we have is now Hermitian. This means that

$$\left(i\frac{d}{dt}[\hat{U}]\hat{U}^\dagger\right) = \hat{H} \tag{2.136}$$

Where $\hat{H}$ is some Hermitian operator. Now suppose we multiply by $\hat{U}$ on both sides:

$$\begin{aligned} i\frac{d}{dt}[\hat{U}]\hat{U}^\dagger\hat{U} &= \hat{H}\hat{U} \\ i\frac{d}{dt}[\hat{U}] &= \hat{H}\hat{U} \end{aligned} \tag{2.137}$$

Rearranging this equation slightly, we are left with exactly the statement in our claim:

$$\frac{d}{dt}\left[\hat{U}\right]\hat{U}^\dagger = -i\hat{H} \tag{2.138}$$

Now returning to Eqn. 2.137, let us multiply from the right by the ket vector $|\psi(t_0)\rangle$, and then apply the definition of $\hat{U}$ as a time evolution operator:

$$\hat{H}\hat{U}\,|\psi(t_0)\rangle = i\frac{\partial}{\partial t}\left(\hat{U}\,|\psi(t_0)\rangle\right) \tag{2.139}$$

$$\hat{H}\,|\psi(t)\rangle = i\frac{\partial}{\partial t}\,|\psi(t)\rangle \tag{2.140}$$

This is the Schrodinger equation, and we see that $\hat{H}$ must then be the Hamiltonian. We see that if we start with the basic assumption that states remain normalized as they time evolve, the Schrödinger equation is a natural consequence.

Suppose that the Hamiltonian is time independent, $\hat{H}(t) = \hat{H}(t_0) = \hat{H}$. In this case, we have a trivial solution, $\hat{U} = e^{-i\hat{H}t}$. One way to show that this is a suitable time-evolution operator is to expand both sides in series and then match them term by term. Another way to show this is to write the operator out in the energy eigenbasis:

$$\hat{U}(t) = \sum_k e^{-iE_k t} \left|\psi_k\right\rangle \left\langle\psi_k\right| \tag{2.141}$$

Where $\hat{H}\left|\psi_k\right\rangle = E_k \left|\psi_k\right\rangle$. Note that this equation is the time independent Schrodinger equation, energy eigenstates are stationary states in time.

Now consider the case where H is time dependent, $[\hat{H}(t), \hat{H}(t_0)] \neq 0$. Let us again begin by stating the solution:

$$\hat{U}(t, t_0) = \mathcal{T}\left(e^{-i\int_{t_0}^{t} H(t')\,dt'}\right) \tag{2.142}$$

Where $\mathcal{T}$ is known as the time ordered product. For two operators, the time ordered product is defined as follows:

$$\begin{aligned} \mathcal{T}[\hat{A}(t_1), \hat{B}(t_2)] &= \begin{cases} \hat{A}(t_1)\hat{B}(t_2) & \text{if } t_1 > t_2 \\ \hat{B}(t_2)\hat{A}(t_1) & \text{if } t_2 > t_1 \end{cases} && (2.143) \\ &= \hat{A}(t_1)\hat{B}(t_2)\Theta(t_1 - t_2) + \hat{B}(t_2)\hat{A}(t_1)\Theta(t_2 - t_1) && (2.144) \end{aligned}$$

Where Θ is the Heaviside step function, also sometimes known as the unit step function:

$$\Theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases} \tag{2.145}$$

Note that we can also define the Heaviside step function via the delta function:

$$\Theta(x) = \int_{-\infty}^{x} \delta(x')\,dx' \tag{2.146}$$

Note that in our case, we have an exponential of an operator, and so we Taylor expand the exponential to get the arguments to the time order product:

$$\mathcal{T}\left[\exp\left(-i\int_{t_0}^{t} \hat{H}(t')\,dt'\right)\right] = \mathcal{T}\left[\mathbf{1} - i\int_{t_0}^{t} \hat{H}(t')\,dt' + \frac{1}{2}\int_{t_0}^{t} \hat{H}(t')\,dt' \int_{t_0}^{t} \hat{H}(t'')\,dt'' + \ldots\right] \tag{2.147}$$

Looking at the quadratic term:

$$\mathcal{T}\left[-\frac{1}{2}\int_{t_0}^{t} \hat{H}(t')\,dt' \int_{t_0}^{t} \hat{H}(t'')\,dt''\right] = \left[\int_{t_0}^{t} dt'\,\hat{H}(t') \int_{t_0}^{t'} \hat{H}(t'')\,dt''\right] \tag{2.148}$$

We see that the factor of $\frac{1}{2}$ out front is killed off by the time ordering, we split the integral and note that both integrals must be the same. We can extend this argument, and claim that for N time orderings, we get $N!$ combinations of time orderings, which cancel the factor of $\frac{1}{N!}$ in the Taylor series. From this, we can show that

$$-i\frac{\partial}{\partial t}\mathcal{T}\left[\exp\left(-i\int_{t_0}^{t} dt''\hat{H}(t'')\right)\right] = \hat{H}\mathcal{T}\left[\exp\left(-i\int_{t_0}^{t} dt''\,\hat{H}(t'')\right)\right] \tag{2.149}$$

Which is proof that this $\hat{U}$ is indeed a solution of our time evolution equation:

$$\hat{H}\hat{U} = -i\frac{\partial}{\partial t}\hat{U} \tag{2.150}$$

Now let us make a connection to statistical mechanics, and we will show that if we consider time to be imaginary, and take some appropriate steps, we will derive the partition function.

Let us take the Fourier transform of our time evolution operator:

$$\int_{-\infty}^{\infty} dt\, e^{i\omega t}\hat{U}(t) \tag{2.151}$$

This should pick out the frequencies in the operator, which in this case are the energies of the eigenstates of the Hamiltonian.

$$\begin{aligned}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\hat{U}(t) &= \int_{-\infty}^{\infty} dt\, e^{i\omega t}\sum_n |n\rangle\langle n|\, e^{-iE_n t} & (2.152)\\ &= \sum_n |n\rangle\langle n| \int_{\infty}^{\infty} dt\, e^{i(\omega-E_n)t} & (2.153)\\ &= 2\pi\sum_n |n\rangle\langle n|\,\delta(\omega-E_n) & (2.154)\end{aligned}$$

Suppose we instead take the Fourier transform of the trace of the operator:

$$\int_{-\infty}^{\infty} dt\, e^{i\omega t}\mathrm{Tr}\left[\hat{U}(t)\right] = \sum_n \delta(\omega-E_n) \tag{2.155}$$

Suppose we now consider

$$\begin{aligned}\int_0^{\infty} e^{-\beta\omega}\, d\omega \int_{-\infty}^{\infty} dt\, e^{i\omega t}\mathrm{Tr}\left[\hat{U}\left(t\right)\right] &= \sum_n \exp(-\beta E_n) & (2.156)\\ &= \mathrm{Tr}\left[e^{-\beta\hat{H}}\right] & (2.157)\\ &= Z(\beta) & (2.158)\end{aligned}$$

We see that we have found the partition function from statistical mechanics. We pick out the frequencies, and then we weight the sum correctly, to recover the partition function. Suppose we instead do the ω integral first:

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, \left[\int_0^{\infty} d\omega\, e^{-\beta\omega}e^{-i\omega t}\right]\mathrm{Tr}\left[\hat{U}\left(t\right)\right] = \int_{-\infty}^{\infty} dt\, \frac{1}{\beta - it}\mathrm{Tr}\left[\hat{U}(t)\right] \tag{2.159}$$

This tells us that $Z(\beta)$ can be written as:

$$Z(\beta) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, \frac{1}{\beta - it}\mathrm{Tr}\left[\hat{U}(t)\right] \tag{2.160}$$

We have a classical statistical mechanics result that we derived from the time evolution operator.

If we compute this as a contour integral that has a pole at $t = -i\beta$, we find that

$$Z(\beta) = \mathrm{Tr}[\hat{U}(-i\beta)] \tag{2.161}$$

Note that all of this could have been done (far quicker) by setting $t = -i\beta$, and we would see that the trace of $\hat{U}(t)$ spits out the partition function.

2.7.1 Heisenberg Picture

Up to this point, we have been implicitly making a distinction on how we represent time dependence in quantum systems. The choice we have made is to have operators be fully time-independent, and have the states depend on time. For example, the time evolution has so far been represented as follows:

$$|\psi(t)\rangle = U(t, t_0)\,|\psi(t_0)\rangle \tag{2.162}$$

This is known as the **Schrödinger picture**. If we instead choose to have states be time-independent, and instead place the time dependence in the operators, we have what is known as the **Heisenberg picture**. In the Heisenberg picture, an operator at time t is given by the time evolution of the operator in the Schrödinger picture:

$$\hat{A}^H(t) = \hat{U}(t)^\dagger \hat{A}\hat{U}(t) \tag{2.163}$$

Changing pictures does not change any of the dynamics of the system, simply how we represent states and operators during time-dependent dynamics.

Given an operator in the Heisenberg picture, what is the equation of motion, that is, how does the operator change as a function of time? Looking at the definition of the operator at some time t (2.163), we can take a time derivative:

$$\frac{d}{dt}\hat{A}^H(t) = \frac{d}{dt}\left(\hat{U}^\dagger\right)\hat{A}\hat{U}(t) + \hat{U}^\dagger\hat{A}\frac{d}{dt}\left(\hat{U}(t)\right) \tag{2.164}$$

Now using Eqn. 2.137 to rewrite the derivatives of $\hat{U}$ and $\hat{U}^\dagger$, we have

$$\begin{aligned}
\frac{d}{dt}\hat{A}^H(t) &= i\left[\hat{U}^\dagger(t)\hat{A}\hat{H}^H(t)\hat{U}(t) - \hat{U}^\dagger(t)\hat{H}^H(t)\hat{A}\hat{U}(t)\right] && (2.165)\\
&= -i\left[\hat{U}^\dagger(t)\hat{A}\hat{U}(t)\hat{U}^\dagger(t)\hat{H}^H(t)\hat{U}(t) - \hat{U}^\dagger(t)\hat{H}^H(t)\hat{U}(t)\hat{U}^\dagger(t)\hat{A}\hat{U}(t)\right] && (2.166)\\
&= -i\left[\hat{A}^H(t), \hat{H}^H(t)\right] && (2.167)
\end{aligned}$$

In the case where the Hamiltonian is time independent, $\hat{H}^H(t) = \hat{H}$, and we are left with what is known as the Heisenberg equation of motion:

$$\frac{d}{dt}\hat{A}^H = -i\left[\hat{A}^H, \hat{H}\right] \tag{2.168}$$

Note that we have an analogous equation from classical mechanics:

$$\frac{dA}{dt} = [A, H]^{\mathrm{PB}} \tag{2.169}$$

Where PB indicates a Poisson bracket.

Let us do a simple example in the Heisenberg picture. Consider the Hamiltonian that represents the motion of a particle in one dimension:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x) \tag{2.170}$$

Now let us look at the Heisenberg equations of motion for $\hat{x}$ and $\hat{p}$:

$$\frac{d}{dt}\hat{x}^H = -i\left[\hat{x}^H, \hat{H}\right] \tag{2.171}$$

$$= \frac{\hat{p}}{m} \tag{2.172}$$

$$\frac{d}{dt}\hat{p}^H = -i\left[\hat{p}^H, \hat{H}\right] \tag{2.173}$$

$$= -V'(\hat{x}) \tag{2.174}$$

We can look at the 3 dimensional case:

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + V(\hat{\boldsymbol{x}}) \tag{2.175}$$

In this case, the only nonzero commutators between operators are:

$$[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i \tag{2.176}$$

Or more compactly:

$$[\hat{x}_i, \hat{p}_j] = i\delta_{ij} \tag{2.177}$$

We can look at the Heisenberg equation of motion for the momentum:

$$\frac{d}{dt}\hat{\boldsymbol{p}} = -i\left[\hat{\boldsymbol{p}}, \hat{H}\right] \tag{2.178}$$

$$= -\boldsymbol{\nabla} V(\hat{\boldsymbol{x}}) \tag{2.179}$$

These are just analogs of the classical Hamilton's equations of motion. From the Heisenberg equation of motion, we can derive the Ehrenfest theorem:

$$m\frac{d^2\langle\hat{x}\rangle}{dt^2} = \langle\hat{F}\rangle \tag{2.180}$$

Where F is the force.

Let us consider a simple system, a spin in an external magnetic field. In the absence of any other interactions, the spin will want to align with the field (minimizing the energy), but since there is no mechanism to remove energy from the system, it will precess instead. Let us begin with the Hamiltonian:

$$\hat{H} = -\boldsymbol{\mu} \cdot \boldsymbol{B} \tag{2.181}$$

Where $\boldsymbol{\mu} = g\mu_B\boldsymbol{S} = \frac{1}{2}g\mu_B\boldsymbol{\sigma}$, and g is the g-factor, while μ_B is the Bohr magneton. Rewriting the Hamiltonian in full:

$$\hat{H} = -\frac{1}{2}(g\mu_B\boldsymbol{B}) \cdot \boldsymbol{\sigma} \tag{2.182}$$

Let us (without loss of generality) assume that the external magnetic field is aligned in the z direction, $\boldsymbol{B} = B_0\hat{z}$. Let us simplify the constants in our problem by defining $\omega = g\mu_B B_0$. Thus we have that

$$\hat{H} = -\frac{1}{2}\omega\hat{\sigma}_z \tag{2.183}$$

Let us consider the time evolution of this system, which is given by the time evolution operator:

$$\hat{U}(t) = \exp\left(i\frac{1}{2}\omega\hat{\sigma}_z t\right) \tag{2.184}$$

Now note that, since $\hat{\sigma}_z$ commutes with the Hamiltonian, it's Heisenberg time evolution is constant, it will not shift in time. However, $\hat{\sigma}_x$ and $\hat{\sigma}_y$ do not commute with the Hamiltonian, and therefore will undergo evolution (giving rise to precession). To see this, let us look at $\hat{\sigma}_x^H(t)$:

$$\begin{aligned}\hat{\sigma}_z^H(t) &= \exp\left(-i\omega t\frac{\hat{\sigma}_z}{2}\right)\hat{\sigma}_x \exp\left(i\omega t\frac{\hat{\sigma}_z}{2}\right) && (2.185)\\ &= \cos(\omega t)\hat{\sigma}_x^H(0) - \sin(\omega t)\hat{\sigma}_y^H(0) && (2.186)\end{aligned}$$

Similarly, we can write out the evolution of $\hat{\sigma}_y^H$:

$$\hat{\sigma}_y^H(t) = \cos(\omega t)\hat{\sigma}_y^H(0) + \sin(\omega t)\hat{\sigma}_x^H(0) \tag{2.187}$$

Now that we have an understanding of how the three Pauli operators evolve in time, we can look at the spin vector evolution:

$$\begin{pmatrix}\hat{S}_x^H(t)\\ \hat{S}_y^H(t)\\ \hat{S}_z^H(t)\end{pmatrix} = \begin{pmatrix}\cos(\omega t) & -\sin(\omega t) & 0\\ \sin(\omega t) & \cos(\omega t) & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\hat{S}_x^H(0)\\ \hat{S}_y^H(0)\\ \hat{S}_z^H(0)\end{pmatrix} \tag{2.188}$$

This is just the classical precession of a spin! Alternatively (since we derived a fancy new equation of motion) we can do this with the Heisenberg equation of motion:

$$\begin{aligned}\frac{d}{dt}\hat{A}^H &= -i\left[\hat{A}^H, \hat{H}\right]\\ &= \frac{i\omega}{2}\left[\hat{A}^H, \hat{\sigma}_z\right] && (2.189)\end{aligned}$$

Writing these out for all three Pauli matrices:

$$\begin{aligned}\frac{d}{dt}\hat{\sigma}_x^H &= \frac{i\omega}{2}\left[\hat{\sigma}_x^H, \hat{\sigma}_z^H\right]\\ &= \omega\hat{\sigma}_y^H && (2.190)\\ \frac{d}{dt}\hat{\sigma}_y^H &= \frac{i\omega}{2}\left[\hat{\sigma}_y^H, \hat{\sigma}_z^H\right]\\ &= -\omega\hat{\sigma}_x^H && (2.191)\\ \frac{d}{dt}\hat{\sigma}_z^H &= \frac{i\omega}{2}\left[\hat{\sigma}_z^H, \hat{\sigma}_z^H\right]\\ &= 0 && (2.192)\end{aligned}$$

Solving these coupled differential equations gives us the exact same solution we found earlier (2.188).

Let us look at another system, this time the harmonic oscillator in 1 dimension, whose Hamiltonian is given by:

$$\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2 \tag{2.193}$$

We can introduce rescaled operators $\hat{\tilde{x}}$ and $\hat{\tilde{p}}$:

$$\hat{\tilde{x}} = \sqrt{m\omega}\hat{x} \tag{2.194}$$

$$\hat{\tilde{p}} = \sqrt{m\omega}\hat{p} \tag{2.195}$$

Note that these are still canonical variables:

$$\left[\hat{\tilde{x}}, \hat{\tilde{p}}\right] = i \tag{2.196}$$

Now we can rewrite the Hamiltonian:

$$\hat{H} = \frac{1}{2}\omega\left(\hat{\tilde{x}}^2 + \hat{\tilde{p}}^2\right) \tag{2.197}$$

We can compute the Heisenberg equations of motion for these two operators:

$$\frac{d}{dt}\hat{\tilde{x}}^H = -i\left[\hat{\tilde{x}}, \hat{H}\right] \tag{2.198}$$

$$= \omega\hat{\tilde{p}}^H \tag{2.199}$$

$$\frac{d}{dt}\hat{\tilde{p}}^H = -i\left[\hat{\tilde{p}}, \hat{H}\right] \tag{2.200}$$

$$= -\omega\hat{\tilde{x}}^H \tag{2.201}$$

The solutions to these coupled equations are the same as the classical solution:

$$\hat{\tilde{x}}^H(t) = \cos(\omega t)\hat{\tilde{x}}^H(0) + \sin(\omega t)\hat{\tilde{p}}^H(0) \tag{2.202}$$

$$\hat{\tilde{p}}^H(t) = -\sin(\omega t)\hat{\tilde{x}}^H(0) + \cos(\omega t)\hat{\tilde{p}}^H(0) \tag{2.203}$$

Things simplify if we rewrite this in terms of non-Hermitian variables $\hat{a}$ and $\hat{a}^\dagger$:

$$\hat{a} = \frac{1}{\sqrt{2}}\left(\hat{\tilde{x}} + i\hat{\tilde{p}}\right) \tag{2.204}$$

$$\hat{a}^\dagger = \frac{1}{\sqrt{2}}\left(\hat{\tilde{x}} - i\hat{\tilde{p}}\right) \tag{2.205}$$

Which we can always solve for the original variables:

$$\hat{\tilde{x}} = \frac{1}{\sqrt{2}}\left(\hat{a} + \hat{a}^\dagger\right) \tag{2.206}$$

$$\hat{\tilde{p}} = \frac{1}{\sqrt{2}}\left(\hat{a} - \hat{a}^\dagger\right) \tag{2.207}$$

Now we can rewrite our equations of motion using these new variables:

$$\hat{a}^H(t) = e^{i\omega t}\hat{a}^H(0) \tag{2.208}$$

$$\hat{a}^{\dagger\,H}(t) = e^{-i\omega t}\hat{a}^{\dagger\,H}(0) \tag{2.209}$$

Note that the equation of motion for $\hat{a}$ only depends on $\hat{a}$ at time zero, and similarly for the $\hat{a}^\dagger$ equation of motion. Also note the commutation relation between these two operators:

$$\left[\hat{a}, \hat{a}^\dagger\right] = 1 \tag{2.210}$$

Now let us consider a new operator, $\hat{N}$:

$$\begin{aligned} \hat{N} &= \hat{a}\hat{a}^\dagger \\ &= \frac{1}{2}\hat{\tilde{x}}^2 + \frac{1}{2}\hat{\tilde{p}}^2 + \frac{1}{2}i\left[\hat{\tilde{p}}, \hat{\tilde{x}}\right] \\ &= \frac{\hat{H}}{\omega} + \frac{1}{2} \end{aligned} \tag{2.211}$$

Rewriting this to solve for $\hat{H}$ in terms of $\hat{N}$:

$$\hat{H} = \omega\hat{N} + \frac{1}{2} \tag{2.212}$$

and we can also see that the Hamiltonian and our new operator commute:

$$\left[\hat{H}, \hat{N}\right] = 0 \tag{2.213}$$

If we can find eigenstates of $\hat{N}$, we have also found eigenstates of $\hat{H}$. We can also look at the commutation relations between $\hat{N}$ and $\hat{a}$ and $\hat{a}^\dagger$:

$$\left[\hat{a}, \hat{N}\right] = \left[\hat{a}, \hat{a}\hat{a}^\dagger\right] \tag{2.214}$$

$$= \hat{a}\left[\hat{a}, \hat{a}^\dagger\right] \tag{2.215}$$

$$= \hat{a} \tag{2.216}$$

$$\left[\hat{a}^\dagger, \hat{N}\right] = \left[\hat{a}^\dagger, \hat{a}\hat{a}^\dagger\right] \tag{2.217}$$

$$= \left[\hat{a}^\dagger, \hat{a}\right]\hat{a}^\dagger \tag{2.218}$$

$$= -\hat{a}^\dagger \tag{2.219}$$

Now let us consider a set of eigenstates of $\hat{N}$, labeled $|n\rangle$, with eigenvalues n:

$$\hat{N}|n\rangle = n|n\rangle \tag{2.220}$$

If we were to look at the expression $\hat{N}\hat{a}|n\rangle$:

$$\hat{N}\hat{a}|n\rangle = \hat{a}\hat{N}|n\rangle + \left[\hat{N}, \hat{a}\right]|n\rangle \tag{2.221}$$

$$= \hat{a}n|n\rangle - |n\rangle \tag{2.222}$$

$$= (n-1)\hat{a}|n\rangle \tag{2.223}$$

We see that $\hat{a}|n\rangle$ is an eigenvector of $\hat{N}$, with eigenvalue $n-1$. If that is the case, then we have that

$$\hat{a}|n\rangle = \eta|n-1\rangle \tag{2.224}$$

Where η is some normalization constant. To find η, we note that

$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle = |\eta|^2 \tag{2.225}$$

And then we note that $\hat{a}^\dagger\hat{a} = \hat{N}$:

$$\langle n|\hat{N}|n\rangle = n \tag{2.226}$$

And thus we have that $|\eta| = \sqrt{n}$. We can choose the phase to be real, so we have that

$$\hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle \tag{2.227}$$

Via an analogous derivation, one can find that

$$\hat{a}^\dagger\,|n\rangle = \sqrt{n+1}\,|n+1\rangle \tag{2.228}$$

These are the raising and lowering operators of the harmonic oscillator. What are the allowed values of n? To find out, let us first note that

$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle = |n|^2\,\langle n-1|n-1\rangle \geq 0 \tag{2.229}$$

So we have that $n \geq 0$.

Claim

n must be an integer.

To prove this, let us first note that if n *is* an integer, than we can apply $\hat{a}$ repeatedly, and the state will decrease by 1 for each application, until we hit $|0\rangle$, and $\hat{a}\,|0\rangle = 0$, and the chain will stop. Suppose that n is instead something like $\frac{15}{2}$. In this case, we can again repeatedly use $\hat{a}$ on our state, until we reach the state $|\frac{1}{2}\rangle$. Now note that

$$\left\langle\frac{1}{2}\middle|\hat{a}^\dagger\hat{a}\middle|\frac{1}{2}\right\rangle = -\frac{1}{2} \tag{2.230}$$

This cannot be allowed, since in Eqn. 2.229, we proved that $n \geq 0$. Thus we have a contradiction, n cannot be anything other than an integer.

We can construct any state via successive applications of $\hat{a}^\dagger$:

$$|n\rangle = \frac{1}{\sqrt{n!}}\left(\hat{a}^\dagger\right)^n|0\rangle \tag{2.231}$$

Recall that $\hat{H}$ and $\hat{N}$ commute (2.213), which means that eigenstates of $\hat{N}$ are also eigenstates of $\hat{H}$:

$$\hat{H}\,|n\rangle = \left(n + \frac{1}{2}\right)\omega\,|n\rangle \tag{2.232}$$

Which gives us the energy spectrum for the quantum harmonic oscillator.

We can look at matrix elements of our original operators, such as $\hat{x}$, by replacing them with their definitions in terms of the raising and lowering operators:

$$\langle n'|\hat{x}|n\rangle = \frac{1}{\sqrt{2m\omega}}\,\langle n'|\hat{a}+\hat{a}^\dagger|n\rangle \tag{2.233}$$

$$= \frac{1}{\sqrt{2m\omega}}\left[\sqrt{n}\delta_{n',n-1} + \sqrt{n+1}\delta_{n',n+1}\right] \tag{2.234}$$

As an example:

$$\langle 8|\hat{x}|7\rangle = \frac{\sqrt{8}}{\sqrt{2m\omega}} \tag{2.235}$$

2.7.2 Interaction Picture

This section is not present in Tom's lecture notes for the course, and is presented for those interested.

For a more thorough discussion of the interaction picture, see section 5.5.2 of Sakurai's Modern Quantum Mechanics.

So far we have discussed the Schrödinger and Heisenberg pictures of quantum mechanics, but there is another picture that will be useful next semester when we do time-dependent perturbation theory and scattering. This is known as the interaction picture. Recall that when doing perturbation theory we split our Hamiltonian into an analytically solvable part and a perturbing part:

$$H = H_0 + H'$$

The interaction picture is a sort of combination of the Schrödinger and Heisenberg pictures that has convenient properties when we decompose our Hamiltonian in this manner. We let

$$|\psi(t)\rangle_I = e^{iH_0t/\hbar} |\psi(t)\rangle_S$$

where the left gives the state ket in the interaction picture and the right gives the state ket in the Schrödinger picture. If we recall that $|\psi(t)\rangle_S = e^{-iHt/\hbar} |\psi(0)\rangle_S$ then we can write $|\psi(t)\rangle_I = e^{-iH't/\hbar} |\psi(0)\rangle_I$. That is, interaction picture state vectors evolve only due to the perturbative Hamiltonian, in contrast to Schrödinger picture state vectors, which evolve with the full Hamiltonian. What about operators? We set

$$A_I = e^{iH_0t/\hbar} A_S e^{-iH_0t/\hbar}$$

This makes it a little clearer what exactly we are doing. Our expectation values evolve like

$$\langle\psi(0)| e^{iHt/\hbar} A e^{-iHt/\hbar} |\psi(0)\rangle$$

In the Schrödinger picture we associate the unitary time evolution matrices with the state vectors. In the Heisenberg picture we associate them with the operator. In the interaction picture, we associate the perturbative half of the unitary time evolution matrices with the state vectors, and the analytic half with the operators.

But why is this useful? Let's derive the time evolution of a state vector in the interaction picture.

$$\begin{aligned} i\hbar\frac{\partial}{\partial t} |\psi(t)\rangle_I &= i\hbar\frac{\partial}{\partial t}\left(e^{iH_0t/\hbar} |\psi(t)\rangle_S\right) \\ &= -H_0 e^{iH_0t/\hbar} |\psi(t)\rangle_S + e^{iH_0t/\hbar} H_S |\psi(t)\rangle_S \\ &= e^{iH_0t/\hbar} H'_S e^{-iH_0t/\hbar} e^{iH_0t/\hbar} |\psi(t)\rangle_S \end{aligned}$$

That is,

$$i\hbar\frac{\partial}{\partial t} |\psi(t)\rangle_I = H'_I |\psi(t)\rangle_I \tag{2.236}$$

Of course, this is the expected result, since states in the interaction picture depend only on H'. We see that splitting apart the time evolution correspondence removes the dependency on H_0. We can "package" the time dependence on H_0 into H'_I in the interaction picture and then retrieve it by moving back to the Schrödinger or Heisenberg picture. This will be extremely useful for some of the lengthier results next semester, but for now it is just another example of how to manipulate the formalism of quantum mechanics for easier problem solving. The math is there to serve you, not the other way around.

2.7.3 Propagators

We have shown that we can evolve a state from time t' to time t via a time evolution operator:

$$|\psi(t)\rangle = \hat{U}(t,t')\,|\psi(t')\rangle \tag{2.237}$$

Suppose we now want to look at the wavefunction instead of the state. To do this, we can simply tack on the position bra from the left:

$$\langle x|\psi(t)\rangle = \langle x|\,\hat{U}(t,t')\,|\psi(t')\rangle \tag{2.238}$$

And we can insert the identity to get the spatial wavefunction at time t in terms of the wavefunction at time t':

$$\begin{aligned}\psi(x,t) &= \int dx'\ \langle x|\hat{U}(t,t')|x'\rangle\,\langle x'|\psi(t')\rangle & (2.239)\\ &= \int dx'\ \langle x|\hat{U}(t,t')|x'\rangle\psi(x',t') & (2.240)\end{aligned}$$

We define the propagator $K(x,t;x',t')$ as the matrix element:

$$K(x,t;x',t') = \langle x|\hat{U}(t,t')|x'\rangle \tag{2.241}$$

Which leaves us with:

$$\psi(x,t) = \int dx'\,K(x,t,;x',t')\,\psi(x',t') \tag{2.242}$$

Think of the propagator as the probability amplitude for the system to propagate from a point in space and time to another point in space and time.

We can also interpret this matrix element in terms of Greens functions. Consider the Schrödinger equation:

$$\left(-\frac{i}{2m}\frac{\partial^2}{\partial x^2} + V(x) - i\frac{d}{dt}\right)\psi(x,t) = 0 \tag{2.243}$$

Suppose we denote the highlighted term as $\mathcal{O}$. We now claim that the propagator has the following property:

Claim

$$\mathcal{O}K(x,t;x',t') = -i\delta(x-x')\delta(t-t') \tag{2.244}$$

subject to the condition that $K(x,t;x',t') = 0$ if $t < t'$.

If we assume this property of the propagator, K can be seen as the Greens function for the operator $\mathcal{O}$. To prove this, let us first enforce the condition that this is the "retarded" Green's function of $\mathcal{O}$ (meaning that we are propagating from the past to the future), by tacking on a Heaviside step function to the wavefunction in Eqn. 2.242:

$$\psi(x,t)\Theta(t-t') = \int dx'\,K(x,t;x',t')\,\psi(x',t') \tag{2.245}$$

Suppose we now apply $\mathcal{O}$ to both sides of this equation:

$$\mathcal{O}\,\psi(x,t)\Theta(t-t') = \int dx'\,\mathcal{O}K(x,t;x',t')\,\psi(x',t') \tag{2.246}$$

Now looking at the left side of the equation, we have to use the product rule because of the Heaviside step function (2.146):

$$\mathcal{O}\,\psi(x,t)\Theta(t-t') = -i\psi(x,t)\delta(t-t') \tag{2.247}$$

Now looking at the right side of Eqn. 2.246:

$$\int dx'\,\mathcal{O}K(x,t;x',t')\psi(x',t') = \int dx'\,\left(-i\delta(x-x')\delta(t-t')\psi(x',t')\right) \tag{2.248}$$

$$= -i\psi(x,t)\delta(t-t') \tag{2.249}$$

And thus both sides of Eqn. 2.246 are equivalent, and thus K is a Green's function for $\mathcal{O}$. Note that we have not made any claim about the propagator being the unique Greens function, just that it is one, so we will wave our hands very rapidly and claim it is unique.

2.7.4 The Feynman Path Integral

Let us consider the simplest Hamiltonian for a system propagating in space in 3 dimensions:

$$\hat{H} = \frac{\boldsymbol{p}\cdot\boldsymbol{p}}{2m} \tag{2.250}$$

Can we find the Greens function for this system? We can write down the propagator, by using the time evolution operator for a time-independent Hamiltonian:

$$K(\boldsymbol{x},t;\boldsymbol{x}',t') = \left\langle \boldsymbol{x}\middle|\exp\left(-i\frac{\boldsymbol{p}^2}{2m}(t-t')\right)\middle|\boldsymbol{x}'\right\rangle \tag{2.251}$$

If we now insert the identity in the momentum eigenbasis twice:

$$K(\boldsymbol{x},t;\boldsymbol{x}',t') = \left\langle \boldsymbol{x}\middle|\left(\int dp\,\left|p\right\rangle\left\langle p\right|\right)\exp\left(-i\frac{\boldsymbol{p}^2}{2m}(t-t')\right)\left(\int dp'\,\left|p'\right\rangle\left\langle p'\right|\right)\middle|\boldsymbol{x}'\right\rangle \tag{2.252}$$

$$= \iint dp\,dp'\,\langle \boldsymbol{x}|\boldsymbol{p}\rangle\exp\left(-i\frac{\boldsymbol{p}^2}{2m}(t-t')\right)\langle \boldsymbol{p}'|\boldsymbol{x}'\rangle\,\delta^3(\boldsymbol{p}-\boldsymbol{p}') \tag{2.253}$$

$$= \int \frac{d^3p}{(2\pi)^3}\exp\left(-i\boldsymbol{p}(\boldsymbol{x}-\boldsymbol{x}')-i\frac{\boldsymbol{p}^2}{2m}(t-t')\right) \tag{2.254}$$

We can solve this integral by completing the square in the exponential, and then using the standard Gaussian integral result. Note that this is the simplest Hamiltonian that we could write down, and the derivation of the propagator is still quite complicated.

As a graduate student, Richard Feynman rewrote quantum mechanics using the action, rather than the Hamiltonian, which is useful in relativistic cases (since the Hamiltonian is not Lorentz invariant, while the action is).

Claim

Suppose we want to compute the propagator between two points, from (x', t') to (x, t). We have some spatial path as a function of time between these two points, $x(t)$, and Feynman stated that the propagator can be defined as follows:

$$K(x,t;x',t') = c \sum_{\text{paths}} e^{iS_{\text{path}}} \tag{2.255}$$

Where c is some constant and S is the action, defined in terms of the Lagrangian $\mathcal{L}$:

$$S = \int_{t'}^{t} dt''\, \mathcal{L}(\dot{x}(t), x(t)) \tag{2.256}$$

Let us now take a look at a simple example. Consider the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V \tag{2.257}$$

Which has corresponding Lagrangian:

$$\mathcal{L} = \frac{1}{2}m\dot{x}^2 - V \tag{2.258}$$

Suppose we take our path, and partition it into infinitely many time steps, each Δt apart. We can look at the propagator between any two time steps, t_j and t_{j-1}:

$$K(x_j, t_j; x_{j-1}, t_{j-1}) = \langle x_j|\hat{U}(t_j, t_{j-1})|x_{j-1}\rangle \tag{2.259}$$

Let us take a closer look at $\hat{U}$:

$$\hat{U}(t_j, t_{j-1}) = \exp\left[-i\left(\frac{\hat{p}^2}{2m} + V\right)(t_j - t_{j-1})\right] \tag{2.260}$$

Now we can use the Suzuki-Trotter decomposition of this exponential:

$$\exp\left[-i\left(\frac{\hat{p}^2}{2m} + V\right)\Delta t\right] = \exp\left[-i\left(\frac{\hat{p}^2}{2m}\right)\Delta t\right]\exp\left[-iV\Delta t\right] + \mathcal{O}((\Delta t)^2) \tag{2.261}$$

Where $\Delta t = t_j - t_{j-1}$. Now let us discard the higher order terms (because who likes those), and we can rewrite our propagator:

$$K(x_j, t_j; x_{j-1}, t_{j-1}) = \left\langle x_j \middle| \exp\left[-i\left(\frac{\hat{p}^2}{2m}\right)\Delta t\right]\exp\left[-iV\Delta t\right] \middle| x_{j-1}\right\rangle \tag{2.262}$$

And then insert the identity in the momentum eigenbasis:

$$K(x_j, t_j; x_{j-1}, t_{j-1}) = \int dp\, \left\langle x_j \middle| \exp\left[-i\left(\frac{\hat{p}^2}{2m}\right)\Delta t\right] \middle| p\right\rangle \langle p|\exp\left[-iV\Delta t\right]|x_{j-1}\rangle \tag{2.263}$$

$$= \int dp\, e^{-i\frac{p^2}{2m}} e^{ip(x_j - x_{j-1})} V(x_{j-1}) e^{iV\Delta t} \tag{2.264}$$

Rearranging terms in the exponentials, completing the square in the exponential, and then utilizing the standard Gaussian integral, we are left with:

$$K(x_j, t_j; x_{j-1}, t_{j-1}) = \text{constant} \cdot e^{i(T-V)\Delta t} \tag{2.265}$$

Where T is shorthand for the kinetic energy. Now we note that $\mathcal{L} = T - V$:

$$\begin{aligned} K(x_j, t_j; x_{j-1}, t_{j-1}) &= \text{constant} \cdot e^{i\mathcal{L}\Delta t} && (2.266) \\ &= \text{constant} \cdot e^{iS} && (2.267) \end{aligned}$$

This was all for one time slice, a single path segment. If we want to compute the propagator from the initial point to the final point, across the entire path:

$$\langle x|\hat{U}(t,t')|x'\rangle = \int dx_1\, dx_2\, dx_3\, \ldots\, dx_n\, \langle x|\hat{U}(t,t_n)|x_n\rangle\, \langle x_n|\hat{U}(t_n,t_{n-1})|x_{n-1}\rangle \ldots \langle x_1|\hat{U}(t_1,t')|x'\rangle \tag{2.268}$$

This is essentially integrating over all paths between x and x'. Note that computing these integrals numerically is very difficult, due to the sign problem, caused by the cancelling out of the exponential terms.

The Sign Problem

In numerical studies of path integrals, observables are estimated by importance sampling with weight

$$\langle \mathcal{O} \rangle = \frac{\int \mathcal{D}\phi\, \mathcal{O}[\phi]\, e^{-S[\phi]}}{\int \mathcal{D}\phi\, e^{-S[\phi]}}.$$

If the Euclidean action $S[\phi]$ is real-valued and the partition function is finite, the Boltzmann factor $e^{-S[\phi]} > 0$ defines a proper probability distribution, enabling efficient Monte Carlo sampling. However, in many systems of interest — e.g. finite-density fermions or real-time dynamics — the sampling weight is complex or sign-indefinite. Phase/sign cancellations then yield an exponentially small average phase/sign, which causes exponentially bad signal-to-noise problems. This *Monte Carlo sign problem* is a central barrier to simulating a wide class of quantum systems numerically, and has in fact been found to be NP-hard, indicating that a *generic* solution is unlikely to be found.

2.8 Gauge Potentials in Electromagnetism

The Hamiltonian for a particle with charge q in an electromagnetic field is given by

$$H = \frac{(\boldsymbol{p} - q\boldsymbol{A})^2}{2m} + q\phi \tag{2.269}$$

In general, we can relate the magnetic and electric fields to the magnetic vector potential and scalar potential:

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A} \tag{2.270}$$

$$\boldsymbol{E} = -\nabla\phi - \frac{\partial \boldsymbol{A}}{\partial t} \tag{2.271}$$

Note that the Hamiltonian is **not** given in terms of $\boldsymbol{E}$ and $\boldsymbol{B}$, only $\boldsymbol{A}$ and ϕ. However, the classical Hamiltonian equation gives the Lorentz force law

$$m\ddot{x} = q(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B})$$

Note moreover that the canonical momentum $\boldsymbol{p}$ is **not** $m\boldsymbol{v}$ and does not correspond to the "mechanical momentum", but this is the **only** way to write a Hamiltonian formalism in terms of local objects. Also note that $\boldsymbol{A}$, ϕ are not of any physical significance: only $\boldsymbol{E}$ and $\boldsymbol{B}$ are.

Now let us consider the following transformations from $\boldsymbol{A}$ to $\boldsymbol{A}'$ and ϕ to ϕ':

$$\boldsymbol{A}(\boldsymbol{x},t) \to \boldsymbol{A}'(\boldsymbol{x},t) = \boldsymbol{A}(\boldsymbol{x},t) + \boldsymbol{\nabla}\Lambda(\boldsymbol{x},t) \tag{2.272}$$

$$\phi(\boldsymbol{x},t) \to \phi'(\boldsymbol{x},t) = \phi(\boldsymbol{x},t) - \frac{\partial\Lambda(\boldsymbol{x},t)}{\partial t} \tag{2.273}$$

If we make these transformations and insert them into Eqns. 2.270 and 2.271, we see that $\boldsymbol{E}$ and $\boldsymbol{B}$ are the same and hence $(\boldsymbol{A},\phi)$ and $(\boldsymbol{A}',\phi')$ are physically identical.

For the following discussion, let us consider the case of static $\boldsymbol{E}$ and $\boldsymbol{B}$ fields and static potentials:

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A} \tag{2.274}$$

$$\boldsymbol{E} = -\nabla\phi \tag{2.275}$$

and principally look at magnetic fields.

What happens if we make a gauge transformation $A \to A' = A + \nabla\Lambda$ in a quantum mechanical context?

Claim

This corresponds to a unitary transformation that leaves all matrix elements of $\hat{\boldsymbol{x}}$ unchanged but can alter $\hat{\boldsymbol{p}}$.

Note that the canonical momentum is not physical; it cannot be measured unless $\boldsymbol{A}$ is specified. To reflect this in quantum mechanics, we can upgrade the momentum and position to operators:

$$\hat{H} = \frac{(\hat{\boldsymbol{p}} - q\boldsymbol{A}(\hat{\boldsymbol{x}}))^2}{2m} + q\phi(\hat{\boldsymbol{x}})$$

Consider a unitary transformation of the form $\hat{U} = \exp(-iq\Lambda(x))$, a "position dependent phase". We can see that this will commute with the position operator, as well as any function of the position operator:

$$\hat{U}^\dagger \hat{x} \hat{U} = \hat{x} \tag{2.276}$$

$$\hat{U}^\dagger f(\hat{x}) \hat{U} = f(\hat{x}) \tag{2.277}$$

If we instead apply the transformation to the momentum operator:

$$\hat{U}^\dagger \hat{\boldsymbol{p}} \hat{U} = \hat{\boldsymbol{p}} - q\boldsymbol{\nabla}\Lambda \tag{2.278}$$

We see that this does not commute with the momentum operator. We can also apply the transformation to $\hat{\boldsymbol{p}} - q\boldsymbol{A}(\hat{x})$, the term in the Hamiltonian:

$$\hat{U}^\dagger \left(\hat{\boldsymbol{p}} - q\boldsymbol{A}(\hat{\boldsymbol{x}})\right) \hat{U} = \hat{\boldsymbol{p}} - q(\boldsymbol{\nabla}\Lambda + \boldsymbol{A}(\hat{\boldsymbol{x}})) \tag{2.279}$$

$$= \hat{\boldsymbol{p}} - q\boldsymbol{A}'(\hat{\boldsymbol{x}}) \tag{2.280}$$

Where we have inserted the gauge transformation $\boldsymbol{A}' = \boldsymbol{A} + \boldsymbol{\nabla}\Lambda$. We see that this unitary transformation is equivalent to our original gauge transformation, and corresponds to a spatially dependent phase.

The gauge principle is very deep. The entire Standard Model of particle physics is built on it (we derive theories that are invariant under local transformations).

Practically, we can choose whichever gauge makes our life easier. For example, consider a constant magnetic field $\boldsymbol{B} = B_0\hat{z}$. Then let $\boldsymbol{A}(x,y,z) = xB_0\hat{y}$. Hence

$$\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}, \qquad B_i = \epsilon_{ijk}\partial_j A_k, \qquad \boldsymbol{B} = B_0\hat{z}.$$

Let us look at the position space Schrödinger equation:

$$\frac{1}{2m}\left(-\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial z^2} + \left(i\frac{\partial}{\partial y} - qB_0 x\right)^2\right)\psi = E\psi. \tag{2.281}$$

Since there is no dependence on z or y, we can separate variables, and pull out the simpler solutions for those variables. This tells us that:

$$\psi \sim e^{ip_z z}e^{ip_y z} f(x) \tag{2.282}$$

Where we have quantum numbers p_x and p_y. We can now introduce the classical cyclotron frequency $\omega_0 = \frac{qB_0}{m}$ to rewrite our equation:

$$\left(\left(-\frac{1}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_0^2\left(x - \frac{p_y}{m\omega_0}\right)^2\right) + \frac{p_z^2}{2m}\right)f(x) = Ef(x) \tag{2.283}$$

We see that our Hamiltonian corresponds to a harmonic oscillator with x shifted by $\frac{p_y}{m\omega_0}$. Hence our energy spectrum is given by

$$E = \frac{p_z^2}{2m} + \omega_0\left(n + \frac{1}{2}\right) \tag{2.284}$$

with the first term corresponding to motion in the z direction, and the second to quantization in the x-y plane. Note that there is no dependence on p_y.

The energy levels of a quantum harmonic oscillator are known as Landau levels. Recall that in the classical picture of a particle in a constant magnetic field, motion in the x–y plane takes the form of circular orbits of arbitrary radius and period ω_0, centered about an arbitrary point. The Landau levels quantize these orbits. The orbits are highly degenerate, since each value of p_y is a distinct solution, but leaves the actual orbit unchanged. The degeneracy is associated with an arbitrary point in the x–y plane about which the particle orbits. For a crude understanding of this degeneracy, assume that the wavefunction is periodic in x, y in a box of length L_x, L_y:

$$\psi(x,y,z) = \psi(x + L_x, y + L_y, z)$$

The allowed p_y in the box are $p_y = \frac{2\pi n_y}{L_y}$ with $n_y \in \mathbb{N}^+$. But the harmonic oscillator has a center moved by $\frac{p_y}{m\omega_0} = \frac{2\pi n_y}{L_y m\omega_0}$. This has to be $\leq L_x$, so the degeneracy N, where N_y is the maximum number of independent levels, is

$$N_d = \frac{L_x p_y m\omega_0}{2\pi} = \frac{\text{Area} \cdot m\omega_0}{2\pi}$$

This is not strictly exact, but approximately valid when $N_d \gg 1$, or in a large box. This degeneracy is particularly relevant when looking at a system of charged fermions.

2.9 Identical Particles

The Hilbert space of a two particle state is spanned by the tensor product of one particles basis states:

$$|a, b\rangle = |a\rangle_1 \otimes |b\rangle_2$$

a and b include space, spin and other internal degrees of freedom. Similarly, three particle states are spanned by states of the form

$$|a, b, c\rangle = |a\rangle_1 \otimes |b\rangle_2 \otimes |c\rangle_3 .$$

Subtle question: What happens if one swaps two particles? Logically there are two possibilities:

1. You get a new state that is distinct from the old.
2. You get back the same state up to a possible phase.

Empirically, nature has chosen the second possibility. Let's introduce the operator P_{ij} which swaps the ith and jth particles in the state.

Claim

In quantum mechanics with identical particles, $P_{ij} |\psi\rangle = e^{i\theta} |\psi\rangle$. In 1D or 3D, $e^i\theta = \pm 1$, with $+1$ for bosons and -1 for fermions.

We have that $P_{ij} P_{ij} = \mathbf{1}$, so the possible eigenvalues are ± 1. But this is not rigorous. Why can't we have a phase times $\mathbf{1}$? It turns out this is possible in two dimensions. We call particles with this property "anyons". But what is special about 2D? In 2D there are two ways to swap particles:

1. Rotate the particles clockwise by π.
2. Rotate the particles counterclockwise by π.

These operations have opposite phases. But there is only one way to swap two particles in 1 or 3 dimensions. Anyons are important in effective degrees of freedom in condensed matter physics. But in our fundamental world of 3 spatial dimensions, there are only fermions and bosons.

2.9.1 Bosons and Fermions

Theorem 2.9.1. *Spin Statistics Theorem*

- *All particles with integer spins are Bosons.*
- *All particles with half-integer spins are Fermions.*

This result is known as the *spin-statistics theorem*, and is achieved by imposing causality, unitarity, and Lorentz invariance. Some examples of bosons include photons, pions, the hydrogen atom, and some examples of fermions include electrons, muons, neutrinos, and protons.

Even in the absence of interactions between particles, the statistics of identical particles can have a dramatic effect. Crudely, bosons “like” to be around other bosons, while fermions “hate” to. One illustrative analogy is “quantum coins”. Imagine you have a box inside of which there are two accessible single particle quantum states. One is called heads, “H”, and the other is called tails, “T”. Put two non-interacting particles into this box and many other boxes so that all possibilities are equally likely.

Now, pick up a box at random, reach in, pull out one particle, and determine the state it was in. The question is: Assuming that one removes a particle at random and determines that it is H, what is the probability that the other is also H? There are 3 cases:

1. Classical coins, or distinguishable particles. There are 4 possibilities: HH, HT, TH, TT. If the first particle removed is H we know that the state cannot be TT. Since we do not know which coin is removed, the box is twice as likely to be HH rather than HT or TH. Hence the probability of being in state HH is 50%, and in HT or TH is 25% each. That is, there is a 50% chance that the other coin is in state H.
2. Fermions. We only have one possibility, HT, or strictly $\frac{1}{\sqrt{2}}$(HT-TH). Therefore there is a 0% chance that the other coin is H. Again, fermions hate to be with fermions of the same kind.
3. Bosons. We now have three possibilities: HH, TT and HT $= \frac{1}{\sqrt{2}}$(HT+TH). We cannot have TT, and we are twice as likely to have HH than HT. Therefore there is a 66% chance that the other coin is in state H. Again, bosons love to hang out with bosons of the same species.

Another remarkable case: Put N bosonic coins in a box. If all possible boxes are equally likely, then it can be shown that in the large N limit, if one coin is removed from the box and found to be H, on average $\frac{2}{3}$ of the remaining coins are also H. Classically, this probability is 50%. Note that this effect occurs with <u>no</u> interactions between particles, this is simply from the intrinsic statistics! Note that under exchange of particles, *all* quantities are exchanged. Position, spin, “internal quantum numbers” (such as quark numbers), are all exchanged. Also note that spatial wavefunctions in 3 dimensions depend on orbital angular momentum L. They are symmetric for even L, and antisymmetric for odd L, where L is the orbital angular momentum. For two spin-$\frac{1}{2}$ particles, we can write out the 4 possible states. The first is the total angular momentum $S = 0$ state:

$$|S=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \tag{2.285}$$

And the 3 states with total angular momentum $S = 1$:

$$|S=1\rangle = |\uparrow\uparrow\rangle\,, |\downarrow\downarrow\rangle\,, \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \tag{2.286}$$

In general, the exchange (anti)symmetry of (fermionic)bosonic systems induces restrictions on the quantum numbers of physical states.

2.9.2 Slater Determinants

It is often useful to describe many body states in terms of single particle levels. There single particle levels should be an orthonormal set. Assume a discrete basis $|\psi_i\rangle$ with $\langle\psi_i|\,|\psi_j\rangle = \delta_{ij}$. Fermions must be in orthogonal single particle states. Let us construct a state where 1 particle is in $|a\rangle$ and the other is in $|b\rangle$:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left[|a\rangle^{(1)} \otimes |b\rangle^{(1)} - |b\rangle^{(1)} \otimes |a\rangle^{(1)}\right],$$

or in simpler notation, $|\psi\rangle = \frac{1}{\sqrt{2}}\left[|ab\rangle - |ba\rangle\right]$. What about 3 particles?

$$|\psi\rangle = \frac{1}{\sqrt{6}}\left[|abc\rangle + |cab\rangle + |bca\rangle - |cba\rangle - |bac\rangle - |acb\rangle\right]$$

These are the 6 possible one and two swap permutations of our three particles. While not all antisymmetric states are of this form, states of this form comprise a complete basis for antisymmetric states. For the case of an arbitrary number of fermions one can represent this as a determinant:

$$|\psi\rangle_N = \frac{1}{\sqrt{N!}}\begin{vmatrix} |a\rangle^{(1)} & |b\rangle^{(1)} & \cdots & |N\rangle^{(1)} \\ |a\rangle^{(2)} & |b\rangle^{(2)} & \cdots & |N\rangle^{(2)} \\ \vdots & & & \\ \vdots & & & \\ |a\rangle^{(N)} & |b\rangle^{(N)} & \cdots & |N\rangle^{(N)} \end{vmatrix}$$

The set of these Slater determinants form a basis for states of N fermions.

The Hartree-Fock approximations uses the “best” Slater determinant; i.e. the one that minimizes the energy. For example, consider a system of two non-interacting identical particles in plane waves in 1D. For simplicity work in center of mass coordinates so that each particle has equal and opposite moomentum when compared to the other particle. Also assume that we have either 2 spinless bosons, or 2 spin-up fermions. In this case, we have plane wave solutions:

$$\psi(x_1, x_2) = A\left[e^{ikx_1}e^{-ikx_2} \pm e^{ikx_2}e^{-ikx_1}\right] \tag{2.287}$$

Where the $+$ is the bosonic case, and the $-$ is the fermionic case. We can rewrite this as a single sinusoid for both cases:

$$\psi(x_1, x_2) = \begin{cases} A' \cos(k(x_1 - x_2)) & \text{Bosons} \\ A'' \sin(k(x_1 - x_2)) & \text{Fermions} \end{cases} \tag{2.288}$$

Now let us consider $\psi^*\psi$ for both of these cases:

$$\psi^*\psi = \begin{cases} c\cos^2(k(x_1 - x_2)) & \text{Bosons} \\ c\sin^2(k(x_1 - x_2)) & \text{Fermions} \end{cases} \tag{2.289}$$

Note that in the bosonic case, the probability is maximized when $x_1 - x_2 = 0$, the two bosons are stacked on top of each other, whereas in the fermionic case, the probability is 0 when $x_1 - x_2 = 0$, the fermions will never be stacked on top of each other (Pauli Exclusion Principle).

2.9.3 Degeneracy Pressure

Suppose we have a rectangular box with sides of length L_x, L_y, L_z. For simplicity assume periodic boundary conditions:

$$\psi(x,y,z) = \psi(x+L_x,y,z) = \psi(x,y+L_y,z) = \psi(x,y,z+L_z)$$

for large boxes ("thermodynamic limit"). The form of the boundary conditions should not matter and will retrieve the same result as the box approaches infinity. Suppose we toss a bunch of non-interacting fermions into the box. We will see that they exert a force on the walls of the box, simply via the properties of fermions. We can write out the single particle Hamiltonian:

$$H_1 = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \tag{2.290}$$

The wavefunction for a single particle will be of the form:

$$\psi_1(x,y,z) = \text{constant} \cdot \left[e^{ik_x x} e^{ik_y y} e^{ik_z z}\right] \tag{2.291}$$

The boundary conditions force momentum quantization in each direction:

$$k_i = \frac{2\pi n_i}{L_i} \qquad i \in \{x,y,z\} \tag{2.292}$$

Where $n_x, n_y, n_z \in \mathbb{Z}$.

At $T = 0$, all states with energy less than some Fermi cutoff E_0 are occupied:

$$E_{\boldsymbol{k}} = \frac{|\boldsymbol{k}|^2}{2m} \leq E_0 \tag{2.293}$$

How many such states are there? We can count them:

$$\begin{aligned} N(E_0) &= d \sum_{n_x,n_y,n_z} \Theta\left(E_0 - \left(\frac{k_x^2 + k_y^2 + k_z^2}{2m}\right)\right) && (2.294) \\ &= d \sum_{n_x,n_y,n_z} \Theta\left(E_0 - \frac{\left(\frac{n_x 2\pi}{L_x}\right)^2 + \left(\frac{n_y 2\pi}{L_y}\right)^2 + \left(\frac{n_z 2\pi}{L_z}\right)^2}{2m}\right) && (2.295) \end{aligned}$$

Here, d is a degeneracy factor that takes spin into account (in the case of spin-1/2 fermions such as electrons, $g = 2$). Now suppose the cutoff E_0 is large, so we take the continuum case of this summation:

$$N(E_0) = Vd \int \frac{d^3k}{(2\pi)^3} \Theta\left(E_0 - \frac{k_x^2 + k_y^2 + k_z^2}{2m}\right) \tag{2.296}$$

Now using the Jacobian, $d^3k = 4\pi k^2\, dk$:

$$\begin{aligned} N(E_0) &= Vd \int_0^{k_F} \frac{dk}{2\pi^2} \frac{k^2}{2m} && (2.297) \\ &= \frac{Vd}{2\pi^2} \frac{k_F^3}{3} && (2.298) \end{aligned}$$

$$= \frac{V d k_F^2}{6\pi^2} \tag{2.299}$$

Where we have defined the Fermi momentum, $k_F = \sqrt{2mE_0}$. In general, we have that

$$\sum_{n_x,n_y,n_z} \Theta(E_0 - E) = V \int_0^{k_F} \frac{dk\, k^2}{2\pi^2} \tag{2.300}$$

We now have an expression for the number of states filled, which we can write in terms of the number density:

$$n = \frac{k_F^2 d}{6\pi^2} \tag{2.301}$$

We can now compute the total amount of energy needed to kick out all of the fermions in the system:

$$E_{\text{total}} = Vd \int_0^{k_F} \frac{dk}{2\pi^2} k^2 \frac{k^2}{2m} \tag{2.302}$$

$$= \frac{3}{5} N d \frac{k_F^2}{2m} \tag{2.303}$$

Suppose we now wanted to compute the pressure. Recall that at 0 temperature, $P = \frac{\partial E}{\partial V}$. How do we take this derivative? We note that k_F is implicitly related to the volume, so we can rewrite it and go through with the derivative, and we find the degeneracy pressure that we see in astronomy textbooks.

3 Statistical Quantities

Historically thermodynamics was developed in the first half of the 19th century (Carnot knowledge). The concept of entropy developed in thermodynamics around this time. During the mid-to-late 19th century, statistical mechanics developed in order to describe thermodynamics in terms of microscopic degrees of freedom, such as atoms and molecules. This work was mainly carried out by Maxwell, Boltzmann and Gibbs. Around this time the existence of atoms and molecules was still controversial, so statistical mechanics was contextualized by classical mechanics. The key notion was that entropy in thermodynamics was the natural logarithm of the number of accessible “microstates”:

$$S = k \ln W \tag{3.1}$$

The concept of a classical microstate is subtle. Instead, we will introduce entropy via von Neumann’s entropy of a quantum system.

Let $\hat{\rho}$ be a density matrix. The von Neumann entropy of $\hat{\rho}$ is given by

$$S = -\operatorname{Tr}\left[\hat{\rho} \ln \hat{\rho}\right] \tag{3.2}$$

Why is the von Neumann entropy a sensible measure of “disorder”? The first reason we choose the von Neumann entropy is that the entropy of a pure state $|\psi\rangle \langle\psi|$ is zero. The second reason is that this is the only measure of disorder which is extensive, as the thermodynamic entropy is.

To prove the extensivity of the von Neumann entropy, suppose that we have 2 uncorrelated systems, $\hat{\rho}^{\text{full}} = \hat{\rho}^{(1)} \otimes \hat{\rho}^{(2)}$. Let’s move to the diagonal basis of each, and compute the von Neumann entropy of each:

$$\hat{\rho}^{(1)} = \sum_j p_j^{(1)} |j\rangle^{(1)}\, {}^{(1)}\langle j| \qquad \hat{\rho}^{(2)} = \sum_k p_k^{(2)} |k\rangle^{(2)}\, {}^{(2)}\langle k| \tag{3.3}$$

$$S_1 = \sum_j -p_j^{(1)} \ln p_j^{(1)} \qquad S_2 = \sum_k -p_k^{(1)} \ln p_k^{(1)} \tag{3.4}$$

We use the tensor product basis for the combined system. The probability that the state is in both $|j\rangle^{(1)}$ and $|k\rangle^{(2)}$ is $p_{(jk)} = p_j^{(1)} p_k^{(2)}$. Hence

$$\hat{\rho} = \sum_{j,k} p_j^{(1)} p_k^{(2)} \left(|j\rangle^{(1)} \otimes |k\rangle^{(2)}\right) \left({}^{(1)}\langle j| \otimes {}^{(2)}\langle k|\right) \tag{3.5}$$

We can then compute the total von Neumann entropy of the system:

$$\begin{aligned} S^{\text{total}} &= -\sum_{j,k} p_{(jk)} \ln(p_{(jk)}) && (3.6)\\ &= -\sum_{j,k} p_j^{(1)} p_k^{(2)} \ln(p_j^{(1)} p_k^{(2)}) && (3.7) \end{aligned}$$

$$= -\sum_{j,k} p_j^{(1)} p_k^{(2)} \left(\ln(p_j^{(1)}) + \ln(p_k^{(2)})\right) \tag{3.8}$$

$$= \left(-\sum_j p_j^{(1)} \ln p_j^{(1)} \sum_k p_k^{(2)}\right) + \left(-\sum_k p_k^{(2)} \ln p_k^{(2)} \sum_j p_j^{(1)}\right) \tag{3.9}$$

$$= S_1 + S_2 \tag{3.10}$$

Where in the second to last line, we note that $\sum_k p_k^{(2)}$ and $\sum_j p_j^1$ are both 1.

We have shown that the definition of von Neumann entropy is additive across uncorrelated subsystems and is a measure of disorder. That is, it is a sensible measure of entropy, and we set $S_\rho = -\operatorname{Tr}[\hat{\rho} \ln \hat{\rho}]$. This depends on the mixed state of interest. Suppose that I now wish to find the mixed state that maximizes S_ρ subject to the constraint that my average energy is fixed to some value.

Claim

The density matrix that maximizes S_ρ given fixed average energy is the one that puts the system into thermal equilibrium.

Systems tend to become as disordered as possible empirically. To find the mixed state that does this is equivalent to finding the density matrix that does this. We vary $\hat{\rho}$ and find the $\hat{\rho}$ such that $\hat{\rho} + \delta\hat{\rho}$ makes no first order change in S subject to the fixed energy constraint. The trick is to introduce a Lagrange multiplier along the fixed energy contour. We will call this Lagrange multiplier $-\beta$:

$$\delta\left[\langle -\beta E\rangle + S\right] = 0 = \delta\left[\beta\left(E - \frac{1}{\beta}S\right)\right] \tag{3.11}$$

Now define

$$F(\beta, \hat{\rho}) \equiv \langle E\rangle - \frac{1}{\beta} S_\rho \tag{3.12}$$

In equilibrium this is the free energy. The condition to maximize (extremize) S subject to fixed $\langle E\rangle$ is equivalent to minimizing F with fixed β.

$$\delta F = \delta\left(\operatorname{Tr}\left[\hat{\rho}\left(\hat{H} + \frac{1}{\beta}\ln(\hat{\rho})\right)\right]\right) = 0 \tag{3.13}$$

Claim

Equation 3.13 is solved when $\rho = \rho_0 = Z^{-1} e^{-\beta H}$ with $Z = \operatorname{Tr}[e^{-\beta \hat{H}}]$.

That is the Boltzmann distribution! To prove this, we need to show invariance under first order shifts in ρ. To begin, we construct some unitary $\hat{U}$ that transforms the state $\hat{\rho}$ to $\hat{\rho}_d$:

$$\hat{\rho} = \hat{U}^\dagger \hat{\rho}_d \hat{U} \tag{3.14}$$

Since $\hat{U}$ is unitary, we can write it as the exponential of some Hermitian matrix $\hat{G}$:

$$\hat{U} = e^{i\hat{G}} \tag{3.15}$$

When we expand $\hat{U}^\dagger$ and $\hat{U}$ in a power series, we can describe a small perturbation in the density matrix:

$$\delta\hat{\rho} = \delta\hat{\rho}_d + i[\hat{\rho}_d, \delta\hat{G}] \quad \text{where} \quad \operatorname{Tr}[\delta\hat{\rho}_d] = 0 \tag{3.16}$$

We can now look at the change in F, which we separate into two terms:

$$\delta F = \mathrm{Tr}\left[\delta\hat{\rho}\hat{H}\right] \tag{3.17}$$

$$+\frac{1}{\beta}\left[(\hat{\rho}+\delta\hat{\rho})\ln(\hat{\rho}+\delta\hat{\rho}) - \hat{\rho}\ln\hat{\rho}\right] \tag{3.18}$$

We have two kinds of shifts, $\delta\hat{\rho}_d$ and $\delta\hat{G}$. We will consider them separately, and both terms must vanish. First, let us consider variations of the form $\delta\hat{G}$. Term 3.18 only depends on the eigenvalues of $\hat{\rho}$ and is therefore independent of $\hat{G}$, so we look at only the term in (3.17):

$$\begin{aligned}
\delta F_G &= \mathrm{Tr}[i[\hat{\rho}_d, \delta\hat{G}]\hat{H}] \\
&= i\,\mathrm{Tr}[\hat{\rho}_d\delta\hat{G}\hat{H} - \delta\hat{G}\hat{\rho}_d\hat{H}] \\
&= i\,\mathrm{Tr}[\delta\hat{G}\hat{H}\hat{\rho}_d - \delta\hat{G}\hat{\rho}_d\hat{H}] \\
&= i\,\mathrm{Tr}[\delta\hat{G}[\hat{H}, \hat{\rho}_d]] \\
&= 0
\end{aligned}$$

We see that this does not change, and thus $\delta F = 0$ for changes of the form $\delta\hat{G}$. Now let us consider changes of the form $\delta\hat{\rho}_d$. Looking back at δF, the second term (3.18) can be rewritten:

$$-\frac{1}{\beta}\mathrm{Tr}\left[(\hat{\rho}_d+\delta\hat{\rho}_d)\log(\hat{\rho}_d+\delta\hat{\rho}_d) - \hat{\rho}_d\log\hat{\rho}_d\right] = -\frac{1}{\beta}\mathrm{Tr}\left[\delta\hat{\rho}_d\log(\hat{\rho}_d) + \hat{\rho}_d\hat{\rho}_d^{-1}\delta\hat{\rho}_d\right] + \mathcal{O}(\delta\hat{\rho}_d^2) \tag{3.19}$$

Now adding the first term (3.17) back in:

$$\delta F = \mathrm{Tr}\left[\delta\hat{\rho}_d\left(\hat{H} + \frac{1}{\beta}\log(\hat{\rho}_d) + \text{const.}\right)\right] \tag{3.20}$$

Now we note that we can add in a constant if we want, since the trace of $\delta\hat{\rho}_d$ is 0, and we are multiplying everything in the trace by $\delta\hat{\rho}_d$. Thus, adding a constant won't change anything here, but we are implicitly adding in a Lagrange multiplier to enforce the condition that the trace of $\hat{\rho}$ is 1. We want this to be zero, and therefore we have that

$$\hat{H} - \frac{1}{\beta}\log\hat{\rho}_d + \text{const.} = 0 \tag{3.21}$$

Which we can rewrite as

$$\hat{H} - \frac{1}{\beta}\log\left(\hat{\rho}_d\cdot\text{const.}\right) = 0 \tag{3.22}$$

Which can be again rewritten:

$$\hat{\rho}_d = \frac{1}{\text{const.}}\exp\left(-\beta\hat{H}\right) \tag{3.23}$$

We denote this constant Z, and we can show, by the condition that $\mathrm{Tr}[\rho_d] = 1$, that Z must be:

$$Z = \mathrm{Tr}\left[e^{-\beta\hat{H}}\right] \tag{3.24}$$

In summary, if we define thermal equilibrium as a system for which the density matrix:

- Maximizes S for fixed $\langle E\rangle$ or equivalently,

- Minimizes $F = \langle E\rangle - \beta S$ for fixed β

we recover the "canonical distribution" (or the Boltzmann distribution), if the particle number is fixed. Why? In practice, when systems are allowed to interact, they tend to explore possibilities and randomize, causing disorder. Equilibrium is achieved with maximum disorder given constraints. The Lagrange multiplier β has a simple interpretation:

$$\beta = \frac{1}{kT} \equiv \frac{1}{T}$$

The function $Z(\beta)$ is called the "partition function". Typical systems tend towards this thermal equilibrium.

To generalize this idea, one can add more constraints. For example, consider a Hilbert space with many different particle numbers and add a constraint for $\langle N\rangle$ with a Lagrange multiplier μ enforcing it (the chemical potential):

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathrm{Tr}[e^{-\beta(\hat{H}-\mu\hat{N})}]} \tag{3.25}$$

We see that in this case:

$$Z = \mathrm{Tr}\left[e^{-\beta(\hat{H}-\mu\hat{N})}\right] \tag{3.26}$$

Returning to the canonical distribution, recall that $Z(\beta) = \mathrm{Tr}[e^{-\beta\hat{H}}] = \mathrm{Tr}[U(-i\beta)]$. Suppose we know Z, how can we find the energy? Using the definition of the expectation value in the density matrix formalism (1.12):

$$\begin{aligned}
\langle E\rangle &= \mathrm{Tr}[\hat{\rho}_{eq}(\beta)\hat{H}] && (3.27)\\
&= \frac{\mathrm{Tr}[e^{-\beta\hat{H}}\hat{H}]}{\mathrm{Tr}[e^{-\beta H}]} && (3.28)\\
&= -\frac{\partial}{\partial\beta}\ln(\mathrm{Tr}[e^{-\beta\hat{H}}]) && (3.29)\\
&= -\frac{\partial}{\partial\beta}\ln(Z(\beta)) && (3.30)
\end{aligned}$$

And what about the entropy, or more specifically, the maximum entropy:

$$\begin{aligned}
S_{max} &= -\,\mathrm{Tr}[\hat{\rho}_{eq}\ln(\hat{\rho}_{eq})] && (3.31)\\
&= -\,\mathrm{Tr}\left[\frac{e^{-\beta\hat{H}}}{Z}\ln\left(\frac{e^{-\beta\hat{H}}}{Z}\right)\right] && (3.32)\\
&= -\,\mathrm{Tr}\left[\hat{\rho}_{eq}(-\beta\hat{H} - \ln Z)\right] && (3.33)\\
&= \beta\langle\hat{H}\rangle + \ln Z && (3.34)\\
&= \beta E + \ln Z && (3.35)
\end{aligned}$$

This lets us consider S as a function of E:

$$S(E) = \beta E + \ln Z \tag{3.36}$$

From this, we can look at dS/dE:

$$\frac{\partial S}{\partial E} = \beta + E\frac{\partial \beta}{\partial E} + \frac{\partial \ln Z}{\partial E} \tag{3.37}$$

$$= \beta + E\frac{\partial \beta}{\partial E} + \frac{\partial \ln Z}{\partial \beta}\frac{\partial \beta}{\partial E} \tag{3.38}$$

$$= \beta + E\frac{\partial \beta}{\partial E} - E\frac{\partial \beta}{\partial E} \tag{3.39}$$

and hence

$$\frac{\partial S}{\partial E} = \beta$$

Now recall that we can write the partition function in terms of the free energy, $Z = e^{-\beta F}$, we can rewrite the entropy:

$$S = \beta F + \log\left(e^{-\beta F}\right) \tag{3.40}$$

$$= \beta(E - F) \tag{3.41}$$

This is the same F that was minimized in going from QM to the Boltzmann distribution. The F here is called the "free energy", or more specifically, the "Helmholtz free energy". Our derivation was quantum in nature, we defined von Neumann entropy as fundamental since it was extensive and defined an equilibrium state as that which maximized it. Now that we have this, we can obtain thermodynamic relations. There are many ways to do this:

- Fix E and determine T, S, F.
- Fix T and determine E, S, F.
- Fix S and determine F, T, E.

Regardless of the path we choose, we find the thermodynamic results:

$$\frac{\partial S(E)}{E} = \frac{1}{T} \tag{3.42}$$

$$-\frac{\partial \ln Z(\beta)}{\partial \beta} = E \tag{3.43}$$

We can relate the energy to the free energy and entropy:

$$E = -\frac{\partial}{\partial \beta}(-\beta F) \tag{3.44}$$

$$= F + \beta\frac{\partial f}{\partial \beta} \tag{3.45}$$

$$= F - \frac{\partial f}{\partial T} \tag{3.46}$$

$$= F - TS - T\frac{\partial F}{\partial T} \tag{3.47}$$

Which gives us

$$TS = -T\frac{\partial f}{\partial T} \tag{3.48}$$

Which gives us an expression for the entropy in terms of the free energy density and the temperature:

$$S = -\frac{\partial f(T)}{\partial T} \tag{3.49}$$

Note that E and F are related by Legendre transforms. This is the type of transformation relating, for example, $\mathcal{H}$ and $\mathcal{L}$ in classical mechanics; given $\mathcal{L}(q, \dot{q})$, $\frac{\partial \mathcal{L}}{\partial \dot{q}} = p$. Then $\mathcal{H}(q, p) = \mathcal{L} - p\dot{q}$ with $\frac{\partial \mathcal{H}}{\partial p} = \dot{q}$. The two formalisms are mathematically equivalent. How does this work for E and F? We have that F is a function of T, and

$$\frac{\partial F}{\partial T} = -S \tag{3.50}$$

And we can write E in terms of F, T, and S:

$$E = F + TS \tag{3.51}$$

And we have

$$\frac{\partial E}{\partial S} = T \tag{3.52}$$

Thus the structure of a Legendre transform is given by

$$\frac{\partial F}{\partial T} = -S \tag{3.53}$$

$$\frac{\partial E}{\partial S} = T \tag{3.54}$$

This structure reoccurs throughout thermodynamics and is a key idea.

3.1 Natural Variables

Natural variables come in pairs. One can always be viewed as the Lagrange multiplier of the other. We describe things in terms of a given pair depending on the circumstance. T and S are used to describe heat. P and V are used for work. μ_i and N_i are used to describe the energy associated with the particle number of species i. These are the pairs primarily used, but there are others depending on circumstance, e.g. M and h, the magnetization and external magnetic field. In thermodynamics, we identify the relevant natural variables depending on the process of interest:

- For isothermal processes (fixed T) we use S.
- For adiabatic processes (no heat in or out, fixed S) we use T.
- for isochoric processes (constant V) we use P
- For constant particle number N we use the chemical potential, μ

Note that for each of these, we can also do the reverse, i.e. for isobaric processes (constant P), we use V. There is a type of free energy associated with each set of natural variables. To illustrate, assume no magnetic field and a fixed particle number, which means we can implicitly ignore N, μ, M, and h. Then we can define multiple different free energies:

$$U(S, V) \quad \rightarrow \quad \text{Internal energy} \tag{3.55}$$

$$F(T, V) \quad \rightarrow \quad \text{Helmholtz free energy} \tag{3.56}$$

$$H(S,P) \quad \rightarrow \quad \text{Enthalpy} \tag{3.57}$$
$$G(T,P) \quad \rightarrow \quad \text{Gibbs free energy} \tag{3.58}$$
$$\tag{3.59}$$

They are related to each other through Legendre transforms and contain the same information. For any given situation, we choose the one that is easiest to work with.

$$\left.\begin{aligned} F &= U - TS \\ U &= F + TS \end{aligned}\right\} \left.\begin{aligned} \left.\frac{\partial F}{\partial T}\right|_V &= -S \\ \left.\frac{\partial U}{\partial S}\right|_V &= T \end{aligned}\right\} \quad \text{constant volume (isochoric)} \tag{3.60}$$

$$\left.\begin{aligned} H &= U + PV \\ U &= H - PV \end{aligned}\right\} \left.\begin{aligned} \left.\frac{\partial H}{\partial P}\right|_S &= -V \\ \left.\frac{\partial U}{\partial V}\right|_S &= -P \end{aligned}\right\} \quad \text{constant entropy (adiabatic)} \quad \Delta Q = 0 \tag{3.61}$$

$$\left.\begin{aligned} G &= H - TS \\ H &= G + TS \end{aligned}\right\} \left.\begin{aligned} \left.\frac{\partial G}{\partial T}\right|_P &= -S \\ \left.\frac{\partial H}{\partial S}\right|_P &= -V \end{aligned}\right\} \quad \text{constant pressure (isobaric)} \tag{3.62}$$

$$\left.\begin{aligned} G &= F + PV \\ F &= G - PV \end{aligned}\right\} \left.\begin{aligned} \left.\frac{\partial G}{\partial P}\right|_T &= V \\ \left.\frac{\partial F}{\partial V}\right|_T &= P \end{aligned}\right\} \quad \text{constant temperature (isothermal)} \tag{3.63}$$

There are grand versions of all of these, if the particle number is not fixed. Let us illustrate with one species of particle. We can define the grand free energy Φ_G:

$$\Phi_G(T,V,\mu) = -T \ln \mathcal{Z} \tag{3.64}$$

We can now write out the grand partition function:

$$\mathcal{Z} = \mathrm{Tr}\left[e^{-\beta(\hat{H}-\mu\hat{N})}\right] \tag{3.65}$$
$$= e^{-\beta\Phi_G} \tag{3.66}$$

We can relate the grand potential to the Helmholtz free energy and the internal energy (note that μ plays the role of the Lagrange multiplier for N):

$$\Phi_G = F_G - \mu N \tag{3.67}$$
$$= U - TS - \mu N \tag{3.68}$$

We can also write a set of Legendre transformation relations:

$$\left.\begin{aligned} \left.\frac{\partial \Phi_G}{\partial \mu}\right|_{T,V} &= -N \\ \left.\frac{\partial F_G}{\partial N}\right|_{T,V} &= \mu \end{aligned}\right\} \quad \text{constant volume, isothermal} \tag{3.69}$$

$$\tag{3.70}$$

$$\left.\frac{\partial \Phi_G}{\partial T}\right|_{V,\mu} = -S \tag{3.71}$$

$$\left.\frac{\partial \Phi_G}{\partial V}\right|_{\mu,T} = -P \tag{3.72}$$

One can generalize this method to other grand free energies (subtract μN from H, G) and get analogous relations. We can generalize to multiple species by having a pair of natural variables (μ_i, N_i) for each species i. We can also obtain similar expressions taking into account magnetization using the variables (M, h). In general, we use the formula $\hat{H} - \lambda\hat{x}$, where λ is a Lagrange multiplier and $\hat{x}$ is some quantity of interest, to obtain a free energy for x.

3.2 Equations of State

If we differentiate any free energy with respect to any natural variable, we get an equation of state, which expresses one thermodynamic quantity in terms of others. The most famous example would be to take the derivative:

$$-P = \left.\frac{\partial F}{\partial V}\right|_{T,N} \tag{3.73}$$

which recovers $P(T, V, N)$. For a classical ideal gas, $P(T, V, N) = T\frac{N}{V}$.

Let us consider the first law of thermodynamics. This is the idea that energy is conserved. Consider a system with variable pressure, volume, particle number, etc. Conservation of energy states that the change in the internal energy, dU, is equal to the heat that we put in, TdS, the mechanical work, $-PdV$, and the chemical potential for each species, dependent on the number of particles, $\sum_{\text{species}} \mu_i dN_i$:

$$dU = TdS - PdV + \sum_i \mu_i dN_i + \sum_j \lambda_j dx_j \tag{3.74}$$

Where the last term is any other quantities that we care about, such as magnetization, isospin, and whatever else there is going on in our system. In the same way, we can define other free energies:

$$dF = -SdT - PdV + \sum_i \mu_i dN_i + \sum_j \lambda_j dx_j \tag{3.75}$$

$$dH = TdS + VdP + \sum_i \mu_i dN_i + \sum_j \lambda_j dx_j \tag{3.76}$$

$$dG = -SdT + VdP + \sum_i \mu_i dN_i + \sum_j \lambda_j dx_j \tag{3.77}$$

We can combine these to obtain expressions for the change in products of thermodynamic quantities:

$$d(PV) = dH - dU = dG - dF \tag{3.78}$$

$$d(TS) = dU - dF = dH - dG \tag{3.79}$$

We can differentiate equations of state in different ways. For simplicity, we work at fixed N, but let every other thermodynamic quantities vary. Take $U(S, V)$. We can look at the mixed partial with respect to S and V:

$$\frac{\partial^2 U}{\partial S \partial U} = \frac{\partial}{\partial S}\frac{\partial U}{\partial V} = \frac{\partial}{\partial V}\frac{\partial U}{\partial S} = -\left.\frac{\partial P}{\partial S}\right|_V = \left.\frac{\partial T}{\partial V}\right|_S \tag{3.80}$$

Similarly, we can look at other free energies:

$$\left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P \quad \text{from} \quad H \tag{3.81}$$

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V \quad \text{from} \quad F \tag{3.82}$$

$$\left.\frac{\partial S}{\partial P}\right|_T = \left.\frac{\partial V}{\partial T}\right|_P \quad \text{from} \quad G \tag{3.83}$$

If we use the grand potential a bit more care is needed. For simplicity we consider one species of particle:

$$\left.\frac{\partial^2 \Phi_G(T,V,\mu)}{\partial \mu \partial V}\right|_T \quad \Longrightarrow \quad -\left.\frac{\partial P}{\partial \mu}\right|_{T,V} = \left.\frac{\partial N}{\partial V}\right|_{T,\mu} \tag{3.84}$$

3.3 Intensive Quantities

Intensive quantities are natural to describe in terms of densities, and natural to use in the thermodynamic limit. We will use lower case for the density form of our variables:

$$N = Vn, \quad U = Vu, \quad S = Vs, \quad F = Vf, \quad \Phi_G = V\phi_G \tag{3.85}$$

We also have quantities that are already intensive, such as μ, T, and P.

Suppose we have the grand potential, $\Phi_G(T,\mu)$, and we want to find the number density, n. To do this, we can take the derivative:

$$n = -\left.\frac{\partial \phi_G}{\partial \mu}\right|_T \tag{3.86}$$

And we can similarly find the entropy density:

$$s = -\left.\frac{\partial \phi_G}{\partial T}\right|_\mu \tag{3.87}$$

What about the pressure? We don't have an intensive quantity to differentiate with respect to. Previously, we stated that

$$P = -\left.\frac{\partial \Phi_G}{\partial V}\right|_{\mu,T} \tag{3.88}$$

This is just the intensive grand potential density, $\Phi_G = V\phi_G$. There is another way to see this. Consider the pressure in terms of the derivative of the free energy:

$$P = -\left.\frac{\partial F}{\partial V}\right|_T \tag{3.89}$$

We know $F = Vf(T,n) = Vf(T,N/V)$, so we can apply the chain rule:

$$-\frac{\partial F}{\partial V}\bigg|_T = -f(T,n) - V\frac{\partial f}{\partial n}\bigg|_T\frac{\partial n}{\partial V}\bigg|_\mu \tag{3.90}$$

$$= -\left(f(T,n) - n\frac{\partial f}{\partial n}\bigg|_T\right) \tag{3.91}$$

$$= -(f - \mu n) \tag{3.92}$$

$$= -\phi_G \tag{3.93}$$

3.4 Fluctuations

Suppose we want to compute the fluctuations in the energy, which we can measure by looking at the variance:

$$\langle E^2\rangle - \langle E\rangle^2 \tag{3.94}$$

We can compute both of these quantities:

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z \tag{3.95}$$

$$= \frac{\mathrm{Tr}[e^{-\beta\hat{H}}\hat{H}]}{\mathrm{Tr}[e^{-\beta H}]} \tag{3.96}$$

$$\langle E^2\rangle = \frac{\mathrm{Tr}[e^{-\beta\hat{H}}\hat{H}^2]}{\mathrm{Tr}[e^{-\beta H}]} \tag{3.97}$$

$$= \frac{1}{Z}\frac{\partial}{\partial\beta^2}Z \tag{3.98}$$

Now we will make a claim about the variance, and then see that it holds for an example system.

Claim

For large systems in equilibrium, the fluctuations are small compared to $\langle E\rangle^2$.

Consider two isolated systems. We can look at the partition function for the two systems treated together:

$$Z(\beta) = \sum_{i,j}\exp(-\beta(E_i^{(1)} + E_j^{(2)})) \tag{3.99}$$

$$= \sum_i e^{-\beta E_i^{(1)}}\sum_j e^{-\beta E_j^{(2)}} \tag{3.100}$$

$$= Z_1(\beta)Z_2(\beta) \tag{3.101}$$

$$\tag{3.102}$$

Note that this implies (via the relationship between Z and F), that

$$F = F_1 + F_2 \tag{3.103}$$

Now let modify the setup slightly. Instead of having two separated systems, we place them in contact with one another. Let us assume that the things away from the contact barrier don't matter, we have a finite correlation length. The difference between this case and the previous case is that we have a small change to the free energy, due to the interactions around the contact. However, if we assume that the volume of the systems is large, then this change in the free energy is small:

$$F = F_1 + F_2 + \delta F \tag{3.104}$$

If the correlations are finite ranged and the box size in all dimensions is much greater than the correlation length, then we ignore this “finite volume effect”:

$$F \approx F_1 + F_2 \tag{3.105}$$
$$Z \approx Z_1 Z_2 \tag{3.106}$$

This justifies the notion that $F \approx fV$. Suppose that the system is large, homogeneous, has finite range correlations, and in equilibrium. In this case, we can again set up a small perturbation to the free energy:

$$F = f(T)V + \delta f \tag{3.107}$$

Where $\lim_{V\to\infty} \frac{\delta f}{V} = 0$. Using the relationship between the free energy and the partition function, $\beta F = -\ln Z$ so $Z = e^{-\beta(fV+\delta f)}$. We can then compute the variance in the energy:

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} \tag{3.108}$$
$$= V\left(f - \beta\frac{\partial f}{\partial \beta}\right) \tag{3.109}$$
$$\langle E^2 \rangle = \frac{\frac{\partial^2 Z}{\partial \beta^2}}{Z} \tag{3.110}$$
$$= V^2\left(f - \beta\frac{\partial f}{\partial \beta}\right)^2 \tag{3.111}$$
$$= \langle E \rangle^2 - V\frac{\partial^2 f}{\partial \beta^2} \tag{3.112}$$

Hence $\langle E^2 \rangle - \langle E \rangle^2 \sim V$ so

$$\frac{\langle E^2 \rangle - \langle E \rangle^2}{\langle E \rangle^2} \sim \frac{1}{V} \tag{3.113}$$

Such systems have fluctuations suppressed as a fraction of the total in the thermodynamic limit $V \to \infty$.

We can now define a quantity that reflects the change in energy at fixed volume and particle number, by leveraging the fact that $\partial S/\partial E = 1/T$:

$$\frac{\Delta S}{\Delta E} = \frac{1}{T} \tag{3.114}$$

From which we have

$$\Delta E = T\Delta S \tag{3.115}$$

We call this Q, or heat. If we call $\langle E \rangle = U$, the internal energy, we have that $\Delta U = T\Delta S$. Note that this holds for fixed T.

Now let us justify our interpretation of T as temperature. Consider two systems that have no correlation but which allow energy to move between them. The von Neumann entropy and energy are additive:

$$S(E) = S_1(E_1) + S_2(E_2) \tag{3.116}$$

$$E = E_1 + E_2 \tag{3.117}$$

To maximize the total entropy S with fixed E, I need to determine the energy E_1 in the first system that maximizes S. Note that this also determines E_2.

$$\frac{\partial S}{\partial E_1} = 0 = \frac{\partial S_1}{\partial E_1} + \underbrace{\frac{\partial E_2}{\partial E_1}}_{-1} \frac{\partial S_2}{\partial E_2} \tag{3.118}$$

i.e. at equilibrium,

$$0 = \frac{1}{T_1} - \frac{1}{T_2} \tag{3.119}$$

This means that if we adopt this interpretation of T, then if two systems are in equilibrium, they have the same temperature.

3.5 Heat Bath

A heat bath is a very large system held at fixed T, that can equilibrate with other systems, without changing its T noticeably. The effective number of accessible quantum states is given by the entropy, $S = -\operatorname{Tr}[\rho \ln \rho]$. These states are spread out in energy, but for large systems, the spread in energy is small. One can visualize the spread in energy as being just a fixed energy, and all states within some distance $\delta E/2$ of this energy, with all states equally likely.

$$S = -\operatorname{Tr}[\rho \ln \rho] \tag{3.120}$$

$$= \sum_{\substack{\text{states}\\ \text{within}\\ \Delta E}} \frac{1}{\omega} \ln \frac{1}{\omega} \tag{3.121}$$

$$= \ln \omega \tag{3.122}$$

where ω is the number of states within ΔE.

4 Statistical Mechanics

4.1 Carnot Cycle

We want to find the maximum efficiency at which we can extract work from a heat bath. Consider two heat baths, one at a higher temperature T_H and one at a lower temperature T_C. We will consider an idealized Carnot cycle, a reversible cycle from which we move heat from the hotter to the colder bath. There are 4 steps, and the T-S diagram is shown in Figure 4.1:

1. We begin with a compressed system in equilibrium with the hot reservoir. Work is done through isothermal expansion.
2. We disconnect from the hot bath. Adiabatic expansion continues to do work.
3. We connect to the cold reservoir. Work is required for isothermal compression.
4. We disconnect from the cold reservoir. Work is required for adiabatic compression, bringing us back to our original system when we again connect to the hot reservoir.

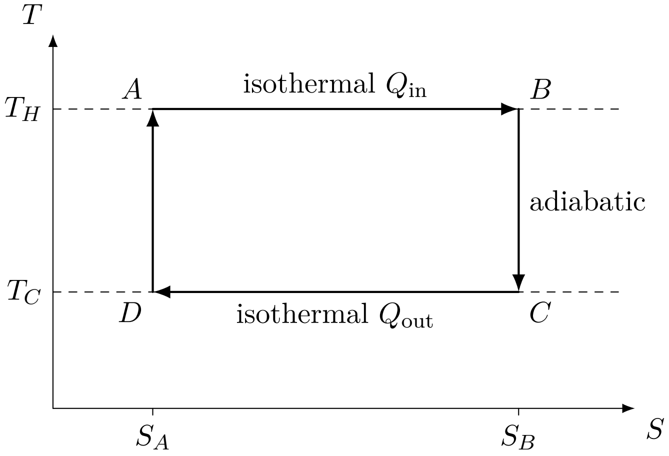


Figure 4.1: The T-S diagram for the Carnot cycle.

We can compute the net work done by this cycle. To begin, let us consider the heat differences during the isothermal processes:

$$\Delta Q_{A\to B} = \int_{S_A}^{S_B} T_H \, dS \tag{4.1}$$

$$= T_H(S_B - S_A) \tag{4.2}$$

$$\Delta Q_{C\to D} = \int_{S_B}^{S_A} T_C \, dS \tag{4.3}$$

$$= T_C(S_B - S_A) \tag{4.4}$$

Adding these two together, we see that the total change in heat is given by

$$\Delta Q = (S_B - S_A)(T_H - T_C) \tag{4.5}$$

We can then relate this to the work done:

$$W = \oint P\,dV \tag{4.6}$$

$$= \oint (T\,dS - dU) \tag{4.7}$$

Now we note that $\oint dU = 0$, since the process is reversible, so the work is exactly equal to the change in heat:

$$W = \Delta Q \tag{4.8}$$

$$= (S_B - S_A)(T_H - T_C) \tag{4.9}$$

We can then define the efficiency of a process, η:

$$\eta = \frac{W}{Q_H} \tag{4.10}$$

Computing this for the Carnot cycle:

$$\eta_{\text{Carnot}} = \frac{(T_H - T_C)(S_B - S_A)}{T_H(S_B - S_A)} \tag{4.11}$$

$$= 1 - \frac{T_C}{T_H} \tag{4.12}$$

This leads to Carnot's theorem: Any reversible cycle transferring heat from hot to cold reservoirs has some efficiency, and $\eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$ is the maximum efficiency for any engine.

4.2 Thermodynamic Stability

Suppose we have a gas in a box. When we look at the pressure of such a system, we think of it as the particles in the gas exerting an outwards force against the walls of the box. In this picture, how could we ever have negative pressure? The particles of the gas cannot hit the wall and somehow exert a pulling force into the system.

Claim

In stable systems, negative pressure is impossible; $P \geq 0$.

Note that this also implies that in stable systems, $\phi_g > 0$, always. Now let us consider a system with total volume V, divided into two subsystems, in thermal equilibrium. The volumes of each system are equal, $V_1 = V_2 = V/2$, and we can write down the number density in each subsystem:

$$n_1 = \frac{N_1}{V/2} \tag{4.13}$$

$$n_2 = \frac{N_2}{V/2} \tag{4.14}$$

Where $N_1 + N_2 = N$. Also note that

$$n_2 = 2n - n_1 \tag{4.15}$$

Now consider the free energy of the two subsystems, and how it relates to the total system:

$$\begin{aligned} F_{\text{split}} &= F_1 + F_2 \qquad (4.16)\\ &= \frac{V}{2}\left(f(T, n_1) + f(T, 2n - n_1)\right) \qquad (4.17) \end{aligned}$$

Now suppose we change the number densities slightly:

$$\begin{aligned} n_1 &= n + \Delta \qquad (4.18)\\ n_2 &= n - \Delta \qquad (4.19) \end{aligned}$$

The free energy then becomes:

$$F_{\text{split}} = \frac{V}{2}\left(f(T, n + \Delta) + f(T, n - \Delta)\right) \tag{4.20}$$

If we dropped the partition between the two subsystems, the system will maximize entropy (with particle number fixed), and minimize the free energy. Thus the free energy of the equilibrated system is lower:

$$F_{\text{split}} \geq V f(T, n) \tag{4.21}$$

Inserting our expression for F_{split} (4.20), we find the following inequality:

$$\frac{V}{2}\left(f(T, n + \Delta) + f(T, n - \Delta)\right) \geq V f(T, n) \tag{4.22}$$

Which can also be written as

$$\frac{V}{2}\Big[f(T, n + \Delta) + f(T, n - \Delta) - 2f(T, n)\Big] \geq 0 \tag{4.23}$$

This is the condition required for stability. Let's look at the limit as $\Delta \to 0$.

$$\frac{\partial^2 f}{\partial n^2}\bigg| T \geq 0 \tag{4.24}$$

We see that f is concave up or flat as a function of n at fixed T, i.e. not concave down.

4.3 Wigner Transforms

Imagine a large number of copies of a system with the same density matrix ρ. This could be one big physical system broken up into regions, one big system averaged over time interacting with a heat bath, etc. Everything we have done so far is quantum, but also works classically. One subtle difference in quantum mechanics is that our density matrix could be the reduced density matrix of a larger system.

In classical mechanics, probabilities are statements of ignorance. In Hamiltonian form, the state of a system is described by a set of q, p:

$$\boldsymbol{q} = (q_1, q_2, \ldots, q_2), \qquad \boldsymbol{p} = (p_1, p_2, \ldots, p_2)$$

For a 3D system with N particles, $n = 3N$. A point $(\boldsymbol{q}, \boldsymbol{p})$ is a point in "phase space" and describes the state of the system completely. The classical Hamiltonian is $\mathcal{H}(\boldsymbol{q}, \boldsymbol{p})$. The equations of motion are given by the Euler-Lagrange equations:

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}$$

Liouville's theorem states that under time evolution, a multidimensional region in phase space will be mapped into a region with the same volume. This is the analogue of local probability conservation in quantum mechanics.

Suppose that we do not know the state of the system but have some probability distribution (i.e. one from the ensemble) $P(\boldsymbol{q}, \boldsymbol{p})$:

$$\int d^N q \, d^N p \, P(\boldsymbol{q}, \boldsymbol{p}) = 1 \tag{4.25}$$

Let us define the entropy

$$S = h^n \int d^n q \, d^n p \, P(\boldsymbol{q}, \boldsymbol{p}) \ln P(\boldsymbol{p}, \boldsymbol{q}) \tag{4.26}$$

This h here is not Planck's constant, but another constant with the same units, needed to get the dimensions right; the value itself is arbitrary. This entropy is also an extensive quantity. Let us now consider the energy:

$$\langle E \rangle = \int d^N q \, d^N p \, \mathcal{H}(\boldsymbol{q}, \boldsymbol{p}) P(\boldsymbol{q}, \boldsymbol{p}) \tag{4.27}$$

Let us define $S_{\text{ef}}(E_0)$ as the entropy of the probability distribution $P(\boldsymbol{q}, \boldsymbol{p})$ that maximizes S subject to the constraint that $\langle E \rangle = E_0$. By the same argument as in the quantum case,

$$P(\boldsymbol{p}, \boldsymbol{q}) = \frac{\exp(-\beta \mathcal{H}(\boldsymbol{q}, \boldsymbol{p}))}{\int d^N q \, d^N p \, \exp(-\beta \mathcal{H}(\boldsymbol{q}, \boldsymbol{p}))} \tag{4.28}$$

The denominator is equal to $CZ(\beta)$, where C is another constant just to get the dimensions right. This formalism leads to exactly the same thermodynamic relations as in quantum mechanical thermodynamics:

$$\langle E \rangle = \frac{\partial \ln Z(\beta)}{\partial \beta} \qquad F = -T \ln Z = E - TS \tag{4.29}$$

$$S = \frac{\partial F}{\partial T} \qquad T = \frac{\partial E}{\partial S} \tag{4.30}$$

To justify this, we note that just as in the quantum mechanical case, the entropy is the only extensive measure of classical disorder. It is also connected to the quantum case through the Wigner transform (the quantum connection to phase space). To understand this transform, let us look at a simple case, the Wigner transform of a single particle in 1D. Suppose we have an operator $\hat{O}$ fully specified by matrix elements $\langle x | \hat{O} | y \rangle$. All this information is contained in

$$O(q, p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}\Delta \, \exp(-ip) \left\langle q + \frac{\Delta}{2} \middle| \hat{O} \middle| q - \frac{\Delta}{2} \right\rangle \tag{4.31}$$

This is the Wigner transform. All information about the operator $\hat{O}$ is contained here, as we can reconstruct a matrix element from this. It is easy to prove that if $\hat{O}$ is Hermitian, O is real. This generalizes to many degrees of freedom.

We can look at the Wigner transform of $\hat{p}$:

$$p(\boldsymbol{q},\boldsymbol{p}) = \frac{1}{2\pi}\int \mathrm{d}\boldsymbol{\Delta}\exp(-i\boldsymbol{p}\cdot\boldsymbol{\Delta})\left\langle \boldsymbol{q}+\frac{\boldsymbol{\Delta}}{2}\middle|\hat{p}\middle|\boldsymbol{q}-\frac{\boldsymbol{\Delta}}{2}\right\rangle \tag{4.32}$$

This acts (sort of) like a phase space distribution, which is easier to see if we look at some of its properties. First, its normalized if we integrate over all of our variables:

$$\int \mathrm{d}^N p\,\mathrm{d}^N q\, p(\boldsymbol{q},\boldsymbol{p}) = 1 \tag{4.33}$$

We can also look at integrating over just one set of variables:

$$\begin{aligned}\int \mathrm{d}^N p\, p(\boldsymbol{q},\boldsymbol{p}) &= p(\boldsymbol{q}) &(4.34)\\ &= \langle \boldsymbol{q}|\,\hat{p}\,|\boldsymbol{q}\rangle &(4.35)\\ \int \mathrm{d}^N q\, p(\boldsymbol{q},\boldsymbol{p}) &= p(\boldsymbol{p}) &(4.36)\\ &= \langle \boldsymbol{p}|\,\hat{p}\,|\boldsymbol{p}\rangle &(4.37)\end{aligned}$$

This is almost a phase space probability distribution, but the form does not prevent $p(\boldsymbol{q},\boldsymbol{p}) < 0$, so it is not really a probability. But, for systems near the "classical limit", $p(\boldsymbol{q},\boldsymbol{p}) \geq 0$ almost everywhere.

A Paradox?

Microscopically, neither classical Hamiltonian evolution nor quantum unitary evolution can change the entropy of a system. If we know the exact microstate that the system is in, the entropy is $S = 0$, and it remains zero under time evolution. How do we reconcile this with the entropy increase observed in macroscopic systems?
One resolution is to note that we never access the exact instantaneous state $p(t)$. Instead, on experimental time scales we effectively sample the system at random times, which corresponds to replacing $p(t)$ with its long–time average

$$\overline{p} = \lim_{T\to\infty}\frac{1}{T}\int_0^T p(t)\,\mathrm{d}t \tag{4.38}$$

This averaged object is still a valid density matrix (quantum) or phase–space distribution (classical), satisfying $\mathrm{Tr}[\overline{p}] = 1$. In this way, entropy growth can be argued to arise not from the microscopic dynamics themselves, but from the coarse–graining of time averaging.

4.4 Ensembles

In statistical mechanics, we have several different ensembles, which in the thermodynamic limit produce the same statistical results, but often allow for more natural descriptions of certain systems. Each ensemble holds certain quantities fixed and allows others to fluctuate. We will define three ensembles, the microcanonical, canonical, and grand canonical ensembles.

To begin, we can consider a system that can (weakly) trade energy with its surroundings, in which case the system can thermalize in a time-averaged sense. In this scenario, we have the canonical ensemble, the temperature is fixed, but the energy can fluctuate. This is often the best ensemble to study equilibrium properties at finite temperature. The microcanonical ensemble describes a system in which the energy, particle number, and volume are all fixed. In this case, we can count the number of accessible microstates, and denote this quantity W. From this, we can define the entropy and temperature:

$$S = \ln W \tag{4.39}$$

$$T = \frac{1}{\frac{\partial S}{\partial E}} \tag{4.40}$$

If we take the microcanonical ensemble to the thermodynamic limit, we will recover the same results as the canonical ensemble.

Finally, we have the grand canonical ensemble. In this case, instead of fixing the number of particles, we allow it to fluctuate. This introduces a Lagrange multiplier that we have already seen, the chemical potential μ. Physically, this corresponds to the amount of energy needed to introduce a particle into the system. The partition function of the system will then depend on μ, recovering the grand partition function (3.65)

$$\mathcal{Z}(\beta, \mu) = \mathrm{Tr}\left[e^{-\beta(\hat{H} - \mu\hat{N})}\right] \tag{4.41}$$

From which we can derive relations between $\mathcal{Z}$ and our system quantities:

$$\frac{\partial \ln \mathcal{Z}}{\partial \mu} = \beta \langle N \rangle \tag{4.42}$$

$$\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \langle E \rangle - \mu \langle N \rangle \tag{4.43}$$

We can also rewrite our partition function in terms of the canonical partition functions, summing over particle counts:

$$\mathcal{Z} = \sum_N e^{\beta\mu N} \mathrm{Tr}_N \left[e^{-\beta\hat{H}}\right] \tag{4.44}$$

$$= \sum_N \left(e^{\beta\mu}\right)^N Z_N(\beta) \tag{4.45}$$

Now we note that if we let $\mu = i\alpha$, we have a Fourier series, and we can extract the coefficients:

$$Z_N(\beta) = \frac{1}{2\pi}\int_0^{2\pi} \mathrm{d}\alpha\, \mathcal{Z}\left(\beta, i\frac{\alpha}{\beta}\right) e^{i\alpha N} \tag{4.46}$$

While these ensembles are fundamentally rooted in statistical mechanics, they are tied to our macroscopic thermodynamic observables. As an aside, we can also define quasistatic processes, which occur slowly enough that the system remains equilibrated at all times. Such processes are reversible, if we run them in reverse, we return to our original state. Not all processes are reversible, and in a practical sense, none are.

4.5 Ideal Gases

Let us now consider an ideal gas, an equilibrated system of non-interacting particles. In essence, we are assuming that the system is dilute, there are no collisions between particles. This is a logically impossible toy model, but is a good representation of particles that are weakly interacting over a long period of time. Let us first work out the simplest case where we have a single species of particle, with no internal degrees of freedom. What regimes is such a model valid for? We expect it to be valid for systems that have temperatures higher than any relevant quantum energies, $k_{\mathrm{Th}}L \gg 1$, where L is the size of the box, and k_{Th} is the thermal momentum, $k_{\mathrm{Th}} = \sqrt{mT}$.

This problem is evaluated simply in the canonical approach. First we find the partition function of 1 particle in a box of volume V:

$$\begin{aligned} Z_1(T,V) &= \frac{1}{\hbar^3}\int \frac{\mathrm{d}^3p}{(2\pi)^3}\int \mathrm{d}^3q e^{-\beta\frac{p^2}{2m}} && (4.47)\\ &= \frac{V}{\hbar^3(2\pi)^3}\int \mathrm{d}^3p e^{-\beta\frac{p^2}{2m}} && (4.48)\\ &= \frac{V}{\hbar^3(2\pi)^3}\int_0^\infty 4\pi p^2 d\mathrm{d}\, e^{-\beta\frac{p^2}{2m}} && (4.49)\\ &= \frac{V}{\hbar^3}\left(\frac{mT}{2\pi}\right)^{3/2} && (4.50) \end{aligned}$$

Now each particle is distinct, having its own independent phase space, so we claim that the partition function for the full system is given by:

$$\begin{aligned} Z(T,N,V) &= (Z(T,V))^N && (4.51)\\ &= \frac{V^N}{\hbar^{3N}}\left(\frac{mT}{2\pi}\right)^{3N/2} && (4.52) \end{aligned}$$

This actually turns out to be wrong, for reasons that we will explore shortly, but let us work with it for now. We can then look at equations of state, beginning with the pressure:

$$\begin{aligned} -P &= -T\frac{d\ln Z}{dV} && (4.53)\\ &= -T\frac{\partial}{\partial V}\left(\ln\left(\frac{V^N}{V_0^N}\right) + \ln\left(\frac{V_0^N}{\hbar^{3N}}\left(\frac{mT}{2\pi}\right)^{3N/2}\right)\right) && (4.54) \end{aligned}$$

Which gives us a familiar result, the ideal gas law:

$$PV = NT \tag{4.55}$$

Or, if we divide out by the volume, $P(T,n) = nT$. This is our equation of state. What about u?

$$\begin{aligned} u &= -\frac{\partial \ln Z}{\partial\beta} && (4.56)\\ &= -\frac{\partial}{\partial\beta}\left[\ln\left(\frac{V^N}{\hbar^{3N}}\left(\frac{m}{2\pi\beta}\right)^{3N/2}\right)\right] && (4.57)\\ &= \frac{3N}{2}\frac{1}{\beta} && (4.58)\\ &= \frac{3}{2}NT && (4.59) \end{aligned}$$

This is a result of what is known as the equipartition theorem.

Theorem 4.5.1. *Equipartition Theorem. If we have a quantity that is quadratic with respect to either q or p, we get a factor of $\frac{1}{2}T$ in the total energy.*

For example, if we have N harmonic oscillators, the equipartition theorem states that the total energy will be $U = NT$. For N particles in 2 dimensions, it predicts $U = NT$. For N particles, each with an internal degree of freedom, we have $U = \frac{5}{2}NT$.

These are all quadratic degrees of equal energy, with Gaussian-type integrals.

The momenta in these systems follow what is known as the Maxwell-Boltzmann distribution. Suppose we have a box with many particles, with a little person inside, who can measure the individual momenta of particles in the box. The distribution of momenta is given by:

$$\text{Prob}(\boldsymbol{p})\, d^3p = -\frac{e^{-p^2 2mT}}{(2\pi mT)^{3N/2}} \tag{4.60}$$

Where the denominator is there so that the probability distribution integrates to 1. This is a distribution in terms of momentum, but we generally write it in terms of the speed:

$$\text{Prob}(v) = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} V^2 \text{exp}\left[-\frac{mv^2}{2T}\right] \tag{4.61}$$

Returning to the ideal gas, everything so far looks good, but recall that we claimed there was something wrong with our partition function, we had claimed that

$$Z(T, N, V) = Z_1(T, V)^N \tag{4.62}$$

We can relate this to the free energy:

$$-\beta F = \ln Z \tag{4.63}$$

$$\frac{F}{V} = -Tn \ln\left(\frac{V}{h^3}(2\pi mT)^{3/2}\right) \tag{4.64}$$

The issue is that f is supposed to be extensive, but it is dependent on the volume! Thus we have that F and S are not extensive. Gibbs noticed this, and for this reason, it is known as the Gibb's paradox.

In quantum mechanics, the notion of indistinguishable particles is well defined: if particles are indistinguishable there is a constraint on the allowed states; the state changes by at most a phase if particles are swapped. In classical mechanics, there is no equivalent notion. As a matter of principle I can follow each particle through phase space and keep track of which is which. This naturally leads to Gibbs' solution: while in principle I can distinguish between particles, in practice I cannot in macroscopic systems. And since entropy is a measure of my ignorance, I should not distinguish between them. If one does this, the entropy and free energy densities do indeed become intensive.

To see this, let us consider a system of two particles. Previously we argued that $Z_2(T, V) = (Z_1(T, V))^2$, i.e. that I get a separate identical copy of the partition function for each particle: $Z_2 = Z_1^{(a)} Z_1^{(b)}$, where $Z_1^{(a)} = Z_1^{(b)}$. But if I cannot distinguish between them, the configurations in phase space are not really independent. Swapping a and b results in the same configuration. So I only get $\frac{1}{2}$ as many independent configurations: $Z_2 = \frac{1}{2}Z_1^2$. If I have 3 particles, there are 3! configurations that are the same. It is easy to see that generally, $Z_N = \frac{1}{N!}Z_1^N$.

If we take this into account for the ideal gas:

$$Z(T,N,V) = \frac{1}{N!}\left(Z(T,V)\right)^N \tag{4.65}$$

$$= \frac{V^N}{N!\,\hbar^{3N}}\left(\frac{mT}{2\pi}\right)^{3N/2} \tag{4.66}$$

Which gives us that

$$\ln Z = -\ln(N!) + N\ln\left(\frac{V}{\hbar^3}\left(\frac{mT}{2\pi}\right)^{3/2}\right) \tag{4.67}$$

Recall Stirling's formula, For large N:

$$N! = \sqrt{2\pi N}N^N e^{-N}\cdot\mathcal{O}\left(e^{\frac{1}{2N}}\right) \tag{4.68}$$

Therefore, solving for f, we have

$$-\ln(N!) = N\ln\left(\frac{1}{N}\right) + N + \text{slowly scaling, non-contributing terms} \tag{4.69}$$

$$-\ln Z = -N\left(\ln\left(\frac{V}{N\hbar^3}\left(\frac{mT}{2\pi}\right)^{3/2}\right)+1\right) \tag{4.70}$$

$$\beta f V = N\left(\ln\left(n\hbar^3\left(\frac{2\pi}{mT}\right)^{3/2}\right)-1\right) \tag{4.71}$$

$$f = nT\left(\ln\left(n\hbar^3\left(\frac{2\pi}{mT}\right)^{3/2}\right)-1\right) \tag{4.72}$$

Now f has become intensive, Gibbs was right about the indistiguishability, without knowing anything about the quantum mechanical property of indistinguishable particles. Now that f is intensive, we can solve for the entropy. We know that $f = u - Ts$, and from Equation 4.59, that $u = \frac{3}{2}nT$.

$$s = \frac{u-f}{T} \tag{4.73}$$

$$= \frac{nT\left(\frac{3}{2} - \ln\left(n\hbar^3\left(\frac{2\pi}{mT}\right)^{3/2}\right)+1\right)}{T} \tag{4.74}$$

$$= n\left(\frac{5}{2} - \ln\left(n\hbar^3\left(\frac{2\pi}{mT}\right)^{3/2}\right)\right) \tag{4.75}$$

$$= n\left(\ln\left(n\hbar^3\left(\frac{mT}{2\pi}\right)^{3/2}\right)+\frac{5}{2}\right) \tag{4.76}$$

$$= n\left(\ln\left(\left(\frac{mT}{2\pi\hbar^2 n^{2/3}}\right)^{3/2}\right)+\frac{5}{2}\right) \tag{4.77}$$

$$= n\left(\frac{3}{2}\ln\left(\frac{mT}{2\pi\hbar^2 n^{2/3}}\right)+\frac{5}{2}\right) \tag{4.78}$$

We can replace T with $\frac{2}{3}\frac{u}{n}$ to retrieve the Sackur-Tetrode formula:

$$s = n\left(\frac{3}{2}\ln\left(\frac{2mu}{3\hbar^2 n^{5/3}}\right)+\frac{5}{2}\right) \tag{4.79}$$

4.5.1 Mixing Entropy

We now encounter a philosophical issue: is it meaningful to ask what s “really is”? Classically, recall that $\hbar$ is arbitrary. Note that if we take a quantum ideal gas to the classical limit we retrieve $\frac{1}{N!}$. Suppose we have a box, with a wall separating it into two parts, with equal volumes, $V/2$. On the left side, we have blue particles, and on the right side we have red particles. Suppose that we have the same density of particles on each side. Also assume that the red particles and blue particles are created equal in all things other than their color. They have the same density on each side of the box:

$$n_{\text{blue}} = n_{\text{red}} = n \qquad\qquad V_{\text{blue}} = V_{\text{red}} = \frac{V}{2} \tag{4.80}$$

We can compute the entropy density on either side, and then we remove the wall and allow the system to evolve for some amount of time. Does the system have the entropy as it did prior to the evolution? Intuitively, the starting state seems more ordered than the ending state, and thus we expect the entropy to have increased. However, we note that if we ignore the color, the entropy should be the same. Is it meaningful to say that the starting system has less entropy than the evolved system? If we know that we will never look at the color, then it isn’t really meaningful to say that the entropy has increased, but if we do look at color, then it does make sense to say that the entropy has increased. How much does the entropy increase by? Let us first compute the entropy of the system in its starting state, when the two species are separated:

$$\begin{align} S_{\text{separated}} &= S_{\text{blue}} + S_{\text{red}} \tag{4.81}\\ &= \frac{V}{2}\left[n\left(\frac{3}{2}\ln\left(\frac{mT}{2\pi\hbar^2 n^{2/3}}\right)+\frac{5}{2}\right)+n\left(\frac{3}{2}\ln\left(\frac{mT}{2\pi\hbar^2 n^{2/3}}\right)+\frac{5}{2}\right)\right] \tag{4.82}\\ &= Vn\left(\frac{3}{2}\ln\left(\frac{mT}{2\pi\hbar^2 n^{2/3}}\right)+\frac{5}{2}\right) \tag{4.83}\end{align}$$

This is the same as if the two particles were a single species uniformly distributed. What happens when the wall is removed and the species mix?

$$\begin{align} n_{\text{blue}} = n_{\text{red}} &\to \frac{n}{2} \tag{4.84}\\ V_{\text{blue}} = V_{\text{red}} &\to V \tag{4.85}\end{align}$$

Now computing the entropy of the mixed system:

$$\begin{align} S &= S_{\text{blue}} + S_{\text{red}} \tag{4.86}\\ &= V\left[\frac{n}{2}\left(\frac{3}{2}\ln\left(\frac{mT}{2\pi\hbar^2\left(\frac{n}{2}\right)^{2/3}}\right)+\frac{5}{2}\right)+\frac{n}{2}\left(\frac{3}{2}\ln\left(\frac{mT}{2\pi\hbar^2\left(\frac{n}{2}\right)^{2/3}}\right)+\frac{5}{2}\right)\right] \tag{4.87}\\ &= Vn\left(\frac{3}{2}\ln\left(\frac{mT}{2\pi\hbar^2 n^{2/3}}\right)+\frac{5}{2}+\ln 2\right) \tag{4.88}\end{align}$$

We see that by removing the wall, the entropy increases by $\Delta S = Vn\ln 2$. This is known as the Gibbs mixing entropy. It makes sense that the entropy has increased; the system is more disordered, but only because we chose to look at the color labels. This generalizes to more than just 2 species of particles:

$$\Delta S = nV\ln\left(N_{\text{species}}\right) \tag{4.89}$$

As an aside, we can also compute the specific heat:

$$c_V = \frac{\partial u}{\partial T}\Big|_V \tag{4.90}$$

For our classical gas with no relevant internal degrees of freedom, which has $u = 3/2nT$, we find:

$$\begin{align} c_V &= \frac{\partial u}{\partial T}\Big|_V \tag{4.91}\\ &= \frac{3}{2}n \tag{4.92}\end{align}$$

What if I keep the pressure constant? In that case as I raise the temperature, the system expands, and work is done which adds to Δu. The work done per unit of initial value is $P\frac{\Delta V}{V}$. To find ΔV use $P\Delta V = nV\Delta T$. This recovers $c_P = c_V + 1$.

4.6 Virial Expansion

Before turning to ideal quantum gases, let us consider a non-ideal classical gas. As we have seen, the equation of state for an ideal gas is $P = nT$. This works for low density, since we have assumed that the particles do not interact. What happens if the density is low but not extremely low? Consider the natural expansion, or virial expansion:

$$P = T\left(n + B_2(T)n^2 + B_3(T)n^3 + \cdots\right) \tag{4.93}$$

The functions $B_i(T)$ are called the virial coefficients. How do we compute them? A general scheme was developed by Joseph and Maria Goeppert Mayer. The basic scheme is known as the "cluster expansion". Each term in the expansion deals with clusters of a certain number of particles. The first term, the ideal gas law, is based on a single particle, B_2 is based on clusters of two particles, B_3 clusters of 3 particles, etc. The Mayers developed a graphical approach to this. The results for B_2 are simple, but the expansion gets very complicated as i increases:

$$\begin{align} B_2(T) &= V\left(\frac{1}{2} - \frac{Z_2}{Z_1^2}\right) = -2\pi\int dr\, r^2\left(e^{-\beta a(r)} - 1\right) \tag{4.94}\\ B_3 &= V^2\left(2\frac{Z_2}{Z_1^2}\left(2\frac{Z_2}{Z_1^2} - 1\right) - \frac{1}{3}\left(6\frac{Z_3}{Z_1^3} - 1\right)\right) = \cdots \tag{4.95}\end{align}$$

Where Z_2 is the partition function for two particles in a box, Z_1 is the partition function for one particle in a box, and $a(r)$ is the potential between the particles, which goes to zero as $r \to \infty$. For simplicity we will only present the derivation of B_2. The derivation begins with the Grand Partition function:

$$\begin{align} \mathcal{Z} &= \sum_N e^{\beta\mu N} Z_N \tag{4.96}\\ &= \sum_N \lambda^N Z_N \tag{4.97}\end{align}$$

where $\lambda = e^{\beta\mu}$ is the fugacity. Let us expand in terms of λ. Prior to this, let us note the relationship between the grand partition function and the grand potential:

$$\mathcal{Z} = e^{-V\phi\beta} \tag{4.98}$$

$$= e^{VP\beta} \tag{4.99}$$

Which, via a logarithm of both sides, implies:

$$\ln \mathcal{Z} = VP\beta \tag{4.100}$$

Dilute systems have low fugacity, since the chemical potential is large and negative. Expanding $\mathcal{Z}$ in powers of λ:

$$\mathcal{Z} = \sum_N \lambda^N Z_N \tag{4.101}$$

$$= (1+\lambda Z_1)\left(1+\frac{\lambda^2 Z_2}{(1+\lambda Z_1)}\right)\left(1+\frac{\lambda^3 Z_3}{(1+\lambda Z_1)\left(1+\frac{\lambda^2 Z_2}{(1+\lambda Z_1)}\right)}\right)(1+\cdots) \tag{4.102}$$

$$\tag{4.103}$$

Now taking the logarithm:

$$\ln \mathcal{Z} = \ln(1+\lambda Z_1) + \ln\left(1+\frac{\lambda^2 Z_2}{(1+\lambda Z_1)}\right) + \cdots \tag{4.104}$$

$$= \left(\lambda Z_1 - \frac{1}{2}\lambda^2 Z_1^2\right) + \lambda^2 Z_2 + O(\lambda^3) \tag{4.105}$$

Now utilizing Eqn. 4.100, to second order in λ, we have

$$VP\beta = \lambda Z_1 + \lambda^2\left(Z_2 - \frac{1}{2}Z_1^2\right) \tag{4.106}$$

Looking at just the first order term:

$$\beta PV = \lambda Z_1 \tag{4.107}$$

If we now leverage the ideal gas law (4.55), we have that $PV\beta = N$, so to lowest order in λ, we have that

$$\lambda = \frac{N}{Z_1} \tag{4.108}$$

If we insert this into Eqn. 4.106, we have

$$\beta PV = \frac{NZ_1}{Z_1} - \left(\frac{N^2}{Z_1^1}\right)\left(\frac{1}{2}Z_1^2 - Z_2^2\right) + \cdots \tag{4.109}$$

We can now isolate the pressure:

$$P = T\left(\left(\frac{N}{V}\right) - \left(\frac{N}{V}\right)^2\left(V\left(\frac{1}{2} - \frac{Z_2}{Z_1^2}\right)\right) + \cdots\right) \tag{4.110}$$

$$\tag{4.111}$$

And we can see that this takes the exact form of the virial expansion (4.93), which allows us to match terms and extract B_2:

$$B_2 = V\left(\frac{1}{2} - \frac{Z_2}{Z_1^2}\right) \tag{4.112}$$

As advertised.

Note that for an ideal gas, $\frac{Z_2}{Z_1^2} = \frac{1}{2}$, which gives us that $B_2 = 0$; similarly for higher orders in the expansion. This justifies the fugacity expansion for the cluster expansion. So the problem of finding B_2 for a non-ideal gas is reduced to the problem of finding Z_2.

We can write out our Hamiltonian, which has a kinetic energy term for each particle, and then an interaction term between every pair of particles, and potentially 3-body and higher forces:

$$H = \sum_i T_i + \frac{1}{2} \sum_{j \neq k} V_{jk} + \cdots \tag{4.113}$$

Note the $\frac{1}{2}$ in the two-body term, this ensures we do not double count the interactions.

Z_1 only involves the kinetic energy. Z_2 involves both kinetic and potential energies. For simplicity, consider a classical gas with one species and central forces independent of spin, $V_{ij} = u|\boldsymbol{r}_i - \boldsymbol{r}_j|$. We can write out Z_2:

$$\begin{aligned} Z_2 &= \frac{1}{2} \int \mathrm{d}^3q_1\, \mathrm{d}^3q_2\, \mathrm{d}^3p_1\, \mathrm{d}^3p_2\, \exp\left(-\beta \left(\frac{1}{2m}\left(p_1^2 + p_2^2\right) + u|\boldsymbol{q}_1 - \boldsymbol{q}_2|\right)\right) && (4.114) \\ &= \frac{1}{2} \int \mathrm{d}^3p_1\, e^{-\beta \frac{p_1^2}{2m}} \int \mathrm{d}^3p_2\, e^{-\beta \frac{p_2^2}{2m}} \int \mathrm{d}^3q_1\, \mathrm{d}^3q_2\, \exp\left(-\beta u|\boldsymbol{q}_1 - \boldsymbol{q}_2|\right) && (4.115) \\ &= \frac{1}{2}\left(\frac{Z_1}{V}\right)^2 \int \mathrm{d}^3q_1\, \mathrm{d}^3q_2\, e^{-\beta u|\boldsymbol{q}_1 - \boldsymbol{q}_2|} && (4.116) \end{aligned}$$

Now the q integrals are bounded by the volume of the box, and the boundary conditions $u(r) \to 0$ as $r \to \infty$. To utilize both of these facts, we can rewrite our exponential:

$$e^{-\beta u|\boldsymbol{q}_1 - \boldsymbol{q}_2|} = 1 + \left(e^{-\beta u|\boldsymbol{q}_1 - \boldsymbol{q}_2|} - 1\right) \tag{4.117}$$

With this, we can rewrite our integral:

$$\int \mathrm{d}^3q_1\, \mathrm{d}^3q_2\, e^{-\beta u|\boldsymbol{q}_1 - \boldsymbol{q}_2|} = \int \mathrm{d}^3q_1\, \mathrm{d}^3q_2\, 1 + \int \mathrm{d}^3q_1\, \mathrm{d}^3q_2\, \left(e^{-\beta u|\boldsymbol{q}_1 - \boldsymbol{q}_2|} - 1\right) \tag{4.118}$$

This first integral is just V^2, and for the second integral, we can do a change of variables to relative coordinates, $\boldsymbol{q} = \frac{1}{2}(\boldsymbol{q}_1 + \boldsymbol{q}_2)$, $\boldsymbol{r} = \boldsymbol{q}_1 - \boldsymbol{q}_2$:

$$Z_2 = \frac{1}{2}\left(\frac{Z_1}{V}\right)^2 \left[V^2 + V \int d^3r\, \left(e^{-\beta u(\boldsymbol{r})} - 1\right)\right] \tag{4.119}$$

From this, we can look at Z_2/Z_1^2:

$$\frac{Z_2}{Z_1^2} = \frac{1}{2} + \frac{1}{2}\frac{1}{V} \int d^3r\, \left(e^{-\beta u(\boldsymbol{r})} - 1\right) \tag{4.120}$$

Now inserting what we have found into the expression for B_2 (4.112):

$$\begin{aligned} B_2 &= V\left(\frac{1}{2} - \frac{Z_2}{Z_1^2}\right) && (4.121) \\ &= \frac{1}{2} \int d^3r\, \left(e^{-\beta u(\boldsymbol{r})} - 1\right) && (4.122) \end{aligned}$$

Since $u(\boldsymbol{r})$ falls to 0 out to infinity, and falls off well within the scale of the box, we can integrate to infinity:

$$B_2 = -2\pi \int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right) \tag{4.123}$$

Note that we have implicitly used the polar Jacobian ($d^3r = 4\pi r^2\, dr$). What does this result mean? It implies that pairs of particles will spend more time near places where $u(r)$ is attractive and will stay away from places where it is repulsive.

We can look at a simple example, the hard sphere gas, the atoms in the gas only interact when the spheres are colliding:

$$u(r) = \infty \cdot \Theta(2R - r) \tag{4.124}$$

This is essentially saying that the closest the centers of two spheres can get is $2R$, they stop each other from getting any closer. We can now compute the B_2 coefficient for this gas:

$$\begin{aligned} B_2 &= -2\pi \int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right) && (4.125)\\ &= \frac{16\pi}{3} R^3 && (4.126) \end{aligned}$$

Which gives us what is known as the excluded volume correction:

$$P = nT\left(1 + \frac{16\pi}{3}R^3 n + \dots\right) \tag{4.127}$$

This can be thought of as saying that part of the system's volume is not available.

Up until now we have neglected quantum effects in our gas. But at low temperatures, quantum effects matter. Recall that in quantum mechanics, there are physical effects due to indistinguishability of particles. The relevant regime for quantum effects is based on the thermal de Broglie wavelength, also known as the thermal wavelength λ_{Th}:

$$\lambda_{\text{Th}} = \sqrt{\frac{2\pi}{mT}} \tag{4.128}$$

Quantum effects are important for our system if $n\lambda_{\text{Th}} > 1$. Let us consider the second virial coefficient for a gas of bosons. This expansion is valid for low n and high T:

$$P = nT(1 + B_2 n + B_3 n^2 + \cdots), \qquad B_2 = V\left(\frac{1}{2} - \frac{Z_2}{Z_1^2}\right)$$

The derivation is the same for classical and quantum gases, Z_1 and Z_2 are again partition functions for 1 and 2 particles. To find the partition functions, we will use a finite box and sum over the modes. Z_1 is easy to find:

$$Z_1 = \sum_i e^{-\beta E_i} \tag{4.129}$$

Finding Z_2 requires knowledge of two particle states. Note that these states are symmetric, so we have to separate them correctly. Looking at an arbitrary two particle state, we have two cases, the first is when they occupy two separate modes, $|i, j\rangle$, and the energy of such a state is the energy of the two modes, $E = E_i + E_j$. Note that this state is only counted once, since it is symmetric under exchange of the two particles. The two particles can also be in the same mode, $|2k\rangle$, in which case the energy is twice the energy of the mode, $E = 2E_k$. This state is also counted once, since it is identical under exchange. We can then compute the two particle partition function:

$$\begin{aligned} Z_2 &= \sum_k e^{-2\beta E_k} + \sum_i \sum_{j>i} e^{-\beta E_i + E_j} && (4.130) \\ &= \frac{1}{2}\sum_{i,j} e^{-\beta(E_i+E_j)} + \frac{1}{2}\sum_k e^{-2\beta E_k} && (4.131) \end{aligned}$$

Now we can note that the first summation is two independent summations:

$$\begin{aligned} Z_2 &= \frac{1}{2}\left(\sum_i e^{-\beta E_i}\right)\left(\sum_j e^{-\beta E_j}\right) + \frac{1}{2}\sum_k e^{-2\beta E_k} && (4.132) \\ &= \frac{1}{2}Z_1^2 + \frac{1}{2}\sum_k e^{-2\beta E_k} && (4.133) \end{aligned}$$

Now that we have the two-particle partition function, we can compute the second virial coefficient B_2:

$$\begin{aligned} B_2 &= V\left(\frac{1}{2} - \frac{Z_2}{Z_1^2}\right) && (4.134) \\ &= -\frac{1}{2}\frac{\int d^3k e^{-2\beta\frac{k^2}{2m}}}{\left(\int d^3k e^{-\beta\frac{k^2}{2m}}\right)^2} && (4.135) \end{aligned}$$

Where we have taken the thermodynamic limit:

$$\sum_k \to V\int \frac{d^3k}{(2\pi)^3} \tag{4.136}$$

Doing some change of variables, if we let $x^2 = \frac{\beta k^2}{m}$, then $k = x\sqrt{mT}$, and $d^3k = d^3x\,(mT)^{3/2}$. The virial coefficient is then:

$$\begin{aligned} B_2 &= -\frac{1}{2}\frac{(2\pi)^3}{(mT)^{3/2}}\frac{\int_0^\infty 4\pi x^2 e^{-x}\,dx}{\left(\int_0^\infty 4\pi x^2 e^{-\frac{x}{2}}\,dx\right)^2} && (4.137) \\ &= -\frac{\pi^{3/2}}{2(mT)^{3/2}} && (4.138) \end{aligned}$$

From this, we can write down the pressure using the second order virial expansion:

$$P = nT\left(1 - \frac{\pi^{3/2}}{2(mT)^{3/2}}n\right) + \mathcal{O}(n^3) \tag{4.139}$$

There are analogous expansions for u, f, s, and other variables of interest.

4.7 Bose Gases

Consider an ideal gas of bosons. What is the best formalism to do this? For the ideal classical gas, we used the canonical ensemble. In this case, we will instead use the grand canonical formulation, which introduces a chemical potential, μ. The next problem is how we should do it. For the classical case, we used phase space. For the Bose gas, we will solve the 1 particle Schrodinger equation for a particle in a box. We impose periodic boundary conditions, because we can always take the thermodynamic limit and make the box very large, and the states near the wall make a tiny fraction of the total states. We are allowed to do the 1 particle equation because we assumed it was an ideal gas, there is no interaction between particles.

Note that the energy spectrum for the particle in a box is discrete, as long as the box is of finite volume. We have discrete energy levels, E_i, which we will refer to as modes. In each mode, we can stick as many bosons as we want. Let us look at a particular mode, mode i. The Hilbert space for this mode is given by $|0\rangle, |1\rangle, |2\rangle$, etc. Note that there is only 1 state with each number of particles as the particles are indistinguishable. Then

$$\hat{H}|0\rangle = 0, \quad \hat{H}|1\rangle = E_i, \quad \hat{H}|2\rangle = 2E_i, \quad \cdots$$

Hence $\hat{H}|n\rangle = nE_i|n\rangle$, similar to the harmonic oscillator, in fact, this is exactly the energy spectrum of the harmonic oscillator (2.232), with the zero point energy removed.

So let us write out the grand partition function for the ith mode:

$$\begin{aligned}
\mathcal{Z}_i &= \mathrm{Tr}_i\left[e^{-\beta(\hat{H}-\mu\hat{N})}\right] && (4.140)\\
&= \sum_{N_1=0}^{\infty} e^{-\beta N_i(E_i-\mu)} && (4.141)\\
&= \sum_{N_1=0}^{\infty}\left(e^{-\beta(E_i-\mu)}\right)^{N_i} && (4.142)\\
&= \frac{1}{1-e^{-\beta(E_i-\mu)}} && (4.143)\\
&= \frac{1}{1-e^{\beta(\mu-E_i)}} && (4.144)
\end{aligned}$$

Where Tr_i is a trace over the Hilbert space of the ith mode. Note that we used the geometric series, which only converges if $E_i - \mu$ is positive (where we assume that β is positive.) If E_0 is the ground state, we can set it to 0, since we can always shift it because all we care about are relative energy differences. This tells us that $\mu < 0$. This is a very important result, and will greatly constrain what we can do.

Now expanding this partition function to all modes:

$$\mathcal{Z} = \prod_i \mathcal{Z}_i \tag{4.145}$$

Now let us ask some simple questions. We can ask what the probability is for the occupation number to be N_i:

$$P(N_i) = \frac{\exp\left(-\beta N_i\left(E_i-\mu\right)\right)}{\mathcal{Z}_i} \tag{4.146}$$

$$= \exp\left(-\beta N_i(E_i - \mu)\right)\left(1 - \exp\left(-\beta(E_i - \mu)\right)\right) \tag{4.147}$$

We can then compute the expectation value of the occupation number, $\langle N_i \rangle$:

$$\begin{aligned} \langle N_i \rangle &= \sum_{N_i} P(N_i) N_i \\ &= \sum_{N} N_i e^{-\beta N_i (E_i - \mu)} \left(1 - e^{-\beta(E_i - \mu)}\right) \\ &= \frac{1}{e^{\beta(E_i - \mu)} - 1} \end{aligned} \tag{4.148}$$

This is known as the Bose distribution.

We expect this to act like a classical system in the high temperature limit, and we expect N_i to be low. Looking at the Bose distribution, when we go to high temperature:

$$N_i = \frac{1}{(1 + \beta(E_i - \mu) + \cdots) - 1} \tag{4.149}$$

$$\approx \frac{1}{\beta(E_i - \mu)} \tag{4.150}$$

This is large! Conversely, when we go to low temperatures, we find that N_i goes to 0! This is the opposite of what we expect! Something is wrong here. The issue is that we have assumed that μ is fixed. Instead, the classical limit can be achieved correctly by expanding in terms of fixed fugacity, which we will see in Section 4.7.1.

What is the maximum occupation if we have a fixed temperature? Well, by the Bose distribution (4.148), $\mu = 0$, since that is the largest we can make μ, since $\mu < 0$. This actually creates a paradox, which can be found by looking at the energy. Consider U_i, the energy of the ith mode:

$$U_i = E_i \langle N_i \rangle \tag{4.151}$$

$$= \frac{E_i}{e^{\beta(E_i - \mu)} - 1} \tag{4.152}$$

We can now look at the grand potential:

$$\beta \Phi_G = \ln \mathcal{Z}_i \tag{4.153}$$

$$= T \ln\left(1 - e^{-\beta(E_i - \mu)}\right) \tag{4.154}$$

$$= U_i - \mu N_i - TS \tag{4.155}$$

If we want to look at all modes, we can just sum over i:

$$E = \sum_i E_i \tag{4.156}$$

$$S = \sum_i S_i \tag{4.157}$$

$$N = \sum_i N_i \tag{4.158}$$

$$\tag{4.159}$$

We can replace the summations with an integral to move to the thermodynamic limit:

$$\sum_i \to V \int \frac{d^3k}{(2\pi)^3} \tag{4.160}$$

And we replace the energy with the kinetic energy:

$$E_i \to \frac{k^2}{2m} \tag{4.161}$$

With these two substitutions, let us look on the total particle number. The number density is given by

$$\begin{aligned} n &= \frac{\langle N \rangle}{V} \\ &= \int \frac{d^3k}{(2\pi)^3} \frac{1}{\exp\left(\beta\left(\frac{k^2}{2m} - \mu\right)\right) - 1} \\ &= \int_0^\infty \frac{dk}{2\pi^2} \frac{k^2}{e^{\beta\left(\frac{k^2}{2m} - \mu\right)} - 1} \end{aligned} \tag{4.162}$$

Note that

$$\int d^3k \to \int_0^K dk\, 4\pi k^2 \tag{4.163}$$

since it is a function of $|\boldsymbol{k}|$ only.

Now what is the highest density we can get? Recall that $\mu \leq 0$. $n_{\max}(\beta)$ occurs for $\mu = 0$ (large $-\mu$ makes n smaller):

$$n_{\max} = \int_0^\infty \frac{dk\, k^2}{2\pi^2} \frac{1}{e^{\beta \frac{k^2}{2m}} - 1} \tag{4.164}$$

This is a convergent integral, since the exponential in the denominator kills off the quadratic growth of k^2. This presents a problem, since it means that we have a maximum number of particles in the box. What happens when we have that maximum and we add more particles?

The issue is when we converted the summation to the integral. The issue is that the maximum number that the ground state can fit is actually ∞, but we don't take that into account because the integral weights it as 0. Thus the true number of particles is this integral, plus the number in the ground state. This is where Bose-Einstein condensates come from, when we have macroscopic occupations of the ground state.

Let us compute the convergent integral. We can first do a change of variables, and then solve the resulting integral however we'd like (ask a graduate student, do it numerically, ask Mathematica). Let us first do the change of variables. Let us define $y = \frac{1}{\sqrt{2mT}}$. From this, $k = \sqrt{2mTy}$, and we can rewrite our integral:

$$n_{\max} = (2mT)^{3/2} \int_0^\infty dy\, \frac{y^2}{2\pi^2 \left(e^y\right) - 1} \tag{4.165}$$

We see that all the dimensionful quantities are out of the integral, and we can compute the integral however we would like:

$$n_{\text{max}} = (2mT)^{3/2} \frac{\zeta\left(\frac{3}{2}\right)}{8\pi^{3/2}} \tag{4.166}$$

Where $\zeta(x)$ is the Riemann zeta function, and is defined as $\zeta(x) = \sum_{n=1}^{\infty} \frac{1}{n^x}$.

This just gives us a number, leaving us with:

$$n_{\text{max}} = (mT)^{3/2} \, (0.165869) \tag{4.167}$$

We can cram an arbitrarily large number of particles into just the ground state, once each excited mode is full to n_{max}, the rest of the added particles must go into the ground state mode (assuming that the particles are not interacting). This is Bose-Einstein condensation.

One can think of a Bose Einstein condensate in two ways. At fixed T this is a "phase transition" as a function of density:

$$n_{crit} = (mT)^{3/2} \frac{\xi\left(\frac{3}{2}\right)}{(2\pi)^{3/2}} \approx (mT)^{3/2}(.165869)$$

i.e. it is a low density phase. At any density higher than n_{crit}, the system is in a Bose-Einstein condensate phase. The other way of thinking about this transition is fixing the density and increasing the temperature:

$$\begin{aligned} T_c &= \frac{2\pi}{m} \left(\frac{n}{\xi\left(\frac{3}{2}\right)} \right)^{2/3} \\ &= \frac{2\pi}{\left(\xi\left(\frac{3}{2}\right)\right)^{2/3}} \frac{n^{2/3}}{m} \\ &\approx 3.3125 \left(\frac{n^{2/3}}{m} \right) \end{aligned} \tag{4.168}$$

Recall that the thermal wavelength (4.128) is given by $\lambda_{\text{Th}} = \sqrt{\frac{2\pi}{mT}}$, so we can define λ_c, the thermal wavelength at T_c, is

$$\lambda_c = \left(\frac{\xi\left(\frac{3}{2}\right)}{n} \right)^{1/3}$$

or $n\lambda_c^3 = \xi\left(\frac{3}{2}\right)$. As advertised, profound quantum effects occur when $n\lambda_T^3 \sim O(1)$. If $\lambda > \lambda_c$, the system Bose condenses. Before it does so, the Bose gas is qualitatively different from a classical gas.

Let us look at the density of condensed particles, $n_0(T)$:

$$n_0(T) = \begin{cases} 0 & n < n_{\text{crit}} \\ n - n_{\text{crit}} & n > n_{\text{crit}} \end{cases} \tag{4.169}$$

Let us define the fraction of condensed bosons, we want to know how many of the bosons in the box are in the ground state:

$$\frac{n_0}{n} = \frac{n - n_{\text{crit}}}{n}$$

$$= 1 - \frac{n_{\text{crit}}}{n} \tag{4.170}$$

This number is always finite, this is a macroscopic quantum effect. Some other examples of macroscopic quantum phenomena include superfluidity and superconductivity.

4.7.1 Classical Limit

Now let us attempt to (correctly) obtain the classical ideal gas from the Bose gas. Previously, we looked at the Bose distribution (4.148) in the limit of high T, and found that we had large occupation, and when we went to low T, we found that N_i went to zero. To correctly obtain the classical ideal gas, we need to look at fixed fugacity instead. It turns out that small fugacity $\phi = e^{-\beta\mu}$ corresponds to the classical limit. To see this, let us first note that for low density (dilute) systems, μ is large and negative. If we fix β, and look at large and negative μ, then $-\mu \gg E_i$, and the fugacity is the dominant term, and $\langle N_i \rangle \ll 1$. In this case, we can look at the number density:

$$\begin{aligned} n(\beta,\mu) &= \int_0^\infty \frac{k^2\,dk}{2\pi^2}\frac{1}{e^{\beta\left(\frac{k^2}{2m}-\mu\right)}-1} \\ &\to \int_0^\infty \frac{k^2\,dk}{2\pi^2}e^{-\beta\left(\frac{k^2}{2m}-\mu\right)} \\ &= \frac{(2mT)^{3/2}}{\pi^2}e^{\beta\mu} \end{aligned} \tag{4.171}$$

From this, we can compute the energy density, $u = \sum_{\text{modes}} E_i N_i$:

$$\begin{aligned} u &= \int_0^\infty dk\,\frac{k^2}{2m}\frac{k^2}{2\pi^2}e^{-\beta\left(\frac{k^2}{2m}-\mu\right)} \\ &= \left(-\frac{\partial}{\partial\beta}n + \mu n\right) \\ &= -\frac{\partial}{\partial\beta}\left(\frac{e^{\beta\mu}}{\pi^2}(2mT)^{3/2}\right) + \mu n \\ &= -\mu\frac{e^{\beta\mu}}{\pi^2}(2mT)^{3/2} + \frac{3}{2}\frac{1}{\beta}\frac{e^{\beta\mu}}{\pi^2}(2mT)^{3/2} + \mu n \\ &= -\mu n + \frac{3}{2}nT + \mu n \\ &= \frac{3}{2}nT \end{aligned} \tag{4.172}$$

This is precisely the classical result! One can similarly show that $P = nT$ for dilute Bose gases by taking the low density limit of ϕ_G:

$$\Phi_{Gi} = T\ln(1 - e^{-\beta(E_i-\mu)}) \tag{4.173}$$

To do this, we can integrate:

$$\Phi_G = V\int \frac{d^3k}{(2\pi)^3}T\ln\left(1 - e^{-\frac{k^2}{2m}\beta+\beta\mu}\right) \tag{4.174}$$

If we now expand the logarithm, and divide by V to get ϕ_G:

$$\phi_G = -T\int \frac{d^3k}{(2\pi)^3}\left(e^{-\beta\left(\frac{k^2}{2m}-\mu\right)}\right) \tag{4.175}$$

Now noting that this integral is just the expression we have for n, and using the relation between ϕ_G and P, we have that

$$P = nT \tag{4.176}$$

Which is the classical equation of state.

4.7.2 Photon Gases

Consider a gas of photons, which have no chemical potential ($\mu = 0$), have no mass ($m = 0$), and move at the speed of light $v = c$. Photons have two possible polarizations (linear and circular), and satisfy the energy relation:

$$\begin{aligned} E_i &= c|\boldsymbol{p}| \qquad (4.177)\\ &= c\hbar|\boldsymbol{k}| \qquad (4.178)\\ &= |\boldsymbol{k}| \qquad (4.179) \end{aligned}$$

Looking at one mode in the gas, we have that

$$\begin{aligned} N_i &= \frac{1}{e^{\beta(E_i-\mu)} - 1} \qquad (4.180)\\ &= \frac{1}{e^{\beta|\boldsymbol{k}_1|} - 1} \qquad (4.181) \end{aligned}$$

Now relating the occupation to the energy:

$$\begin{aligned} U &= \sum_i E_i N_i \qquad (4.182)\\ &= \sum_i |\boldsymbol{k}_i| N_i \qquad (4.183) \end{aligned}$$

In summing over the modes, remember for each k_i there are two modes, one for each of the 2 polarizations. We replace $\sum_i$ with $Vg\int \frac{d^3k}{(2\pi)^3}$ to move to the thermodynamic limit. $g = 2$ is a degeneracy factor accounting for the 2 modes:

$$U = V\left(2\int \frac{d^3k}{(2\pi)^3}\frac{k}{e^{\beta|\boldsymbol{k}|} - 1}\right) \tag{4.184}$$

Which gives the energy density:

$$u = \int \frac{dk}{\pi^2}\frac{k^3}{e^{\beta k} - 1} \tag{4.185}$$

Now, it is more convenient to think in terms of ω instead of k, but $\omega = k$, so this is a simple change:

$$u = \int d\omega\, u(\omega, T) \tag{4.186}$$

Where

$$u(\omega, T) = \frac{\omega^3}{\pi^2\left(e^{\beta\omega} - 1\right)} \tag{4.187}$$

This is Planck's black body spectrum written in units with $\hbar = c = 1$ and in terms of ω rather than frequency. $u(\omega, T)\Delta\omega$ is the energy density contained in an angular frequency bin of width $\Delta\omega$. If we integrate this from $\omega = 0$ out to infinity:

$$u = \int_0^\infty d\omega \frac{\omega^3}{\pi^2 \left(e^{\beta\omega} - 1\right)} \tag{4.188}$$

To solve this, we can do a change of variables and let $y = \beta\omega$, so that $\omega = Ty$. This gives us the integral:

$$u = T^4 \int_0^\infty \frac{dy}{\pi^2} \frac{y^3}{e^y - 1} \tag{4.189}$$

$$= \frac{\pi^2}{15} T^4 \tag{4.190}$$

Note that T^4 was obvious on dimensional grounds with units $\hbar = c = k = 1$. This is because u has dimensions of energy per unit volume, which in natural units is temperature per inverse temperature cubed, giving T^4. Note that T is the only dimensionful parameter in our theory. If one did classical Maxwell theory instead of looking at photons, $n(\omega, T)$ becomes the high T version:

$$n(\omega, T) = \frac{\omega^3}{\pi^2 \left(e^{\beta\omega} - 1\right)} \underset{\text{classical}}{\longrightarrow} \frac{\omega^3}{\pi^2 \beta\omega} = \frac{T\omega^2}{\pi^2}$$

From which we can find the classical energy density:

$$u_{\text{classical}}(T) = \int_0^\infty d\omega \, u_{\text{classical}}(\omega, T) \tag{4.191}$$

$$= \int_0^\infty d\omega \frac{T\omega^2}{\pi^2} \tag{4.192}$$

$$= \infty \tag{4.193}$$

This is the ultraviolet catastrophe, and is precisely why QM was invented!

4.7.3 Phonons

Crystalline solids have vibrations, which we can naively model as a square lattice, where each site is connected to its neighbor sites via a spring, as shown in Figure 4.2.

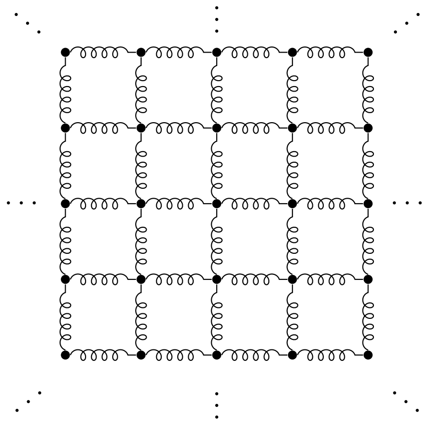


Figure 4.2: Two dimensional lattice of coupled harmonic oscillators.

On this lattice, we can have classical collective modes of oscillation characterized by a wave number $\boldsymbol{k}$ and a dispersion relation $\omega(\boldsymbol{k})$. Each of these modes is basically a harmonic oscillator. Working quantum mechanically, we can look at a single mode, whose partition function is of the form:

$$Z_i = \sum_n e^{-\beta\omega_i(n+\frac{1}{2})} \tag{4.194}$$

$$= e^{-\beta\omega_i/2}\frac{1}{1-e^{-\beta\omega_i}} \tag{4.195}$$

We can compute the average energy of the mode, but to do that we will want $\ln Z_i$:

$$\ln Z_i = -\beta\omega_i/2 - \ln(1-e^{-\beta\omega_i}) \tag{4.196}$$

Which then allows us to compute the energy:

$$\langle E_i\rangle = -\frac{\partial \ln Z_i}{\partial\beta} \tag{4.197}$$

$$= \frac{\omega_i}{2} + \frac{\omega_i e^{-\beta\omega_i}}{1-e^{-\beta\omega_i}} \tag{4.198}$$

$$= \frac{\omega_i}{2} + \frac{\omega_i}{e^{\beta\omega_i}-1} \tag{4.199}$$

We can also leverage the fact that each mode is just a harmonic oscillator, and we know the spectrum of the harmonic oscillator (2.232). We can take averages of the energy spectrum:

$$\langle E_i\rangle = \omega_i\left(\langle N_i\rangle + \frac{1}{2}\right) \tag{4.200}$$

Therefore, combining our two computations for the average energy, we can solve for the average occupation of each mode:

$$\langle N_i\rangle = \frac{\omega_i}{e^{\beta\omega_i}-1} \tag{4.201}$$

This is exactly the same as the occupation number of a bosonic gas with $\mu = 0$! We see that we can think of phonons as bosonic "quasiparticles", they're not really particles, but the collective modes have the same behavior as the bosonic modes. The general dispersion relation for phonons is complicated, and has a ultraviolet (UV) cutoff. The UV cutoff is easiest to understand in a one dimensional lattice. In this case, only positions where $x = na$ are physical, where a is the lattice spacing and n is an integer. e^{ikna} are the only physical parts of the wave, with $-\pi < ka < \pi$ corresponding to distinct values. Outside of this range, we begin to cover the same points again; $k \to k + 2\pi/a$ is physically equivalent.

Phonons have the property that the dispersion relation $\omega(\boldsymbol{k})$ is linear in k for small k. This is a general feature of spontaneous symmetry breaking, crystals break translation symmetry. For small k,

$$\omega(\boldsymbol{k}) = v_s|\boldsymbol{k}| + \mathcal{O}(|\boldsymbol{k}|) \tag{4.202}$$

where v_s is the speed of sound. Note that in real materials, sound need not be isotropic, but it often is. For very low temperatures, the calculation is identical to the photon gas, but without the factor of 2 for polarizations, and we cannot use units where $c = 1$ (looking at longitudinal "sound" modes). Hence

$$u = \int d\omega u(\omega, T) \tag{4.203}$$

where

$$u(\omega, T) = \frac{\omega^3}{2v_s^3 \pi^2 \left(e^{\beta\omega} - 1\right)}$$

This is only valid for $\omega \ll \omega_{UV}$, where ω_{UV} is the frequency of the UV cutoff. For materials near room temperature, the UV cutoff dominates over the quantum cutoff. This derivation is identical to the photon gas derivation, both are examples of massless Bose gases with linear dispersion relations. The modelling of atomic vibrations as phonon excitations in a harmonic oscillator lattice is known as the Debye model.

Now let us finish up y computing the pressure in this model of phonons. To begin, we will look at the grand potential of a single mode:

$$\Phi_{G,i} = T \ln\left(1 - e^{-\beta(E_i - \mu)}\right) \tag{4.204}$$

In this case, $\mu = 0$, and $E_i = |\boldsymbol{k}_i|$, so we have that

$$\Phi_G = \sum_i T \ln\left(1 - e^{-\beta|\boldsymbol{k}_i|}\right) \tag{4.205}$$

We can take this to the thermodynamic limit:

$$\Phi_G = 2V \int \frac{d^3k}{(2\pi)^3} T \ln\left(1 - e^{-\beta|\boldsymbol{k}|}\right) \tag{4.206}$$

Note that this is equivalent to the Helmholtz free energy (since $\mu = 0$), so we have that

$$f = \frac{F}{V} \tag{4.207}$$

$$= \int \frac{dk}{\pi^2} k^2 T \ln\left(1 - e^{-\beta k}\right) \tag{4.208}$$

Once again changing variables to frequency, and then doing another change of variables, with $y = \beta\omega$:

$$f = T^4 \int_0^\infty \frac{dy}{\pi^2} y^2 \ln\left(1 - e^{-y}\right) \tag{4.209}$$

$$= -\frac{\pi^2}{45} T^4 \tag{4.210}$$

Note that again, we could have found the T^4 dependence just by dimensional analysis. Now that we have the free energy density, we can compute the entropy, by first relating the free energy to the internal energy:

$$f = -\frac{1}{3} u \tag{4.211}$$

And then noting that $f = u - Ts$, so

$$s = \frac{u - f}{T} \tag{4.212}$$

$$= \frac{4\pi^2}{45}T^3 \tag{4.213}$$

Once again, we could have intuited this from dimensional analysis. Finally, we can compute the pressure:

$$P = -\Phi_G \tag{4.214}$$

$$= -f \tag{4.215}$$

$$= \frac{\pi^2}{45}T^4 \tag{4.216}$$

4.8 Fermi Gases

Now looking at a gas of fermions, we have a derivation that is analogous to the derivation for Bose gases, we work in the grand canonical ensemble, focus on a single mode (which takes into account spin), and the Hilbert space for each mode has two states, either the mode is occupied or unoccupied. We can write out the grand partition function for the ith mode:

$$\mathcal{Z}_i = \mathrm{Tr}_i\left[e^{-\beta(H_i - \mu N)}\right] \tag{4.217}$$

$$= \left[1 + e^{-\beta(E_i - \mu)}\right] \tag{4.218}$$

Where the first term is the case where there is no particle in the mode, and the second term is when we have the mode full (for fermions we can only have a single particle in a mode). We can now look at the average occupation:

$$\langle N_i \rangle = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}_i}{\partial \mu} \tag{4.219}$$

$$= \frac{e^{-\beta(E_i - \mu)}}{1 + e^{-\beta(E_i - \mu)}} \tag{4.220}$$

$$= \frac{1}{e^{\beta(E_i - \mu)} + 1} \tag{4.221}$$

This is known as the Fermi-Dirac distribution. Comparing this to the Bose distribution (4.148), we see that the only difference is the sign in the denominator. We can compute the average energy of each mode:

$$\langle E_i \rangle = E_i \langle N_i \rangle \tag{4.222}$$

$$= \frac{E_i}{e^{\beta(E_i - \mu)} + 1} \tag{4.223}$$

We can now write down the grand potential for one mode:

$$\Phi_{G,i} = -T \ln \mathcal{Z}_i \tag{4.224}$$

$$= -T \ln\left(1 + e^{-\beta(E_i - \mu)}\right) \tag{4.225}$$

Recall that in the boson case, $\mu < 0$ was required for convergence. This is not true for the fermionic case, and can easily be understood by looking at $\langle N_i \rangle$ at both extremes of μ. If $\mu \to -\infty$, then the average occupation will be zero. On the other hand, if $\mu \to \infty$, the average occupation will saturate at 1.

Let us consider two basic regimes of the Fermi gas:

1. $E_i - \mu < 0$
2. $E_i - \mu > 0$

In the first regime where $E_i - \mu < 0$, if β is large (so T is low), the exponential in the denominator becomes large, so $\langle N_i \rangle \to 0$. For small β (large T), the exponential goes to 1, and $\langle N_i \rangle \to \frac{1}{2}$, as shown in Figure 4.3.

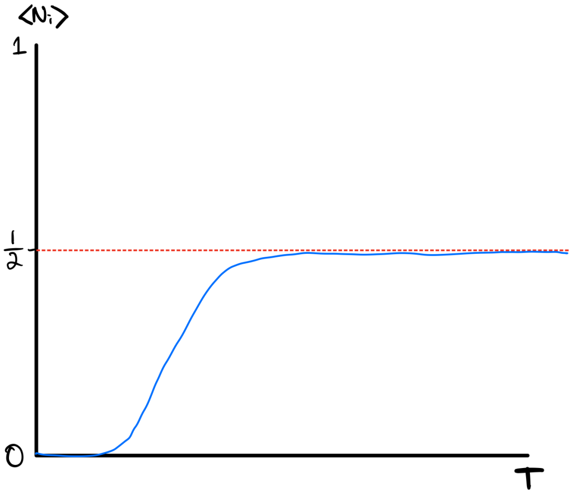


Figure 4.3: Fermi-Dirac distribution in the regime where $E_i - \mu < 0$.

In the second regime, where $E_i - \mu > 0$, if β is large (low T), then the exponential becomes small, and $\langle N_i \rangle \to 1$. If β is small (high T), then $\langle N_i \rangle \to \frac{1}{2}$, as shown in Figure 4.4.

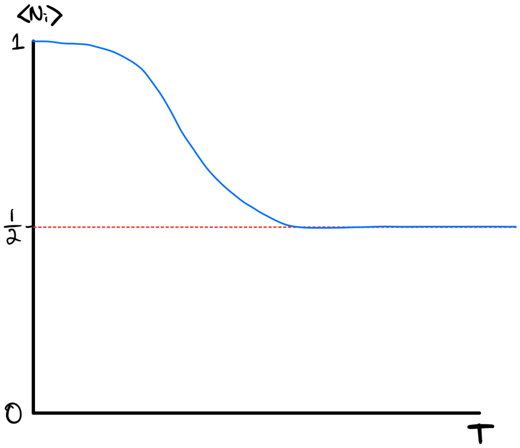


Figure 4.4: Fermi-Dirac distribution in the regime where $E_i - \mu > 0$.

Now let us derive the number density, but first we introduce a shorthand function to simplify our notation:

$$n_F(x) = \frac{1}{e^x + 1} \tag{4.226}$$

We can then compute the number density:

$$n = g \int \frac{d^3k}{(2\pi)^3}\, n_F\left(\beta\left(\frac{k^2}{2m} - \mu\right)\right) \tag{4.227}$$

$$= g \int \frac{dk}{2\pi^2}\, k^2 n_F\left(\beta\left(\frac{k^2}{2m} - \mu\right)\right) \tag{4.228}$$

Where $g = 2s + 1$ is the spin degeneracy. For electrons, $s = 1/2$. It is sometimes useful to replace integrals over k with integrals over energy. Let $E = \frac{k^2}{2m}$, then $k = \sqrt{2mE}$, and

$$dk = \frac{1}{2}\frac{\sqrt{2m}}{\sqrt{E}} dE \tag{4.229}$$

From this, we define

$$\int \frac{dk\, k^2}{2\pi^2} = \int dE\, d(E) \tag{4.230}$$

Where $d(E)$ is the density of states:

$$d(E) = \frac{(2m)^{3/2} E^{1/2}}{4\pi^2} \tag{4.231}$$

From which we can write the energy density and the number density:

$$n = g \int dE\, d(E) n_F(\beta(E - \mu)) \tag{4.232}$$

$$u = g \int dE\, d(E)\, E\, n_F(\beta(E-\mu)) \tag{4.233}$$

Now in general, we just shut up and integrate. It is also useful to consider the cases when T is large or small. We will only consider the small T case, as it is markedly different from the bosonic case (the large T case is similar to the large T bosonic case, just with the key sign difference in the distribution). Suppose we have small T and positive μ. If we look at a plot of the distribution, we see that the small T regime is almost a step function. The only place where we diverge from a step function is when μ is close to the Fermi energy, which is defined as:

$$E_F = \frac{k_F^2}{2m} \tag{4.234}$$

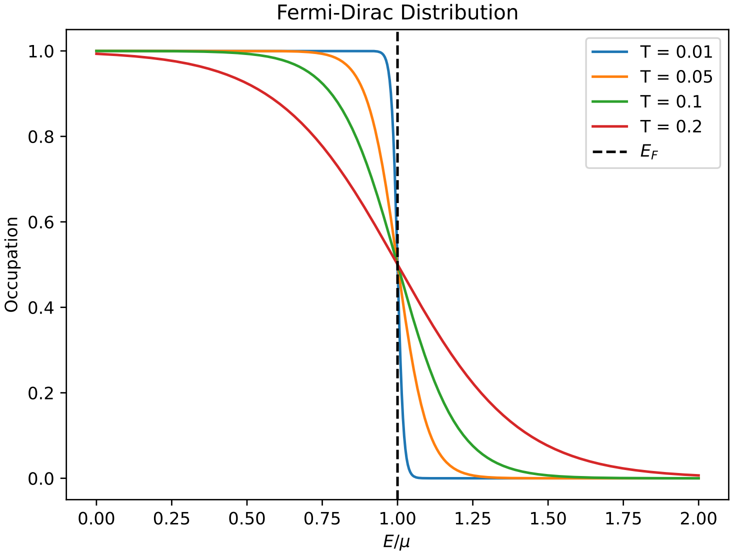


Figure 4.5: Fermi-Dirac distribution (Eqn. 4.221) plotted at decreasing energies. We see that as the temperature decreases, the distribution approaches a step function.

One can think of these thermal excitations as “particle-hole” states, there is a “hole” in the “Fermi sea” where a particle below E_F is vacated, and a particle above E_F is occupied. The vast bulk of particle-hole pairs are “near” E_F when T is small.

Let us try to find what contribution this makes to the energy at small T. We can write out the change in the occupation:

$$\Delta n_F = n_F\left(\frac{E-\mu}{T}\right) - \Theta(\mu - E) \tag{4.235}$$

One can show for fixed n:

$$u = \frac{3}{5} n E_F \left(1 + \frac{5}{12}\pi^2 \left(\frac{T}{E_F}\right)^2 + \cdots\right) \tag{4.236}$$

This second term in the expansion is the contribution of the particle-hole excitations.

We can also compute the heat capacity at fixed volume:

$$C_V = \left.\frac{dU}{dT}\right|_{N,V} \tag{4.237}$$

$$= \frac{N\pi^2 T}{2E_F}\left(1 + \mathcal{O}\left(\frac{T}{E_F}\right)\right) \tag{4.238}$$

And the specific heat at fixed volume:

$$c_V = \left.\frac{du}{dT}\right|_{N,V} \tag{4.239}$$

$$= \frac{n\pi^2 T}{2E_F}\left(1 + \mathcal{O}\left(\frac{T}{E_F}\right)\right) \tag{4.240}$$

In general the specific heat is quite useful, since it is much easier to measure than u.

Before showing how we derive these quantities, we need to discuss a mathematical trick, known as the Sommerfeld expansion. Suppose we have a function $\Delta(x)$ with the property that the expression

$$\int_{-\infty}^{\infty} \mathrm{d}x\, \Delta(x) x^n \tag{4.241}$$

is finite for all non-negative integers n; that is, $\Delta(x)$ falls off exponentially.

Suppose that I am interested in approximating the integral $I(\lambda)$:

$$I(\lambda) = \int_{-\infty}^{\infty} dx\, f(x) \Delta\left(\frac{x - x_0}{\lambda}\right) \tag{4.242}$$

for small λ, where $f(x)$ is analytic over x_0 and independent of λ. Now we note that as λ gets small, $\Delta((x - x_0)/\lambda)$ is only sizable near x_0, as shown (schematically) in Figure 4.6.

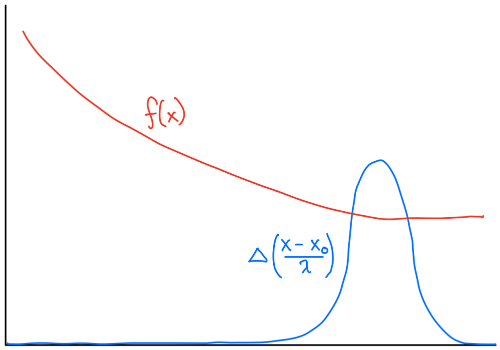


Figure 4.6: Schematic plot of the functions in the integrand of $I(\lambda)$, in Eqn. 4.242.

We can now Taylor expand $f(x)$ in the vicinity of x_0:

$$I(\lambda) = \int_{-\infty}^{\infty} dx \left(f(x_0) + f'(x_0)(x - x_0) + \frac{1}{2}f''(x_0)(x - x_0)^2 + \cdots\right) \Delta\left(\frac{x - x_0}{\lambda}\right) \tag{4.243}$$

Now doing a change of variables, defining $y = \frac{x-x_0}{\lambda}$, we have that

$$I(\lambda) = \int_{-\infty}^{\infty} dx\, \Delta(y) \left(\lambda f(x_0) + \lambda^2 f'(x_0) y + \frac{\lambda^3}{2} f''(x_0) y^2 + \cdots \right) \tag{4.244}$$

$$= \sum_{n=0}^{\infty} \frac{\lambda^{n+1}}{n!} \left(\left. \frac{d^n f}{dx^n} \right|_{x=x_0} \right) \int_{-\infty}^{\infty} dy\, y^n \Delta(y) \tag{4.245}$$

Now let us define c_n, the "moments" of $\Delta(y)$:

$$c_n = \int_{-\infty}^{\infty} dy\, y^n \Delta(y) \tag{4.246}$$

Which leaves us with

$$I(\lambda) = \sum_{n=0}^{\infty} \frac{\lambda^{n+1} c_n}{n!} \left. \frac{d^n f}{dx^n} \right|_{x=x_0} \tag{4.247}$$

In effect, we are replacing $\Delta(y)$ by a series of delta functions and derivatives of delta functions that preserve the moments of $\Delta(y)$:

$$\Delta(y) \approx \sum_{n} \frac{c_n (-1)^n}{n!} \delta^{(n)}(y) \tag{4.248}$$

This is of course a terrible approximation of Δ, but is a very good one when used in integrals for small λ.

Missing Terms?

Note that this approximation can be used to get an expansion in powers of λ. There may be corrections to $I(\lambda)$ that cannot be written in that form, such as $\exp(-c/\lambda)$, where c is a constant. This vanishes to all orders of λ, and therefore cannot be expressed as a term in the expansion. However, we claim that these terms will all be incredibly small for small λ, and thus we are fine to ignore them.

Let us now apply this expansion to our original expression of interest:

$$\Delta n_F = n_F(x) - \Theta(x) \tag{4.249}$$

Where $x = \mu - E_F$. We can look at the c_0 coefficient:

$$c_0 = \int_{-\infty}^{\infty} dx\, \Delta n_F(x) \tag{4.250}$$

$$= \int_{-\infty}^{0} dx \left(\frac{1}{e^x + 1} - 1 \right) + \int_{0}^{\infty} \frac{dx}{e^x + 1} \tag{4.251}$$

$$= 0 \tag{4.252}$$

Where we note that the first integral can be rewritten:

$$\int_{-\infty}^{0} dx \left(\frac{1}{e^x + 1} - 1 \right) = \int_{-\infty}^{0} dx\, \frac{(-1)}{e^{-x} + 1} \tag{4.253}$$

$$= -\int_0^\infty \frac{dx}{e^x + 1} \tag{4.254}$$

Which is just the second integral. Since this coefficient is zero, we can look at the next coefficient:

$$\begin{aligned}
c_1 &= \int_{-\infty}^{\infty} dx\, x \Delta n_F(x) && (4.255)\\
&= \int_{-\infty}^{0} dx\, x \left(\frac{1}{e^x + 1} - 1\right) + \int_0^\infty dx\, \frac{x}{e^x + 1} && (4.256)\\
&= 2\int_0^\infty dx\, \frac{x}{e^x + 1} && (4.257)\\
&= \frac{\pi^2}{6} && (4.258)
\end{aligned}$$

Where we again rewrite the first integral:

$$\begin{aligned}
\int_{-\infty}^{0} dx\, x \left(\frac{1}{e^x + 1} - 1\right) &= -\int_{-\infty}^{0} dx\, \frac{x}{e^x + 1} && (4.259)\\
&= \int_0^\infty \frac{x\, dx}{e^x + 1} && (4.260)
\end{aligned}$$

Let us truncate at this order, and see what we can extract using this expansion. We want to find u at fixed n, and we have expressions with fixed μ. To convert between them:

$$u = n\left(\frac{u(T,\mu)}{n(T,\mu)}\right) \tag{4.261}$$

We can compute $u(T,\mu)$ and $n(T,\mu)$ to the lowest nontrivial order:

$$\begin{aligned}
n &= n_{T=0} + g\int_0^\infty dE\, d(E) \Delta n_F && (4.262)\\
&= n_{T=0} + g\int_0^\infty dE\, d(E) \left(n_F\left(\frac{E-\mu}{T}\right) - \Theta(\mu - E)\right) && (4.263)\\
&= gT^2 c_1\, d'(E)_{E=\mu} + \mathcal{O}(T^4) && (4.264)
\end{aligned}$$

And similarly for u:

$$\begin{aligned}
u &= u_{T=0} + g\int_0^\infty dE\, d(E) E \left(n_F\left(\frac{E-\mu}{T}\right) - \Theta(\mu - E)\right) && (4.265)\\
&= gT^2 c_1 \frac{d}{dE}\left[E d(E)\right]\Bigg|_{E=\mu} + \mathcal{O}(T^4) && (4.266)
\end{aligned}$$

Putting these together:

$$\frac{u(\mu)}{n(\mu)} = \frac{\mu_0 + T^2 c_1 \mu d'(\mu) + T^2 c_1 d(\mu)}{n_0 + T^2 c_1 d'(\mu)} + \mathcal{O}(T^4) \tag{4.267}$$

Looking at the expansion of the denominator:

$$\frac{1}{n_0 + T^2 c_1 d'(\mu)} = \frac{1}{n_0}\left(1 - \frac{T^2 c_1}{n_0} d'(\mu)\right) + \mathcal{O}(T^4) \tag{4.268}$$

Using this, we can rewrite our ratio:

$$\frac{u(\mu)}{n(\mu)} = \frac{u_0}{n_0}\left(1 + T^2 c_1 d'(\mu)\left(\mu - \frac{u_0}{n_0}\right) + d(\mu)\right) + \mathcal{O}(T^4) \tag{4.269}$$

Now note that $\mu = E_f(1 + \mathcal{O}(T^2))$, and recall that $u_0/n_0 = 3E_F/5$. Inserting these, along with our previously computed c_1 coefficient, as well as the density of states $d(E)$, we find that

$$\frac{u}{n} = \frac{3}{5}E_F\left(1 + \frac{5}{12}\pi^2\left(\frac{T}{E_F}\right)^2 + \cdots\right) \tag{4.270}$$

From which the results for the heat capacity (4.238) and specific heat (4.240) follow.

5 Lattices

Many systems of particles form crystals. Mathematically, structure of these crystals are called “lattices”. Each atom (or molecule) is approximately at a fixed position, and will oscillate around this position. The physics of these oscillations is naturally described by phonons (as we saw in Section 4.7.3). However, in many cases the motion of particles around the crystal position is only weakly coupled to the behavior at each site. In this case, at each site the state of the particle can depend on the spin of the particle at the site, and possibly other properties, such as the occupation of the site or external fields.

5.1 Paramagnetism

Let us begin with the simplest example, a model for paramagnetism. This is the phenomenon of spins in a material aligning with an external magnetic field for as long as they are subjected to the field. Let us for now assume that interactions between sites are negligible. For the purposes of illustration, let us consider spin-1/2 particles. At each site, we have the Hamiltonian:

$$\hat{H} = -\boldsymbol{m} \cdot \boldsymbol{B} \tag{5.1}$$

Where $\boldsymbol{m} = g\mu_B \boldsymbol{s}$, in which g is the gyromagnetic factor, μ_B is the Bohr magneton, and $\boldsymbol{s}$ is the spin. Suppose that the external $\boldsymbol{B}$ field is given by $\boldsymbol{B} = B\hat{z}$, which gives us the Hamiltonian:

$$\begin{aligned} \hat{H} &= \sum_{\text{sites}} -g\mu_B B s_z && (5.2) \\ &= \sum_{\text{sites}} \frac{1}{2} g\mu_B B \sigma_z && (5.3) \end{aligned}$$

Let us now condense the constant factors into $\tilde{b}$:

$$\hat{H} = \sum_i \tilde{b}\sigma_z^i \tag{5.4}$$

It is easy to apply statistical mechanics to this system because each site is independent of the other sites, and has a two dimensional Hilbert space. The probability that the spin at a site will be spin up is given by the Boltzmann factor:

$$P_\uparrow = \frac{e^{-\beta\tilde{b}}}{e^{-\beta\tilde{b}} + e^{\beta\tilde{b}}} \tag{5.5}$$

Which then gives us the probability that the spin will be down:

$$P_\downarrow = 1 - P_\uparrow \tag{5.6}$$

Now looking at the average spin at the site:

$$\begin{aligned}\langle\sigma_z^i\rangle &= P_\uparrow - P_\downarrow &(5.7)\\ &= \frac{e^{-\beta\tilde{b}} - e^{\beta\tilde{b}}}{e^{-\beta\tilde{b}} + e^{\beta\tilde{b}}} &(5.8)\\ &= \tanh(\beta\tilde{b}) &(5.9)\end{aligned}$$

Now that we have the average spin, we can find the average magnetization:

$$\begin{aligned}\langle\boldsymbol{m}\rangle &= \hat{z}g\,\langle\sigma_z\rangle\, n_{\text{sites}} &(5.10)\\ &= \hat{z}\left(\frac{1}{2}g\mu_B n_{\text{sites}}\right)\tanh\left(\frac{1}{2}\frac{g\mu_B B}{T}\right) &(5.11)\end{aligned}$$

Note that at high temperatures, this goes to zero, as expected, there is no aligning of the spins in the material at high temperatures.

An interesting thing to note is that the external magnetic field $\boldsymbol{B}$ is actually modified by the site itself, $\boldsymbol{B} = \boldsymbol{H} + \boldsymbol{m}$, where $\boldsymbol{H}$ is associated with external macroscopic currents, and $\boldsymbol{m}$ is based on the magnetization of the material. For small magnetizations, this is irrelevant, and we can just consider an external $\boldsymbol{B}$, but for larger fields, we have to calculate “self-consistently”. For small fields, we can write out the average magnetization:

$$\langle\boldsymbol{m}\rangle = \frac{\boldsymbol{H}}{|\boldsymbol{H}|}\left(\frac{1}{2}g\mu_B n_{\text{sites}}\right)\tanh\left(\frac{1}{2}\mu_B g\frac{H}{T}\right) \tag{5.12}$$

A useful way to characterize $\boldsymbol{m}$ is in terms of the magnetic susceptibility χ_m:

$$\chi_m = \frac{\partial m}{\partial H}$$

at small fields where $H \ll m$. It is generally computed for $\beta = 0$. Near $H = 0$ one can Taylor expand the tanh in H:

$$\boldsymbol{m} \approx \left(\frac{1}{2}g\mu_B\right)^2 \frac{n_{\text{sites}}}{T}H \tag{5.13}$$

From which we find χ_m:

$$\chi_m = \left(\frac{1}{2}g\mu_B\right)^2 \frac{n_{\text{sites}}}{T} \tag{5.14}$$

We see that χ_m is small at high T.

5.2 Ising Model

The model we just looked at was made simpler by the lack of interactions between sites, we could treat each site separately. However, there are many models that encode interactions between sites. Some are good approximations of real materials, while others illustrate qualitative behaviors. Typically these models use “nearest neighbor interactions”. This is often justified for very short range interactions. The simplest such model is the Ising model. In this model, spins are restricted to eigenstates of σ_z, which we will write as σ:

$$\sigma = \pm 1 \tag{5.15}$$

Some crystals behave this way to a reasonable approximation, but they are rare. However, as we stated above, this is a useful model to illustrate qualitative behaviors. We start by labeling each lattice site with an index i. The value of the spin at i is σ_i. Then the Hamiltonian takes the form

$$\hat{H} = -\frac{1}{2}J\sum_{\text{NN}}\sigma_i\sigma_j - h\sum_i \sigma_i \tag{5.16}$$

Where NN implies i and j are adjacent sites. The $-$ out front indicates that adjacent spins "want" to align, and the h governs the strength of the external field. This system is analytically solvable in 1 dimension and in 2 dimensions (with great effort), but not in 3 dimensions. After 2 dimensions, we have to use numerical methods (such as Monte Carlo, which we discuss in Section 5.6) or approximations, such as Mean Field Theory, which we discuss in Section 5.2.2.

At $T = 0$, the system is in its ground state. What does the ground state look like? For $h \neq 0$, this is easy to see. If $h > 0$, all of the spins will be $+1$, and if $h < 0$, all the spins will be -1. But what about if $h = 0$? In this case, it is not that half of the spins will be $+1$ and the other half -1, we need each spin to be exactly the same spin as its neighbors, otherwise we can decrease the energy by making the spins align. Therefore we have two degenerate ground states, the all up state and the all down state. The system "chooses" one of the two ground states based on the history of the system (start with $h > 0$ and let $h \to 0$ for all spins up, and vice versa for the all spins down).

This is an example of *spontaneous symmetry breaking*: for $h = 0$, the theory is invariant under $\sigma_i \to -\sigma_i$ for all i. This is a symmetry, but in practice, the ground states depend on the history. The system will always choose one of the two ground states, even though both ground states are functionally identical. By the way, if J had the opposite sign, the ground state would be "antiferromagnetic", with all neighbors having opposite spins. There would still be two degenerate ground states, and we would still have spontaneous symmetry breaking.

Now, what happens at $h = 0$ and $T \neq 0$? Clearly at $T = \infty$, $\langle\sigma\rangle = 0$. The system is random, but how does it go to zero as T increases in the ferromagnetic case? We will focus on $\langle\sigma\rangle$ which is the "order parameter" of the system. There are several cases:

1. **Crossover:** The order parameter smoothly changes as we change the temperature, for all temperatures.
2. **First Order Phase Transition:** There is a discontinuity in the order parameter at some critical point T_c.
3. **Second Order Phase Transition:** At the critical point, the order parameter is continuous, but the derivative of the order parameter has a discontinuity.

These are schematically shown in Figure 5.1.

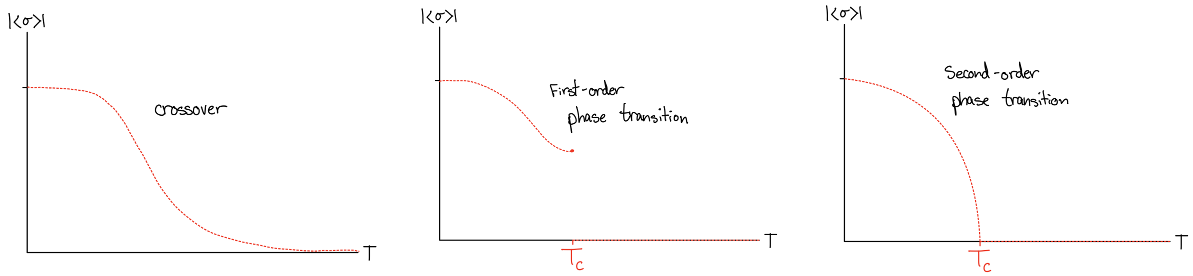


Figure 5.1: Schematic diagrams of the order parameter (in this case, the magnetization) as a function of a dynamical variable (in this case, the temperature) in the 3 different cases. In the case of a crossover, the order parameter changes smoothly for all T. In a first order phase transition, the order parameter has a discontinuity at the critical point. In a second order phase transition, the order parameter is continuous, but its derivative has a discontinuity.

This gives us a way to classify phase transitions based on the behavior of the order parameter (and its derivatives) in the system.

5.2.1 1D Ising Model

Let us now solve the Ising model in 1 dimension, and demonstrate that there is no phase transition, spontaneous symmetry breaking does not occur. First, let us think about the 2D case. We have two symmetry-broken ground states, how does the system pick which one to occupy? Well, we think about turning on the external field, which biases the system to picking one solution. We then take the limit as the external field goes to 0.

Now let us consider the 1 dimensional case, and see if we can drive the system to break the symmetry. Suppose we have a chain of linked spins, formed in a closed loop. Each spin has two nearest neighbors. This is imposing periodic boundary conditions on our lattice. We can do so because in the thermodynamic limit, the details of our boundary conditions will not matter.

Next, we will focus on the interactions between spins as degrees of freedom rather than spins themselves. We have the Hamiltonian:

$$\hat{H} = \sum_{\langle i,i+1\rangle} J\sigma_i\sigma_{i+1} - h\sigma \tag{5.17}$$

Let us first consider the $h = 0$ case. In this case, we can write out the Boltzmann factor:

$$e^{-\beta H} = \exp\left[-\beta J(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_4 + \cdots + \sigma_N\sigma_1)\right] \tag{5.18}$$

We can write this as a product of exponentials:

$$e^{-\beta H} = \exp\left[-\beta J\sigma_1\sigma_2\right]\exp\left[-\beta J\sigma_2\sigma_3\right]\cdots\exp\left[-\beta J\sigma_N\sigma_1\right] \tag{5.19}$$

Now let us consider what $\exp\left[-\beta J\sigma_1\sigma_2\right]$ looks like. In the case where we know what σ_1 and σ_2 are, then this is a number, but if we don't, we have 4 possibilities for the product. To write them down, we can define the transfer matrix t_{12}:

$$t_{12} = \begin{bmatrix} e^{-\beta J} & e^{\beta J} \\ e^{\beta J} & e^{-\beta J} \end{bmatrix} \tag{5.20}$$

Now looking back at Equation 5.19, we can see that this is a series of matrix products:

$$e^{-\beta H} = t_{12} t_{23} \cdots t_{N1} \tag{5.21}$$

In braket notation, we can define $t_{i,i+1} = \langle \sigma_i | t | \sigma_{i+1} \rangle$. We can now look at the partition function in this notation:

$$\begin{aligned} Z(\beta) &= \sum_{\sigma_1} \sum_{\sigma_2} \cdots \sum_{\sigma_N} e^{-\beta H} && (5.22) \\ &= \sum_{\sigma_1, \ldots, \sigma_N} \langle \sigma_1 | t | \sigma_2 \rangle \langle \sigma_2 | t | \sigma_3 \rangle \cdots \langle \sigma_N | t | \sigma_1 \rangle && (5.23) \\ &= \sum_{\sigma_1} \langle \sigma_1 | \, t \sum_{\sigma_2} | \sigma_2 \rangle \langle \sigma_2 | \, t \sum_{\sigma_3} | \sigma_3 \rangle \langle \sigma_3 | \, t \cdots \sum_{\sigma_N} | \sigma_N \rangle \langle \sigma_N | \, t \, | \sigma_1 \rangle && (5.24) \end{aligned}$$

We see that we have rewritten this to *extract* the identity (rather than inserting it for once!). From this, we see that the partition function is:

$$\begin{aligned} Z(\beta) &= \sum_{\sigma_1} \langle \sigma_1 | t^N | \sigma_1 \rangle && (5.25) \\ &= \mathrm{Tr}\left[t^N(\beta) \right] && (5.26) \end{aligned}$$

Now let us reinsert the external field. This changes the transfer matrix:

$$t = \begin{bmatrix} e^{-\beta J} e^{-\beta h} & e^{\beta J} \\ e^{\beta J} & e^{-\beta J} e^{-\beta h} \end{bmatrix} \tag{5.27}$$

We can diagonalize this in order to get something that is easy to exponentiate, which then gives us a partition function of the form:

$$Z(\beta, h) = (\lambda_+)^N + (\lambda_-)^N \tag{5.28}$$

Where $\lambda_\pm$ are the eigenvalues of t.

Now suppose we wanted to compute the average value of a spin, $\langle \sigma \rangle$. To do this, note that differentiating the log of the partition function with respect to h drops down the factor of σ that we want:

$$\begin{aligned} \langle \sigma \rangle &= -\frac{1}{N} \frac{\partial}{\partial h} \log Z && (5.29) \\ &= \frac{\sinh(\beta h)}{\sqrt{\cosh^2(\beta h) - 2e^{-2\beta J} \sinh(2\beta h)}} && (5.30) \end{aligned}$$

Now let us see if there is spontaneous symmetry breaking. We can by inspection see that it does not occur, since as $h \to 0$, the numerator goes to 0, but the denominator does not, and thus we have that $\lim_{h \to 0} \langle \sigma \rangle = 0$, which means that we have no spontaneous symmetry breaking. However, we do have a caveat, which is the case where $T \to 0$. In this case, $\beta \to \infty$, and we have that

$$\langle \sigma \rangle \to \lim_{h \to 0} \lim_{\beta \to \infty} \tanh(\beta h) \tag{5.31}$$

We have a double limit, but we take $h \to 0$ before we take $\beta \to \infty$. If we do this, we see that if $h > 0$, then $\langle \sigma \rangle \to +1$, and if $h < 0$, then $\langle \sigma \rangle \to -1$. This is spontaneous symmetry breaking, achieved only when $T = 0$.

These transfer matrix methods allow us to compute any quantity of interest in the 1D Ising model, but are completely useless in higher dimensions. In order to consider higher dimensional Ising models, one must general resort to either approximations or numerics.

5.2.2 Mean Field Theory

Now let us consider phase transitions in the 2D Ising model. To do so, we will begin by looking at a mean-field solution. In essence, mean-field theory will allow us to approximate the interactions in our system, by having each spin interact with the *average* spin of the spins surrounding it. This will greatly simplify our calculations.[1]

Recall the Ising Hamiltonian (5.16):

$$\hat{H} = -\frac{1}{2}J\sum_{\text{NN}}\sigma_i\sigma_j - h\sum_i \sigma_i \tag{5.32}$$

We want to find out what happens when $h = 0$ and $T \neq 0$. At all times, the system will attempt to minimize the free energy:

$$F = U - TS \tag{5.33}$$

The energy is easy to compute, we can look at all the interactions between the sites. Now we will pick an ansatz, and then vary it to minimize the free energy. The simplest ansatz we can pick is one in which the sites are independent of each other, which is useful in the large h and low T limit. In this case, the spins will all align, and local fluctuations at a site will not affect its neighbors. However, in the case of second order phase transitions, as we approach criticality, correlation lengths go to infinity, which means that spins at one site influence sites that are very far away. Thus this ansatz is a very poor choice when near the critical temperature T_c. We will ignore this, and continue with our ansatz for now. The density matrix for the system is the product of the per-site density matrices (each of which is a two-level system):

$$\hat{\rho} = \prod_i \hat{\rho}_i \tag{5.34}$$

Our approximation will imply that $\hat{\rho}_i = \hat{\rho}_0$ for all i, all the spins are the same. If we now compute the free energy and attempt to choose the $\hat{\rho}_0$ that minimizes it, this will be the result that mean field theory gives us. How do we compute S? Well, since each site has the same density matrix, it will be the number of sites times the entropy of a single site:

$$S_0 = -P_\uparrow \log P_\uparrow - P_\downarrow \log P_\downarrow \tag{5.35}$$

We can now define the average spin at a site:

$$\sigma_0 = P_\uparrow - P_\downarrow \tag{5.36}$$

Note that this also gives us expressions for $P_\uparrow$ and $P_\downarrow$ in terms of σ_0:

$$P_\uparrow = \frac{1}{2}(\sigma_0 + 1) \tag{5.37}$$

$$P_\downarrow = \frac{1}{2}(1 - \sigma_0) \tag{5.38}$$

Now let us consider the expectation value of a single particle pair (where i and j are nearest neighbors), $\langle H_{i,j}\rangle$:

$$\langle H_{i,j}\rangle = -J\langle\sigma_i\sigma_j\rangle \tag{5.39}$$

---

[1] As previously mentioned, the 2D Ising model can be solved analytically, as was famously done by Lars Onsager in 1944.

$$= -J \langle \sigma_0 \rangle^2 \tag{5.40}$$

$$= -J\sigma_0^2 \tag{5.41}$$

Where we utilize the fact that σ_i and σ_j must (by our ansatz) have no correlation, and take on the average spin value. We can then write out the energy of the entire lattice:

$$\langle U \rangle = -h \sum_i \langle \sigma_0 \rangle - \frac{1}{2} J \sum_i N_{\text{NN}} \langle \sigma_0 \rangle^2 \tag{5.42}$$

Where N_{NN} is the number of nearest neighbors. In the case of a 2D lattice, we have $N_{\text{NN}} = 4$, and in a cubic 3D lattice we would have $N_{\text{NN}} = 6$. With the average energy, we can now compute the free energy:

$$F = \langle U \rangle - TS \tag{5.43}$$

$$= \sum_i \left(-h \langle \sigma_0 \rangle - \frac{N_{\text{NN}} J}{2} \langle \sigma_0 \rangle^2 + T \langle \hat{\rho}_0 \log \hat{\rho}_0 \rangle \right) \tag{5.44}$$

We want to minimize this value:

$$\frac{\partial F}{\partial \rho_0} = 0 \tag{5.45}$$

This is a functional derivative, but it boils down to minimizing with respect to σ_0:

$$\frac{\partial F}{\partial \rho_0} = (-h - N_{\text{NN}} \langle \sigma \rangle J) \frac{\partial \langle \sigma \rangle}{\partial \rho_0} + \frac{\partial}{\partial \rho_0} \text{Tr} \left[\rho_0 \log \rho_0 \right] \tag{5.46}$$

If we define the constant prefactor h_{MF}:

$$h_{\text{MF}} = -h - N_{\text{NN}} \langle \sigma \rangle J \tag{5.47}$$

We can see that this is very similar to the case of uncoupled spins in an external field, which we have already solved. Thus we can utilize our solution of $\langle \sigma \rangle = \tanh(\beta h)$:

$$\langle \sigma \rangle = \tanh(\beta h_{\text{MF}}) \tag{5.48}$$

$$= \tanh \left(\beta (h + N_{\text{NN}} \langle \sigma \rangle J) \right) \tag{5.49}$$

This is a transcendental equation, it has no analytic solution. However, we can still work with this. Let us define $\tilde{\sigma}$:

$$\tilde{\sigma} \equiv (h + J N_{nn} \langle \sigma \rangle) \beta \tag{5.50}$$

Rewriting this to solve for $\langle \sigma \rangle$:

$$\langle \sigma \rangle = \frac{T\tilde{\sigma} - h}{J N_{nn}} \tag{5.51}$$

Now equating this to Equation 5.49:

$$\frac{T\tilde{\sigma} - h}{J N_{\text{NN}}} = \tanh(\tilde{\sigma}) \tag{5.52}$$

Now let us consider the case where $h = 0$. In this case, we can physically graph these two functions and look at their intersection points. We see that that at low T and $h = 0$, we have 3 solutions.

Two of these have equivalent (minimal) F, and these are the two physical solutions, and are the degenerate ground states.

As T gets larger, $|\langle\sigma\rangle|$ gets smaller. At some critical T the 3 solutions merge and $\langle\sigma\rangle = 0$. T_c occurs when the slope of the left-hand expression equals 1, that is, $T_c = JN_{\text{NN}}$. For $T > T_c$ the only solution is $\langle\sigma\rangle$.

This is a classic 2nd order phase transition. Physical properties (the magnetization) are continuous, but derivatives have a discontinuity. It is straightforward to calculate the energy, free energy, entropy density, etc. once one has $\langle\sigma\rangle$. It is particularly interesting to compute behavior near the critical point.

Let us again look at the equation for the magnetization (5.52), with $h = 0$:

$$\frac{T\tilde{\sigma}}{JN_{nn}} = \tanh(\tilde{\sigma}) \tag{5.53}$$

If we now note that $T_c = JN_{\text{NN}}$:

$$\frac{T}{T_c}\tilde{\sigma} = \tanh(\tilde{\sigma}) \tag{5.54}$$

From this, we have that

$$\sigma = \tanh\left(\frac{T}{T_c}\sigma\right) \tag{5.55}$$

Regardless of T there is always a solution at $\sigma = 0$. We want to see if other solutions exist, and if so what the behavior is. Near the critical point σ is small, so we can Taylor expand the tanh:

$$\tanh\left(\frac{T_C}{T}\sigma\right) = \frac{T_C}{T}\sigma - \frac{1}{3}\left(\frac{T_C}{T}\sigma\right)^3 + \cdots \tag{5.56}$$

Now utilizing Equation 5.55, we have an expansion for σ:

$$\sigma = \frac{T_C}{T}\sigma - \frac{1}{3}\left(\frac{T_C}{T}\sigma\right)^3 + \cdots \tag{5.57}$$

Now let us assume that there exists a solution other than $\sigma = 0$. In this case, we can divide out by σ, and then solve for σ:

$$\sigma = \pm\sqrt{3\left(\left(\frac{T}{T_C}\right)^2 - \left(\frac{T}{T_C}\right)^3\right)} \tag{5.58}$$

By assumption T is close to T_c, and we can write $T = T_c + (T - T_c)$, and define the reduced temperature t:

$$t = \frac{T - T_c}{T_c} \tag{5.59}$$

Then we have

$$\left(\frac{T}{T_C}\right)^2 = 1 + 2t + \mathcal{O}(t^2) \tag{5.60}$$

$$\left(\frac{T}{T_C}\right)^3 = 1 + 3t + \mathcal{O}(t^3) \tag{5.61}$$

$$\tag{5.62}$$

Which gives us that

$$\sigma = \pm\sqrt{-3t} \tag{5.63}$$

Note that for $t > 0$, there are no real solutions other than the $\sigma = 0$ solution we identified before. For $t < 0$, we have found the behavior of the magnetization near criticality:

$$|\sigma| \sim Ct^{-1/2} \tag{5.64}$$

This is known as critical exponent, and these are *universal.* Note that only the exponent is universal, not the constant out front. However, it turns out that the critical exponents we find from MFT are universally *wrong* (if we are in less than 5 dimensions), as we will discuss in the next section. If we continued to use MFT for other quantities in our system, such as the specific heat c and the susceptibility χ, we would (like the magnetization) have two values, depending on the sign of t.

5.3 Landau Theory

Let us write down new notation for our order parameter, call it ψ, which means that we have that $\psi = \sigma$. The mean field approach has shown us that the order parameter in the disordered phase is zero, and in the ordered phase, goes as $t^{-1/2}$. We can also define critical exponents for our specific heat and magnetic susceptibility. In the disordered phase, with $t > 0$:

$$c \sim t^{-\alpha} \qquad \psi = 0 \qquad \chi \sim t^{-\gamma} \tag{5.65}$$

And in the ordered phase, with $t < 0$:

$$c \sim t^{-\alpha'} \qquad \psi \sim t^{-\beta} \qquad \chi \sim t^{-\gamma'} \tag{5.66}$$

We have already found that $\beta = 1/2$ in 2 dimensions. If we wanted to compute the exponent γ, we can use the definition of the susceptibility:

$$\chi = \left.\frac{\partial \sigma}{\partial h}\right|_{h=0} \tag{5.67}$$

We can then use Equation 5.52 and analyze the resulting equation for χ to get the critical exponent, $\gamma = \gamma' = 1$. Doing similar work for the specific heat, we find that $\alpha = \alpha' = 0$. These are our critical exponents for the 2D Ising model, computed using mean field theory. These exponents are universal to MFT, any version of a theory in MFT will have this if the theory has finite range forces. It turns out that the exponents (for lattice theories with short range interactions) are dependent on the dimensions of space, the order parameter, and the symmetry of the system. Also note that while the critical exponents are universal around the critical point, the location of the critical point is not universal, nor is any of the behavior away from the critical point.

Theories that have the same critical exponents are in the same “universality class”. For example, if we have a scalar order parameter, we are in the **Ising universality class**. In this universality class, we can define the critical exponents of all systems in this class, as shown below.

	α	β	γ
MFT	0	1/2	1
2D	0	1/8	7/4
3D	0.110	0.328	1.24

Note that 2D and MFT are different, because (as stated before) MFT turns out to give the *wrong* critical exponents in less than 5 dimensions. Why is behavior across different systems the same near the critical point? Why is mean field theory wrong? The answers to these two questions are connected. Recall the 1D case, where we demonstrated that there is no phase transition except at $T = 0$. If a single spin is "wrong", it blocks information from its left from propagating to the right. So how does the symmetry breaking at $T = 0$ come about?

One expects that as $T \to 0$, there are larger and larger regions of aligned spins. As $T \to 0$, these regions must go to infinite area. The key concept here is the correlation length. To understand this, we will introduce the concept of a correlation function. Let us work in the high T, disordered phase, where $\langle \sigma_i \rangle = 0$ for all i. Now consider $\langle \sigma_i \sigma_j \rangle$. This need not be zero, and in general will not be zero. When j is close to i, it is more likely to have the same sign, due to the ferromagnetic behavior, and typically, at long distances:

$$\langle \sigma_i \sigma_j \rangle \sim \exp\left(\frac{|r_i - r_h|}{\xi}\right) \tag{5.68}$$

The quantity ξ is known as the correlation length. Our claim will be that as we approach the critical temperature, ξ increases, and the correlations between far away spins increase in magnitude.

Claim

As we approach the critical temperature, $T \to T_c$, the correlation length diverges, $\xi \to \infty$.

To investigate this, we can recall the reduced temperature t (5.59), and look at how ξ changes as we take $t \to 0$. We find that $\xi \sim t^{-\nu}$ for high T, and $\xi \sim (-t)^{-\nu'}$ for low T. How do we extract ν and ν'? This is where Landau theory comes in.

Lev Landau attempted to develop a general theory of second order phase transitions. It turns out to be wrong for the same reason that mean field theory is, but it is instructive about long range correlations. Let ψ be a generic order parameter. Let us assume that near the phase transition point, ψ is small, which will allow us to take an expansion in ψ. Also, we assume that short range correlations in ψ are unimportant (since ψ is some quantity averaged over space), so we will look at a series in gradients of ψ. We also couple $\psi(x)$ to an external field.

Here is the scheme we will follow: we will write a series expression for the free energy as a function of $\psi(x)$, with parameters dependent on the temperature:

$$F = \int d^D x \, f(\psi(x), \nabla \psi(x)) \tag{5.69}$$

Where D is the spatial dimensionality. We see that f is a function of the order parameter and the gradient of the order parameter. Now we can write out f:

$$f = a(T) + r(T)\psi(x)^2 + s(T)\psi(x)^4 + h(x)\psi(x) + f(T)|\nabla\psi|^2 \tag{5.70}$$

Note that the order parameter is position dependent, but is also an averaged quantity over space (such as average magnetization), and therefore we must average ψ over a region that is large enough to define it. However, spatial dependence implies that ψ must be averaged over a small region! This is only self-consistent if we focus on long-range spatial variation, and the theory averages over all short-range physics.

As usual, we will try to minimize this free energy, and to do so we can make some arguments as to the parameters in $f(\psi(x), \nabla\psi(x))$. The first argument is that the linear term vanishes ($h(x) = 0$), since $\psi = 0$ should be an extremum (as seen in the Ising model). In general, cubic terms are allowed, but in the case of the Ising model, where we have "flip" symmetry, where $\psi = -\psi$, the cubic terms must vanish. We can also bound $f(T)$ to be non-negative, since if this is not the case, the system can gain a lower free energy by becoming more "crumpled", contrary to our assumption. Let us assume that $g(T) > 0$. Stability requires that $s(T) > 0$. First, consider the case where there is no external field, and $\psi(x) = \psi_0$, some constant. If we make these assumptions, we find that

$$F = V\left(a(T) + r(T)\psi^2 + s(T)\psi^4\right) \tag{5.71}$$

Now looking at this expression, we have 3 cases:

1. $r > 0$, $T > T_c$
2. $r = 0$, $T = T_c$
3. $r < 0$, $T < T_c$

A schematic diagram of the free energy in each of these cases is shown in Figure 5.2.

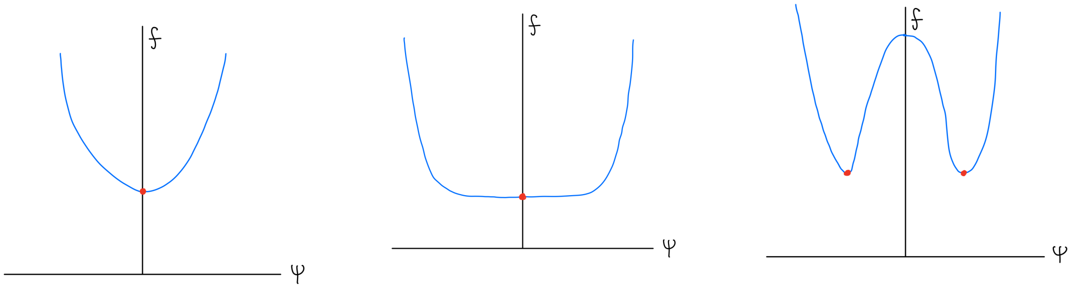


Figure 5.2: Each of the three cases for f. The minima of f are labeled by red points.

We can Taylor expand $r(T)$ around T_c:

$$\begin{aligned} r(T) &= r(T_c) + (T - T_c)r'(T_c) && (5.72)\\ &= T_c\left(\frac{T - T_c}{T_c}\right)r'(T_c) && (5.73)\\ &= ct && (5.74) \end{aligned}$$

Where we define $c = r'(T_c)T_c$, and we note that $r(T_c) = 0$. If we now insert this into our expression for the free energy (5.71), and look at ψ in two cases, based on the reduced temperature:

$$\psi = \begin{cases} 0 & t > 0 \\ \pm\sqrt{\frac{4c}{4s(T_c)}(-t)} & t < T_c \end{cases} \tag{5.75}$$

We see that we recover the exact same critical exponent as we did in MFT, $\beta = 1/2$. Landau theory reduces to MFT when we assume there is no spatial variation and we have no external potential.

What happens if we do allow spatial variation? To deal with this case, we will utilize a method analogous to the Euler-Lagrange equations for minimizing the action. When we do this, we set the boundary conditions such that the start and end points are held fixed. In this case, we will say that ψ goes to a fixed value at boundary of the volume.

We have that $\delta F = 0$:

$$\int \mathrm{d}^D x f(\psi, \nabla\psi) = \int d^D x \left(\frac{\partial f}{\partial \psi}\delta\psi + \sum_i \frac{\partial f}{\partial\left(\partial_i \psi\right)}\delta\left(\partial_i\psi\right)\right) \tag{5.76}$$

Now in classical mechanics, we would integrate by parts, and we do the same thing here. We get two terms, one at the boundary (which vanishes), and we get a minus sign from moving the derivative:

$$0 = \int \mathrm{d}^D x \left[\left(\frac{\partial f}{\partial \psi} - \sum_i \delta_i \frac{\partial f}{\partial\left(\delta_i \psi\right)}\right)\delta\psi\right] \tag{5.77}$$

Now we use the same argument as in classical mechanics, in order for this to work for all $\delta\psi$, this implies that:

$$\frac{\partial f}{\partial \psi} - \sum_i \partial_i \frac{\partial f}{\partial\left(\partial_i\psi\right)} = 0 \tag{5.78}$$

We can insert our definition of f (5.70), and we have that

$$-2f(T)\nabla^2\psi + 2r\psi + 4s(T)\psi^3 = 0 \tag{5.79}$$

$$-\nabla^2\psi + \frac{r(T)}{f(T)}\psi + \frac{2s(T)}{f(T)}\psi^3 = 0 \tag{5.80}$$

This is nonlinear and has no analytic solution. To solve this, we will linearize it, $\psi = \psi_0 + \delta\psi$:

$$\frac{r(T)}{f(T)}\psi_0 + \frac{2s(T)}{f(T)}\psi_0^3 - \left(\nabla^2 + \frac{r(T)}{f(T)} + \frac{6s(T)}{f(T)}\psi_0^2\right)\delta\psi + \mathcal{O}\left(\delta\psi^2\right) = 0 \tag{5.81}$$

We now claim that the first term is 0, since that is the equation that we solved to find the minimum originally. Thus we are left with

$$\left(-\nabla^2 + \frac{r(T)}{f(T)} + \frac{6s(T)}{f(T)}\psi_0^2\right)\delta\psi = 0 \tag{5.82}$$

This is Landau's equation. Recall that in the high temperature phase, $\psi_0 = 0$, and thus the ψ_0^2 term would drop out. Let us define a function $\xi(T)$:

$$\xi^2(T) = \left(\frac{r(T)}{f(T)} + \frac{6s(T)}{f(T)}\psi_0^2(T)\right)^{-1} \tag{5.83}$$

Which turns Landau's equation into:

$$\left(-\nabla^2 + \xi^{-2}(T)\right)\delta\psi = 0 \tag{5.84}$$

We can now solve this subject to the boundary condition that $\lim_{r\to\infty} \delta\psi(r) = 0$. Let us work in 3 dimensions, under the assumption that we have a large volume, and with spherical symmetry. In this case, the ∇^2 becomes:

$$-\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) \tag{5.85}$$

So the solution will be of the form

$$\delta\psi = \frac{e^{-r/\xi}}{r} \tag{5.86}$$

We see that the fluctuation falls off exponentially based on ξ, which we denote the correlation length (as one might have been able to foresee based on our choice of variables).

Recall that we claimed that the correlation length had critical exponents, given by ν and ν'. Looking at the high temperature phase, with no symmetry breaking, we have that

$$\xi^{-2} = \frac{2r(T)}{f(T)} \tag{5.87}$$

If we assume these functions are smooth:

$$f(T) = f(0) + f'(T) \tag{5.88}$$

$$r(T) = \cancelto{0}{r(T_c)} + r'(T_c)(T - T_c) + \mathcal{O}((T - T_c)^2) \tag{5.89}$$

We can now look at ξ^{-2}:

$$\xi^{-2} = t\left(\frac{2T_c r'(T_c)}{f(T_c)}\right) \tag{5.90}$$

From which we find that

$$\xi \sim t^{-1/2} \tag{5.91}$$

And we have our high temperature critical exponent for the correlation length. A similar computation can be done for the symmetry broken phase.

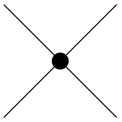
Note that the only place that the dimension came in was the Laplacian, which has the same type of exponential solution no matter the dimension. However, in the real world, the dimension does matter. To analyze this, we use what are known as critical dimensions. The upper critical dimension states that mean field theory or Landau theory is accurate if $D >$ UCD. For the Ising model, UCD $= 4$, and thus once we have 5 spatial dimensions, we obtain the right critical exponents. Exactly at the critical dimension, we are almost correct, but there are logarithmic corrections that are necessary. There is also the lower critical dimension. If $D <$ LCD, there is no phase transition, and no spontaneous symmetry breaking. The LCD for the Ising model is 2, so in 1 dimension, we will not get a phase transition (as we have proven), and MFT will give the wrong result.

5.4 The Renormalization Group

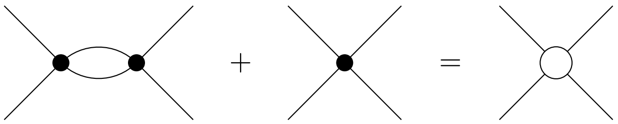
A formal tool to analyze universality classes is the Renormalization Group (RG). RG relies on the fact that the order parameter is only defined by averaging over scales that are large compared to microscopic lattice scale, but small compared to spatial variations studied (i.e. ξ) This means that we can look at the physics of the system at different levels of "zoom", and each level, we have an *effective* theory that models the physics. RG provides a systematic method to see how the parameters of the theory (coupling constants, masses, temperatures, etc) "flow" as we change the scale of observation.

An intuitive way to visualize this is in terms of diagrams. We use lines to represent things that connect to ψ with ψ. The terms in the free energy that go like $r(T)\psi^2 + f(T)|\nabla\psi|^2$ are represented as lines:

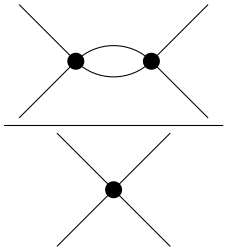
Terms that go like ψ^4 are represented by crosses:



But suppose that some "long range" behavior is declared to be short range (change of scale). Then the ψ^4 term is



One "renormalizes" the coefficient $s(T)$ when one changes scale. Once can develop equations quantifying this. Note that when



$\rightarrow$ 0 as scale gets large

and similar behavior for all couplings, one expects MFT to work, because the long range correlations vanish. These equations depend on dimension since we need to integrate over position. How does one implement this?

To handwave, let us consider the the Ising model, where we rewrite things in terms of blocks of spins, rather than individual spins. We redefine the spin of each block as up or down by "majority rule" (blocks are chosen to have an odd number of sites). We then rewrite $\hat{H}$ in terms of blocks so that all long range observables (appropriately scaled) are the same.

To put it slightly more formally: we define the new order parameter as a spatial average over some length scale:

$$x^{\text{new}} = bx^{\text{old}} \tag{5.92}$$

Where b is a factor that is larger than 1. This gives us:

$$\psi^{\text{new}} = C \int \mathrm{d}^D x^{\text{new}} \psi(x^{\text{new}}) \tag{5.93}$$

A basic trick is to choose a new H (or a new F function like in Landau theory) that reproduces long range physics. Suppose we write an F as we did in Landau theory:

$$F = \int \mathrm{d}^D x f \tag{5.94}$$

$$f = f_0 + c_1\psi^2 + c_2\psi^4 + c_3\psi^6 + \cdots + h\psi \tag{5.95}$$

$$+ d_1(\nabla\psi)^2 + d_2(\nabla\psi)^4 + \cdots \tag{5.96}$$

$$+ e_1(\nabla\psi^2)\psi_1^2 + \cdots \tag{5.97}$$

with all coefficients changing under scale transformations as distances and ψ are renormalizable. Formal studies of this sort show that when $d > 4$, MFT works. Analysis of this sort can give real insights into how critical phenomena works. One important result that can be obtained from RG is that the critical exponents are not independent, they in fact obey certain relations:

$$\alpha + 2\beta + \gamma = 2 \tag{5.98}$$

And, for dimensions less than or equal to 4, $d \leq 4$:

$$\nu = \frac{2 - \alpha}{d} \tag{5.99}$$

We can see whether these relations hold for the cases that we have discussed, in Figure 5.3.

	α	β	γ	ν	$\alpha + 2\beta + \gamma$	$\frac{2-\alpha}{d} - \nu$
MFT	0	1/2	1	1/2	2 ✓	
2d	0	1/8	7/4	1	2 ✓	0 ✓
3d	0.110	0.326	1.24	0.630	2 ✓	0 ✓

Figure 5.3: Table showing that Equations 5.98 and 5.99 hold for the case of the Ising Model in 2D MFT, 2 dimensions solved analytically, and 3 dimensions solved numerically. Note that the 2D MFT exponents do not satisfy Equation 5.99, recall that MFT only becomes accurate starting in $d = 4$.

5.5 First Order Transitions

We have discussed second order transitions through the lens of Landau theory and the renormalization group. Let us now briefly discuss first order transitions.

Let us say that we have some relevant order parameter ψ, and we have the free energy density $\tilde{f}$. Let us also assume that we are in the thermodynamic limit. Let us also assume that the system is homogeneous, all points are created equal. When we were doing second order transitions, we saw that at high T, we had 1 minimum. At low T, we had more than 1 (in the Ising model we had 2). At the critical temperature, its flat. To be slightly more concrete:

- at high T, $\tilde{f}$ at $\psi = 0$ was a local minimum

- at low T, $\tilde{f}$ at $\psi = 0$ was a local maximum
- at T_C, $\tilde{f}$ at $\psi = 0$ had vanishing 2nd derivatives

The behavior was local in order parameter "space". As one gets closer to the phase transition point this becomes obvious. This same behavior is not true for first order phase transitions. In a Landau theory style description, we need higher order terms for this. For first order transitions, the behavior as a function of temperature can be schematically shown in Figure 5.4. Suppose we have two wells in the free energy as a function of the order parameter. In the high T phase, one of these wells is lower than the other. As we decrease the temperature, the depth of the two wells shifts, and in the low T phase, the other well is now the deepest. The critical temperature is the point at which both wells are equally deep.

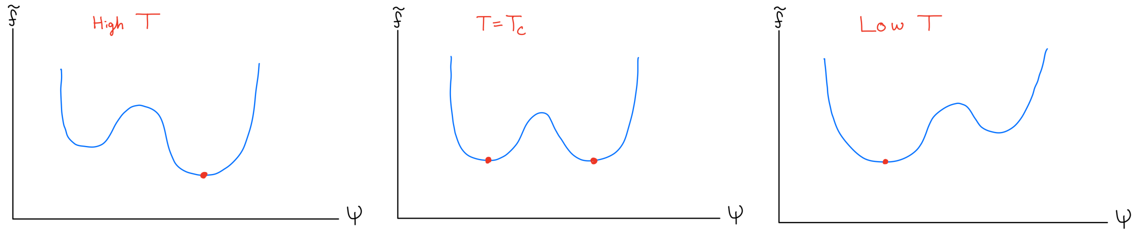


Figure 5.4: Free energy density $\tilde{f}$ as a function of the system's order parameter ψ, at high T, $T = T_c$, and low T.

Note that unlike for second order transitions, there is no indication that a phase transition is coming since nothing local has happened (correlations lengths don't diverge like in the second order transition). Also note that the two phases are totally different, so apart from the free energy, everything is different in two phases at T_c:

- low T phase: low u, low S
- high T phase: high u, high S

At the critical temperature, the free energies are equal at both minima:

$$u_L - T_c S_L = u_H - T_c S_H \tag{5.100}$$

where L and H indicate low and high temperature phases. Thus u and s both change discontinuously at T_c. We define the latent heat based on the change in internal energy across phases:

$$\begin{aligned} \Delta u &= u_H - u_L && (5.101) \\ &= T_C s_H - s_L && (5.102) \end{aligned}$$

We could also ask: what phase is our system in at T_c? This question is in fact misleading! When we introduced the schematic shown in Figure 5.4, one of the assumptions we made was that the system was homogeneous. This assumption breaks down at T_c. Let us see why this is the case. For the sake of simplicity, assume $\psi_L < \psi_H$. Suppose I ask what happens if I force $\psi_L < \psi < \psi_h$, i.e. an order parameter between these two values. Naively I look at Figure 5.4 and say $\tilde{f} > \tilde{f}_L = \tilde{f}_H$ (which are the same at T_c by default), but this is wrong! If I allow the system to do what it wants, it can keep psi (defined as an average over the whole system) to be between ψ_L and ψ_H and still lower the free

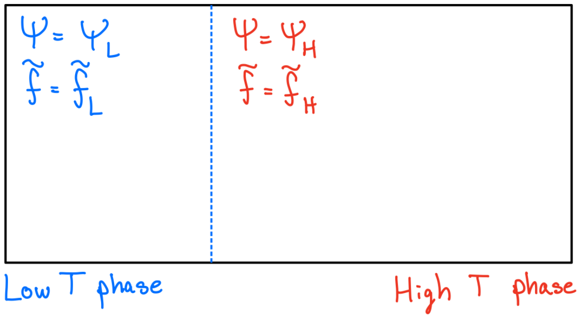


Figure 5.5: Schematic of the system at the critical temperature $T = T_c$. The system is in both phases, with some interface between the two phases. Note that for the purposes of illustration, the interface is drawn as a straight line, which is not necessarily the case. The system will attempt to minmize the area of the interface, to minimize the free energy cost.

energy below what is in the schematic provided. We are actually in both phases at the same time when we are at $T = T_c$! Consider the system as a large box, with both phases coexisting, with some interface between them, as shown in Figure 5.5

This system is still being considered in the thermodynamic limit, but we no longer assume homogeneity (and in practice we cannot!).

Of course dividing the system like this requires an interface, and that costs free energy. But, the interface is a surface and scales like L^2, where L is the characteristic size of the system, while the bulk transitions scale as L^3. So in the thermodynamic limit,

$$\frac{f_{\text{interface}}}{f_{\text{bulk}}} \sim \frac{1}{L} \to 0 \tag{5.103}$$

so the free energy of the interface is ignorable. Therefore the system fractionates, i.e. the schematic in Figure 5.4 is wrong if we consider non-translationally invariant solutions. We can "correct" our diagram for for the transition at $T = T_c$, where the region between the two minima is a non-homogenous region, as shown in Figure 5.6

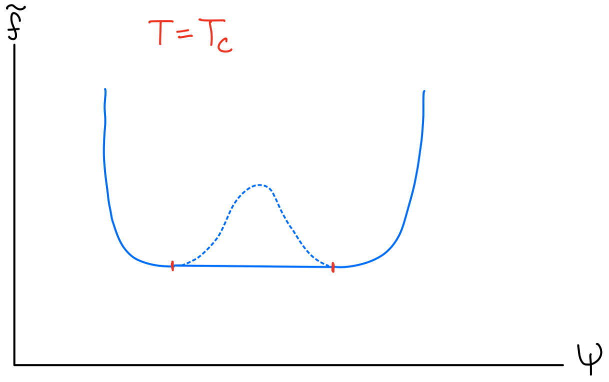


Figure 5.6: A corrected schematic of the first order phase transition at the critical temperature.

As heat is added to the system, starting at low temperature, the temperature of the system temporarily remains the same at T_C, as shown in Figure 5.7. The amount of heat needed to begin raising the temperature once more is exactly the latent heat defined in Equation 5.102.

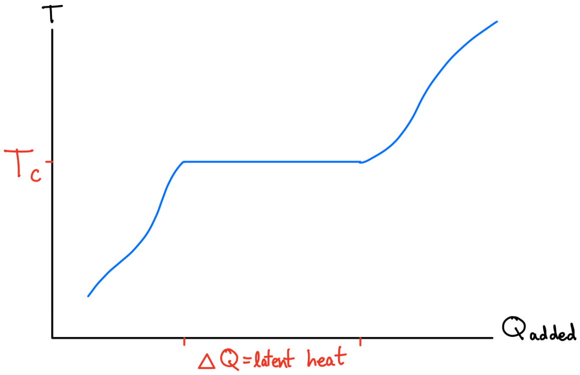


Figure 5.7: Temperature as a function of the heat added to the system. Note that once $T = T_c$, $\Delta Q = u_H - u_L$ is needed to continue increasing the temperature of the system.

How do we think of this in terms of the energy density u and the entropy density s (as we have in microcanonical statistics)? Recall that we have the relationship:

$$\frac{\partial s}{\partial u} = \frac{1}{T} \tag{5.104}$$

Recall that s is the maximum entropy density subject to the constraint of u. If one allows inhomogeneity, this implies that

$$\frac{\partial^2 s}{\partial u} \leq 0 \tag{5.105}$$

Why? If we allow the second derivative to be positive:

$$\frac{\partial^2 s}{\partial u} > 0 \tag{5.106}$$

then a system with the same total u can have a larger total s, a system can gain entropy by dividing. Suppose that the system is broken into two even parts:

$$u_{\text{total}} = V\left(\frac{1}{2}u_1 + \frac{1}{2}u_2\right) \tag{5.107}$$

$$s_{\text{total}} = V\left(\frac{1}{2}s_1 + \frac{1}{2}s_2\right) \tag{5.108}$$

Now let us compare this entropy, which resulted from the system separating, against the entropy of the case where the system remains together. In this case, we see that the entropy is lower (Here s is being treated as a function of the internal energy, $s(u)$):

$$s\left(\frac{1}{2}(u_1 + u_2)\right) < \frac{1}{2}(s(u_1) + s(u_2)) \tag{5.109}$$

Therefore it is entropically favorable for the system to split, and separate into two subsystems. From this, we have shown that a homogeneous system becomes unstable if $\frac{\partial^2 s}{\partial u^2} > 0$, and the limit of stability is if this second derivative is zero.

What does the function $s(u)$ look like when the system is undergoing a first order phase transition? A diagram of $s(u)$ is shown in Figure 5.8.

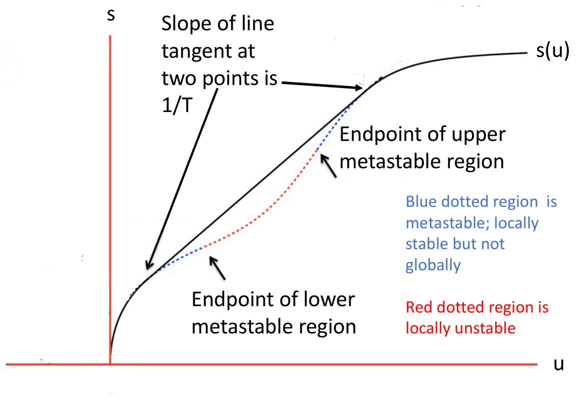


Figure 5.8: A diagram of $s(u)$ for a system undergoing a first order phase transition. The two metastable regions are drawn with blue dashed lines, and the locally unstable region is drawn with red dashed lines.

At T_c, the two phases coexist, thus the tangent lines to $s(u)$ must have the same slope, since the derivative of s gives us β. T_c occurs in the region between the two points where the tangent lines have the same slope. In this region, it is more entropically favorable for the system to split into two subsystems.

Suppose we are in the low T phase, and we heat up the system past T_c, without undergoing a phase transition. In this case, we are in what is known as the metastable superheated phase. This phase is locally stable, which means that local fluctuations in the system cannot allow the system to enter the mixed phase. However, this phase is globally unstable, large fluctuations, such as an external impulse on the system can force the system into the phase transition. Similarly, we have a metastable supercooled phase, which occurs if we start in the high T phase and cool the system below T_c without entering the phase transition. In between these two metastable regions, we have a region that is both locally and globally unstable.

We can describe these metastable phases qualitatively by thinking about the free energy $\tilde{f}$. As is shown in Figure 5.9, a system in the low T phase can remain in the low T phase even when it is not energetically favorable.

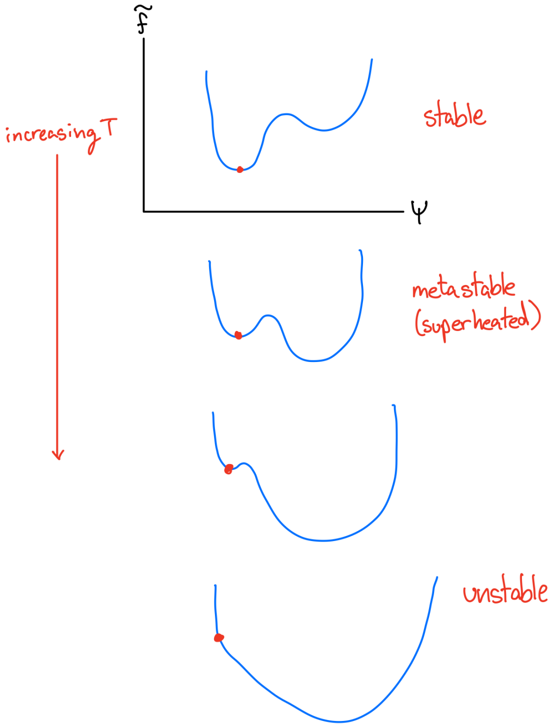


Figure 5.9: A diagram of a system in the low T phase heating up and remaining in the metastable superheated phase. As the temperature increases even further, the metastable state becomes unstable, and we undergo a phase transition.

Recall our description of the mixed phase, which had an interface. The energy cost of the interface is akin to a surface tension, the cost is proportional to the surface area of the interface, with some proportionality constant σ. Consider a system that is metastable, and in phase 1 with energy f_1. We have a second phase, phase 2, with free energy f_2. Suppose a small bubble of phase 2 forms inside a sea of phase 1, as shown in Figure 5.10.

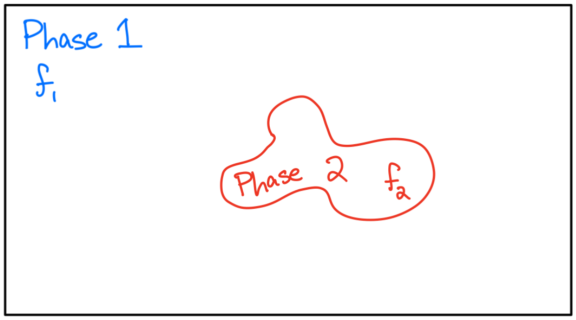


Figure 5.10: Schematic diagram of a phase 2 bubble nucleating inside a region of phase 1. Note that the interface shape is drawn as an arbitrary region.

What is the free energy of the phase 2 region? We can measure this relative to just phase 1:

$$\Delta F = -V(f_2 - f_1) + \sigma A \tag{5.110}$$

Where A is the surface area of the region and V is the volume. If we fix the volume of the region of phase 2, then the shape of the region that maximizes the surface area is a sphere, so let us assume that the region is spherical, with radius R. In this case, we can rewrite the change in free energy:

$$\Delta F = -\frac{4\pi}{3} R^3 (f_2 - f_1) + 4\pi\sigma R^2 \tag{5.111}$$

$$\tag{5.112}$$

Looking at the derivative:

$$\frac{\partial \Delta F}{\partial R} = 4\pi(2\sigma R - R^2(f_2 - f_1)) \tag{5.113}$$

From this, we see that if $R(f_2 - f_1) > 2\sigma$, then the derivative is negative, and the free energy decreases as the bubble of phase 2 grows in size. This defines a critical radius, above which any nucleated bubble of phase 2 will always grow in size:

$$R_c = \frac{2\sigma}{f_2 - f_1} \tag{5.114}$$

Any bubble smaller than this will shrink in size. Note that the creation of these bubbles arises from random fluctuations in our system. This means that if we have fluctuations on the order of the critical radius, the system is unstable. We can see that if we keep the system very close to T_c, then f_2 is very close to f_1, and the critical radius goes to infinity. This means that we can have metastable phases that last for a long time, since large fluctuations are unlikely to occur unless we have a very large system or we wait a very long time. One particularly famous example of this is nitroglycerin, which has a metastable liquid state. When nitroglycerin in this liquid state receives a external shock, it undergoes a phase transition (a particularly violent one).

5.6 Monte Carlo

This section is not present in Tom's lecture notes for the course, and is presented for those interested.

Monte Carlo methods are a class of computational techniques that rely on random sampling to evaluate high-dimensional sums or integrals. In statistical mechanics, many observables are expressed as thermal averages,

$$\langle \mathcal{O} \rangle = \frac{\sum_{\{s\}} \mathcal{O}(s)\, e^{-\beta H(s)}}{\sum_{\{s\}} e^{-\beta H(s)}},$$

where s denotes a microscopic configuration, $H(s)$ the Hamiltonian, and $\beta = 1/T$. For large systems, the configuration space is exponentially large, making direct evaluation of these integrals infeasible.

Monte Carlo sampling addresses this by generating a sequence of N configurations $\{s_i\}$ according to the Boltzmann weight $e^{-\beta H(s)}$. Expectation values can then be estimated as

$$\langle \mathcal{O} \rangle \approx \frac{1}{N} \sum_{i=1}^{N} \mathcal{O}(s_i),$$

with statistical error decreasing as $1/\sqrt{N}$.

The Ising model provides a canonical example. Recall the Ising Hamiltonian (5.16):

$$\hat{H} = -\frac{1}{2} J \sum_{\mathrm{NN}} \sigma_i \sigma_j - h \sum_i \sigma_i \tag{5.115}$$

To probe observables in this system numerically, we can use the Metropolis algorithm to sample configurations of the lattice. The Metropolis algorithm takes in several parameters. N_{samples} is the number of configurations that we wish to produce. In order to ensure that the configurations are independent of each other (in other words, to mitigate autocorrelation), we skip every N_{skip} configurations. We also allow the Markov chain[2] to "thermalize", by discarding the first $N_{\text{thermalization}}$ configurations. We also have the probability distribution that we wish to sample from, $\pi(x)$, and the "step size" of the algorithm. The pseudocode for the algorithm is shown in Algorithm 1.

Algorithm 1: Metropolis Algorithm

```
Input: $N_{\text{samples}}$, $N_{\text{thermalization}}$, $N_{\text{skip}}$, $\pi(x)$, $v$
Output: $N_{\text{samples}}$ samples from the distribution $\pi(\boldsymbol{x})$
samples = [ ]
$\boldsymbol{x}$ = uniform$(-1, 1)$
for $i = 0$ to $N_{samples} \cdot N_{skip} + N_{thermalization}$ do
    $\boldsymbol{x}' = \boldsymbol{x}$ + uniform$(-v, v)$
    prob = $\frac{\pi(\boldsymbol{x}')}{\pi(\boldsymbol{x})}$
    if $prob \geq uniform(0, 1)$ then
        $\boldsymbol{x} = \boldsymbol{x}'$
    end
    if $i \,\%\, N_{skip} == 0$ and $i \geq N_{thermalization}$ then
        samples.append$(\boldsymbol{x})$
    end
end
return samples
```

Essentially, each iteration of the algorithm produces a proposal configuration, which modifies the previous configuration by a perturbation, whose strength is governed by the step size. The algorithm then either accepts or rejects this proposal, based on the magnitude of the probability distribution given the proposed configuration. We then repeat this process until we have a set of sample configurations. With these, we can now compute per-configuration observables, and then average them to produce approximations for expectation values. We must mitigate autocorrelation between samples because neighboring configurations in the Markov chain are very highly correlated, for example, they might different only by the value of a single spin on the lattice. Skipping configurations before taking another sample then reduces the correlation between our samples. Thermalization is required because the initial state of the Markov chain does not resemble sampling from the target probability distribution, the chain takes some time before taking states from the chain represent sampling from the target distribution. Thus we allow the chain to thermalize, by ignoring the first $N_{\text{thermalization}}$ samples.

In the case of the Ising model, we can sample lattice configurations using the Boltzmann distribution $e^{-\beta H(s)}$, and then compute observables such as the average magnetization over the set of samples. If

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[2] The "Markov" label indicates that each element of the chain only depends on the previous element of the chain.

we set a temperature T, and compute average observables such as magnetization and energy based on those samples, we can plot these as a function of temperature, as shown in Figure 5.11.

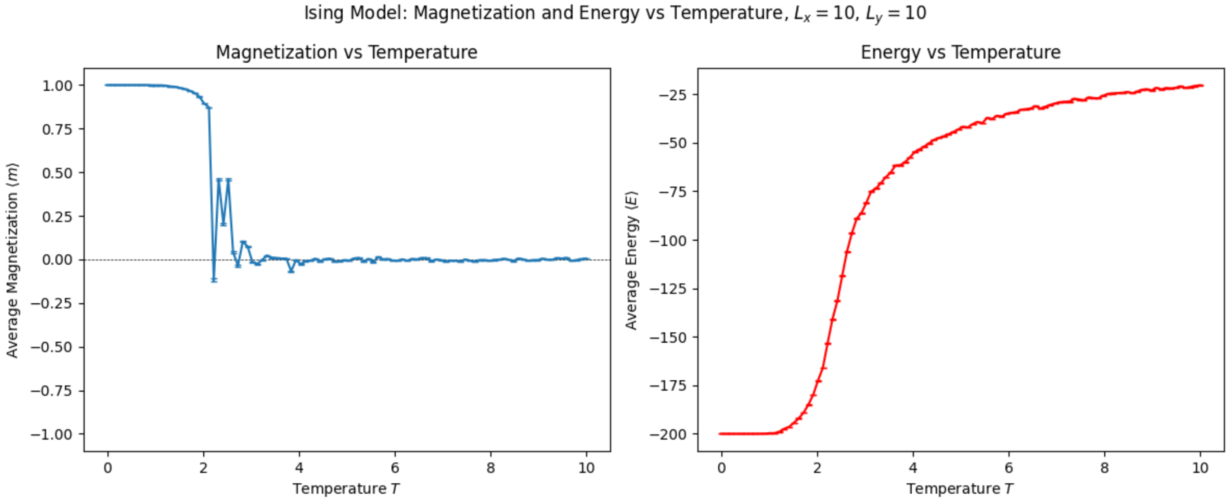

Figure 5.11: Average magnetization $\langle m \rangle$ and average energy $\langle E \rangle$ plotted as functions of temperature T for the 2D Ising model. In this system, $J = 1, h = 0$, and the lattice consists of 100 sites. Each data point is computed using 10^4 Monte Carlo samples, with 10^3 thermalized samples, and taking every 10th sample to reduce autocorrelation. Note that around T_c, even though the statistical error bars are small, increasing correlation lengths mean that local updates of spins become insufficient to accurately describe the observables.