PHYS612 Notes

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Contents

1 Linear Algebra Recap

1.1 Vectors and Dirac Notation

Coordinate systems that are used to describe vectors are not physical, they are created by man to describe the vector, which exists as an abstract physics object. Quantum mechanics is nothing more than applied linear algebra.

We have some abstract vector $|\psi\rangle$, which is a vector in a Hilbert space. The Hilbert space is complex, in that the components in any given eigenbasis can be complex valued. Dirac invented the notation we used, and $|\psi\rangle$ is known as a ket vector, and vectors of the form $\langle\psi|$ are known as bra vectors.

For every ket vector, there exists a bra vector, and the two of them are duals of each other. These are both two parts of the same vector, they encode the same information and we can switch between the two of them.

Suppose we have a vector $|\Phi\rangle = a\,|\phi\rangle$. Suppose we take the dual of $|\Phi\rangle$, which is $\langle\Phi|$. We obtain

$$\langle\Phi| = \langle\phi|\,a^*$$

Where the star denotes complex conjugation.

Let us now define an inner product:

$$\langle\alpha|\beta\rangle$$

This is the quantum mechanical moral equivalent of the dot product of two vectors. It eats two vectors and outputs a complex number:

$$\langle\alpha|\beta\rangle = c$$
$$\langle\beta|\alpha\rangle = c^*$$

In fact, by definition:

$$\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle^*$$

Let us now consider the inner product of a vector with itself:

$$\langle\alpha|\alpha\rangle$$

This must be real (via the definition of the inner product above), and ≥ 0.

Suppose we have a vector $|\alpha\rangle$ such that $\langle\alpha|\alpha\rangle > 0$. Now consider a new vector $|\overline{\alpha}\rangle = \frac{|\alpha\rangle}{\sqrt{\langle\alpha|\alpha\rangle}}$. This new vector has the property that $\langle\overline{\alpha}|\overline{\alpha}\rangle = 1$. This is a normalized vector.

In QM, $|\psi\rangle$ represents the physical state of a system, and we require that $\langle\psi|\psi\rangle = 1$. This is the reason that only unitary operators can do time evolution, since they preserve the norm of the coordinate system.

When picking coordinate systems, we always like to use orthonormal basis states. Given two basis states $|i\rangle$ and $|j\rangle$:

$$\langle i|j\rangle = \delta_{ij}$$

Where δ_{ij} is the Kronecker delta.

Now we introduce completeness:

$$|\alpha\rangle = \sum_i c_i |i\rangle$$

If we write this as a column vector:

$$|\alpha\rangle = \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_i \\ \vdots \end{bmatrix}$$

And the analogous row vector:

$$\langle\alpha| = \begin{bmatrix} c_1^* & c_2^* & \dots & c_i^* & \dots \end{bmatrix}$$

Now let us look at writing out the inner product:

$$\begin{aligned} \langle\alpha|\alpha\rangle &= \sum_{i,j} \langle j| c_j^* c_i |i\rangle \\ &= \sum_{i,j} c_j^* c_i \langle j|i\rangle \\ &= \sum_i c_i^* c_i \end{aligned}$$

Note that since $c_i^* c_i$ must be a real positive number, we have the same condition that we required earlier, $\langle\alpha|\alpha\rangle \geq 0$. If we instead use a normalized state, then we know that $\sum_i c_i^* c_i = 1$.

1.2 Operators

Linear operators can always be written in the form:

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

Which directly leads to the following:

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

Where A_{ij} is a matrix element of A. We can represent A in terms of a matrix:

$$A = \begin{bmatrix} A_{11} & A_{12} & \dots \\ A_{21} & A_{22} & \dots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

If we have $|\beta\rangle = A|\alpha\rangle$, and $|\beta\rangle = \sum_i b_i |i\rangle$ and $|\alpha\rangle = \sum_j a_j |j\rangle$. From this, we have that $b_i = \sum_i A_{ij} c_j$. As we can see, we can map Dirac notation directly onto vector-matrix manipulations.

Suppose we have a matrix A operating on a state $|\alpha\rangle$, and we want to convert it to its dual. The ket vector becomes a bra vector, and the operator becomes the Hermitian adjoint:

$$A|\alpha\rangle \to \langle\alpha| A^\dagger$$

Thinking of this a matrix, if we know that $\langle i|A|j\rangle = A_{ij}$, and the corresponding adjoint's matrix element is $\langle i|A^\dagger|j\rangle = A^*_{ji}$. Another straightforward to prove property is that

$$(AB)^\dagger = B^\dagger A^\dagger$$

Suppose we have an operator product, $C = AB$. The matrix elements of this are of the form:

$$\begin{aligned}\langle i|C|j\rangle &= \sum_k \langle i|A|k\rangle \langle k|B|j\rangle \\ &= \sum_k A_{ik}B_{kj}\end{aligned}$$

Let us now introduce some useful operators, starting off with the identity operator:

$$\mathbb{I} = \sum_i |i\rangle \langle i|$$

Applying this to an arbitrary state $|j\rangle$:

$$\begin{aligned}\mathbb{I}|j\rangle &= \sum_i |i\rangle \langle i| |j\rangle \\ &= |j\rangle\end{aligned}$$

This in fact allows us to prove the matrix product relationship.

Let us now discuss projection operator, $\mathcal{O}_p$. The defining characteristic of the projection operator is that $\mathcal{O}_p^2 = \mathcal{O}_p$. Projection operators map vectors from the full space onto a limited section of the space. In this sense, the identity operator is in fact also a projection operator.

Consider the projection operator $|\alpha\rangle \langle\alpha|$. We can show that this has the property necessary to be a projection operator:

$$|\alpha\rangle \langle\alpha|\alpha\rangle \langle\alpha| = |\alpha\rangle \langle\alpha|$$

Where we have assumed that $|\alpha\rangle$ is normalized.

Let us consider the operator:

$$|i\rangle \langle i| + |j\rangle \langle j|$$

This is a projection operator since $|i\rangle$ and $|j\rangle$ are orthonormal, so if we square the operator, the cross terms go away, since the inner product between $|i\rangle$ and $|j\rangle$ is 0.

Let us now define a Hermitian operator. An operator A is Hermitian if $A^\dagger = A$. Hermitian operators have some nice properties. If we take the expectation value of the operator in a state $|\alpha\rangle$:

$$\langle\alpha|H|\alpha\rangle$$

This is going to be real if H is Hermitian. To prove this, we note that we can group the operator with the bra:

$$\langle\alpha|H|\alpha\rangle = \langle\alpha|H^\dagger|\alpha\rangle$$

Now we note that this means that the complex conjugate of the inner product must equal itself, which is the definition of a real number.

The definition of a Hermitian operator when considering the matrix representation is that $H_{ij}^* = H_{ji}$.

Another nice property is that the eigenvalues of a Hermitian operator are real, which can be immediately derived from the previous property:

$$H\,|\psi_j\rangle = h_j\,|\psi_j\rangle$$

$$\begin{aligned}\langle\psi_j|H|\psi_j\rangle &= \langle\psi_j|h_j|\psi_j\rangle \\ &= h_j\,\langle\psi_j|\psi_j\rangle\end{aligned}$$

Which must be real.

Now looking at the eigenvectors of a Hermitian operator with distinct eigenvalues, we can form an orthogonal basis. To prove this, we begin with the eigenvalue condition:

$$H\,|\psi_j\rangle = h_j\,|\psi_j\rangle$$

We can go to the dual space:

$$\langle\psi_j|\,H = \langle\psi_j|\,h_j$$

We can do the same thing with a second eigencondition:

$$\begin{aligned}H\,|\psi_k\rangle &= h_k\,|\psi_k\rangle \\ \langle\psi_k|\,H &= \langle\psi_k|\,h_k\end{aligned}$$

Now let us look at

$$\langle\psi_k|H|\psi_j\rangle$$

We can look at this in two ways. First let us operate H on $|\psi_j\rangle$, which will get us $h_j\,\langle\psi_k|\psi_j\rangle$. If we instead use H on $\langle\psi_k|$, we get $h_k\,\langle\psi_k|\psi_j\rangle$. By the transitive property, we have that they are equal:

$$\begin{aligned}h_k\,\langle\psi_k|\psi_j\rangle &= h_j\,\langle\psi_k|\psi_j\rangle \\ (h_k - h_j)\,\langle\psi_k|\psi_j\rangle &= 0\end{aligned}$$

We know that for this to be true, one of these has to be 0. since h_j and h_k are distinct, this tells us that the eigenvectors are orthogonal. In the case of degenerate eigenvalues, we can use the Gram-Schmidt process to obtain a new set of vectors that are orthogonal.

Let us now discuss unitary operators. An operator U is unitary if $UU^\dagger = U^\dagger U = \mathbb{I}$. This can also be written as $U^{-1} = U^\dagger$.

These are known as unitary operators as they preserve the norm, if $\langle\alpha|\alpha\rangle = 1$, then $U\,|\alpha\rangle$ will also have norm 1. This tells us that unitary operators take physical states to other physical states. An important example of this is the time evolution operator. Unitary operators also preserve orthonormal bases. If $\langle i|j\rangle = \delta_{ij}$, and we make a new orthonormal basis set, $|i'\rangle = U|i\rangle$ and $|j'\rangle = U|j\rangle$, then $\langle i'|j'\rangle = \langle i|j\rangle = \delta_{ij}$. Unitary operators map orthonormal bases into other orthonormal bases.

Let us now look at the eigenvalues of a unitary operator. The claim is that the eigenvalues of a unitary operator have a norm of 1, it is of the form $e^{i\theta}$. If $U|\psi_j\rangle = u_j|\psi_j\rangle$, we can move to the dual:

$$\langle\psi_j| U^\dagger = \langle\psi_j| u_j^*$$

Now we note that $\langle\psi_j|U^\dagger U|\psi_j\rangle = 1$, and thus looking at the right hand side:

$$\langle\psi_j|u_j^* u_j|\psi_j\rangle = 1$$

Which tells us that $u_j^* u_j = 1$.

1.3 Measurements and Uncertainty

Suppose we have some Hermtian operator A, written in its eigenbasis:

$$\begin{aligned} A &= \sum_i a_i |i\rangle\langle i| \\ &= \sum_i a_i \rho_i \end{aligned}$$

When we measure, we will project onto state i with probability $\langle\psi|\rho_i|\psi\rangle = |\langle\psi|i\rangle|^2$. We can also consider the expectation value of the operator:

$$\begin{aligned} \langle A\rangle &= \sum_i a_i P_i \\ &= \sum_i a_i \langle\psi_i|\rho_i|\psi_i\rangle \\ &= \langle\psi|A|\psi\rangle \end{aligned}$$

Suppose we have $|\psi\rangle = \sum_j c_j|j\rangle$. We can write the dual vector, $\langle\psi| = \sum_k \langle k| c_k^*$. Now let us write out the expectation value:

$$\begin{aligned} \langle\psi|A|\psi\rangle = \langle\psi|\mathbb{I}A\mathbb{I}|\psi\rangle \\ &= \langle\psi|k\rangle\langle k|A|j\rangle\langle j|\psi\rangle \\ &= \sum_{j,k} c_k A_{kj} c_j \end{aligned}$$

We can write out the expectation value in multiple different ways, from the probabilistic method to the matrix multiplication representation.

Suppose we have the vector $|\psi\rangle$, and the associated projection operator, $\rho_\psi = |\psi\rangle\langle\psi|$. What if we want to find the expectation value of A while only using ρ_ψ? We can do this via the trace:

$$\begin{aligned} \langle A\rangle &= \mathrm{Tr}[A\rho] \\ &= \mathrm{Tr}[\rho A] \end{aligned}$$

This is the sum over any set of orthonormal basis vectors:

$$\begin{aligned}\mathrm{Tr}[A\rho] &= \sum_j \langle j|\, A\rho\, |j\rangle \\ &= \sum_{j,k} \langle j|\, A\, |k\rangle \langle k|\, |\psi\rangle \langle\psi|\, |j\rangle \\ &= \sum_{j,k} \langle\psi|j\rangle \langle j|A|k\rangle \langle k|\psi\rangle \\ &= \langle\psi|A|\psi\rangle \\ &= \langle A\rangle\end{aligned}$$

Where we have inserted the identity, $\sum_k |k\rangle\langle k|$.

ρ is an example of a density matrix.

Let us quickly discuss commutators and anticommutators:

$$\begin{aligned}[A,B] &= AB - BA \\ \{A,B\} &= AB + BA\end{aligned}$$

Listing a few more properties:

$$\begin{aligned}[A,B] &= -[B,A] \\ [A,BC] &= [A,B]C + B[A,C] \\ [AB,C] &= [A,C]B + A[B,C] \\ [A,[B,C]] + [B,[C,A]] + [C,[A,B]] &= 0\end{aligned}$$

Suppose we have two observables, A and B. Under what circumstances can we measure both of them at the same time? If they are compatible for measurements, they commute. This is because they must share eigenvectors, for them to be simultaneously measurable. This is because if we measure A, we cannot modify the state, it must be an eigenvector. Then we can measure B. By the same logic, we must be able to measure B and then A and not mess with the state. This tells us that the commutator must be zero, because $AB\,|i\rangle$ must be the same as $BA\,|i\rangle$.

Now how do we meaningfully quantify our ignorance? We use the variance, σ^2 for a particular operator:

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

The claim is that there is a relationship between the uncertainty in two observables, A and B in the state $|\psi\rangle$:

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

This is the generalized uncertainty principle.

To prove this, the basic idea is to use the Cauchy-Schwartz identity:

$$\langle\alpha|\alpha\rangle\,\langle\beta|\beta\rangle \geq |\,\langle\alpha|\beta\rangle\,|^2$$

We then construct:

$$\begin{aligned} |\alpha\rangle &= (A - \langle A\rangle)\, |\psi\rangle \\ |\beta\rangle &= (B - \langle B\rangle)\, |\psi\rangle \end{aligned}$$

We then apply the CS identity and out pops the uncertainty principle.

2 Two Level Systems

There are many different systems that can be represented in terms of two basis vectors, such as spins, qubits, energy of a particle in a magnetic field, but all of them can be treated the exact same way mathematically.

Consider an arbitrary two level system. There are 4 (linearly independent) Hermitian operators:

$$\begin{aligned} \mathbb{I} &= |\uparrow\rangle\, \langle\uparrow| + |\downarrow\rangle\, \langle\uparrow| \\ &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \\ \sigma_x &= |\downarrow\rangle\, \langle\uparrow| + |\uparrow\rangle\, \langle\downarrow| \\ &= \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ \sigma_y &= -i\, |\uparrow\rangle\, \langle\downarrow| + i\, |\downarrow\rangle\, \langle\uparrow| \\ &= \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \\ \sigma_z &= |\uparrow\rangle\, \langle\uparrow| - |\downarrow\rangle\, \langle\downarrow| \\ &= \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \end{aligned}$$

These are also all unitary matrices. We can write the most general Hermitian operator as a linear combination of these 4:

$$H = h_1\mathbb{I} + h_x\sigma_x + h_y\sigma_y + h_z\sigma_z$$

Where h_1, h_x, h_y and h_z are complex numbers. Let us list a few more properties:

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = \mathbb{I}$$

We can also define the anticommutator between two of the operators:

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij}$$

And the commutator:

$$[\sigma_i, \sigma_j] = i2\epsilon_{ijk}\sigma_k$$

Where ϵ_{ijk} is the Levi-Civita symbol. This is a Lie algebra, specifically $SU(2)$, or $SO(3)$.

We can also think about the spin operators:

$$S_i = \frac{\sigma_i}{2}$$

And the associated commutation relations for angular momentum:

$$[S_j, S_k] = i\epsilon_{ijk}S_l$$

Let us now define a 3D vector, $\boldsymbol{\sigma}$ whose components are 2D operators:

$$\boldsymbol{\sigma} = n_x\sigma_x + n_y\sigma_y + n_z\sigma_z$$

Where $n_x^2 + n_y^2 + n_z^2 = 1$.

Our claim, which is easy to prove, is that $(\hat{n}\cdot\boldsymbol{\sigma})^2 = 1$. We can write out our arbitrary Hermitian operator in a more compact form:

$$H = h\mathbb{I} + \boldsymbol{h}\cdot\boldsymbol{\sigma}$$

This is a two dimensional matrix:

$$\begin{bmatrix} h_1 + h_z & h_x + h_y \\ h_x - ih_y & h_1 - h_z \end{bmatrix}$$

Let us find the eigenvalues of this operator. We need the determinant and the trace. The trace is simple, and the determinant is a bit harder:

$$\begin{aligned} \text{Tr}[H] &= 2h_1 \\ \det H &= h_1^2 - (h_x^2 + h_y^2 + h_z^2) \end{aligned}$$

We can then write out the characteristic equation:

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

Which leads to $\lambda = h_1 \pm |\boldsymbol{h}|$. There is an easier way to compute this though. We will first note that the eigenstates of the identity matrix will be the same as the eigenstates of $\boldsymbol{\sigma}$. Thus we can look at only the $\boldsymbol{h}\cdot\boldsymbol{\sigma}$ term. Let us first set up the eigenvalue equation:

$$\begin{aligned} (\boldsymbol{h}\cdot\boldsymbol{\sigma})\,|\psi\rangle &= a\,|\psi\rangle \\ (\boldsymbol{h}\cdot\boldsymbol{\sigma})^2\,|\psi\rangle &= a^2\,|\psi\rangle \end{aligned}$$

Where we have squared both sides. Now we note that the left side will be just $|\boldsymbol{h}|^2$:

$$|\boldsymbol{h}|^2 = a^2\,|\psi\rangle$$

Thus we have that the eigenvalue is $a = \pm|\boldsymbol{h}|$, and thus we can now tack on the eigenvalue of $\mathbb{I}$, which is 1, so we have $h_1 \pm |\boldsymbol{h}|$.

Let us now show how these are related to rotations in 3D. Consider the operator:

$$\sigma^{x-y}(\phi) = \cos(\phi)\sigma_x + \sin(\phi)\sigma_y$$

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

Suppose we now want to rotate this around the z axis. Let us consider the commutator:

$$\begin{aligned} \left[\frac{\sigma_z}{2}, \sigma^{x-y}(\phi)\right] &= i\left(\cos(\phi)\sigma_y - \sin(\phi)\sigma_x\right) \\ &= -i\frac{d}{d\phi}\sigma^{x-y}(\phi) \end{aligned}$$

We see that σ_z generates an infinitesimal rotation about the z axis. This is why we say that the Pauli matrices encode rotations in three dimensions.

One can also show that

$$e^{i\theta\sigma_z/2}\sigma^{x-y}(\phi)e^{-i\theta\sigma_z/2} = \sigma^{x-y}(\phi+\theta)$$

Where we have generated a finite rotation, rather than an infinitesimal one.

We can now write out the most general unitary operator:

$$\begin{aligned} U(\delta,\theta,\hat{n}) &= e^{i\delta}e^{i\theta\hat{n}\cdot\frac{\boldsymbol{\sigma}}{2}} \\ &= e^{i\delta}e^{i(n_x\sigma_x/2+n_y\sigma_y/2+n_z\sigma_z/2)} \end{aligned}$$

Where $n_x = \hat{n}_x\theta$, and similarly for n_y and n_z.

We can also show that $U(\delta,\theta,\hat{n}) = e^{i\delta}\left[\cos\theta\mathbb{I} + i\sin\theta\hat{n}\cdot\boldsymbol{\sigma}\right]$

2.1 Tensor/Outer Products

Tensor products allow us to represent the state of multiple systems at the same time:

$$|a\rangle^{(1)} \otimes |b\rangle^{(2)} = |a,b\rangle$$

There are some states in our Hilbert space that cannot be written in terms of tensor products, such as $|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle$ (neglecting normalization). This state cannot be written as any form of $|a\rangle \otimes |b\rangle$. This is why we use the tensor product states as a basis to discuss the combination of the two systems.

Consider the state

$$\frac{1}{2}(|\uparrow\uparrow\rangle + |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle + |\downarrow\downarrow\rangle)$$

This can in fact be written as a tensor product state:

$$\frac{1}{\sqrt{2}}\left(|\uparrow\rangle + |\downarrow\rangle\right) \otimes \frac{1}{\sqrt{2}}\left(|\uparrow\rangle + |\downarrow\rangle\right)$$

Note that if a state cannot be written as a tensor product, we consider that to be an entangled state.

This leads to two questions, how can we determine whether a state can be written as a tensor product, and the other is why should we care?

The reason entanglement matters is that we cannot do QM on an entangled system, the outcome of a measurement on one part of the system influences the rest of the system.

Let us now consider the operators that act on this joint system. Consider the operator

$$A = A^{(1)} \otimes A^{(2)}$$

Given two states:

$$\begin{aligned} |\phi\rangle &= |x\rangle^{(1)} \otimes |y\rangle^{(2)} \\ |\psi\rangle &= |v\rangle^{(1)} \otimes |w\rangle^{(2)} \end{aligned}$$

We define $\langle\phi|A|\psi\rangle$ to be

$$\langle\phi|A|\psi\rangle = \langle x|A^{(1)}|v\rangle \langle y|A^{(2)}|w\rangle$$

Suppose $A = \sigma_x^{(1)} \otimes \sigma_y^{(2)}$, and we want to compute

$$\begin{aligned} \langle\uparrow\downarrow|A|\downarrow\uparrow\rangle &= \langle\uparrow|\sigma_x|\downarrow\rangle \langle\downarrow|\sigma_y|\uparrow\rangle \\ &= 1 \cdot i \\ &= i \end{aligned}$$

Consider the operator $O = \sigma_x^{(1)} \otimes \mathbb{I}$. Suppose we have the basis states $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, and $|\downarrow\downarrow\rangle$, and we want to write O as a matrix in this basis: O =

$$\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}$$

Note that σ_x appears in the corners, and the 0 submatrix appears in the other two corners.

Let us introduce an operator $\rho_\psi^{(1)} = \text{Tr}_2[\rho_\psi]$, where $\rho_\psi = |\psi\rangle\langle\psi|$. This is the sum over the diagonal elements of the second system, ignoring the elements of the first system. This is essentially obtaining the information that we have if we ignore the first system. This is known as the reduced density matrix.

Suppose we have an operator $O^{(1)} \otimes \mathbb{I}$, and we apply the full trace:

$$\begin{aligned} \text{Tr}\left[\rho_\psi \left(O^{(1)} \otimes \mathbb{I}^{(2)}\right)\right] &= \text{Tr}_1\left[\rho_\psi^{(1)} O^1\right] \\ &= \langle O^{(1)} \rangle \end{aligned}$$

Where ρ_ψ is the full density operator, and we see that it is replaced with the reduced density operator.

The full trace over the system turns into a trace over just the first part of the system.

Looking at the trace of the full density operator:

$$\begin{aligned} \text{Tr}[\rho_\psi] &= \text{Tr}\left[|\psi\rangle\langle\psi|\right] \\ &= 1 \end{aligned}$$

Note that $|\psi\rangle\langle\psi|$ is a projection operator, and those have eigenvalues of 1 and 0. We can get the reduced operators from the trace over the other space:

$$\mathrm{Tr}_2\left[\rho_\psi\right] = \rho_\psi^{(1)}$$

Consider the trace of the reduced density operator:

$$\mathrm{Tr}\left[\rho_\psi^{(1)}\right] = 1$$

Note that this means that the sum of the eigenvalues of the reduced density matrix is 1, and they are all nonnegative. This is because they act like probabilities.

Consider $\rho^{(1)}$:

$$\rho^{(1)} = \sum_k p_k \left|k\right\rangle^{(1)} \left\langle k\right|^{(1)}$$

Where p_k is the probability that we find ourselves in state $|k\rangle$.

We can think of the expectation value of an operator:

$$\langle O^{(1)}\rangle = \sum_k p_k \left\langle k|O|k\right\rangle^{(1)}$$

If the eigenvalues of the reduced density operator are all either 1 or 0, then we have a non-entangled system, and vice versa, if we have eigenvalues other than 1 or 0, then we have an entangled system.

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2.2 Canonical Commutation Relations

We have that $e^{-ipx_0}\hat{x}e^{ipx_0} = \hat{x} - x_0\mathbb{I}$. From this, let us derive the canonical commutation relations of QM.

Let us Taylor expand for small x_0:

$$\begin{aligned}
e^{-ipx_0}\hat{x}e^{ipx_0} &= \left(1 - i\hat{p}x_0 - \frac{x_0^2\hat{p}^2}{2} + \dots\right)\hat{x}\left(1 + i\hat{p}x_0 - \frac{x_0^2\hat{p}}{2} + \dots\right)\\
&= \hat{x} - ix_0\left(\hat{p}\hat{x} - \hat{x}\hat{p}\right) - \frac{x_0^2}{2}\left(\hat{p}^2\hat{x} + \hat{x}\hat{p}^2 - 2\hat{p}\hat{x}\hat{p}\right)\\
&= \hat{x} + ix_0[\hat{x},\hat{p}] - \frac{x_0^2}{2}[\hat{p},[\hat{p},\hat{x}]] + \dots
\end{aligned}$$

This is supposed to be $\hat{x} - x_0\mathbb{I}$. Now to make both sides equal, let us conjecture that $[\hat{x},\hat{p}] = i\mathbb{I}$. If so, then we can account for the $-x_0$ term. The other terms are zero, because it is the commutator of an operator with a constant, since we have nested commutators. Thus we have derived the canonical commutation relation between $\hat{x}$ and $\hat{p}$.

Recall that we have previously learned that $\hat{p}$ operating in the position basis is $-i\frac{\partial}{\partial x}$, but if we look at $\hat{p}\,|x\rangle$:

$$\hat{p}\,|x\rangle = i\frac{\partial}{\partial x}\,|x\rangle$$

Consider the relation that we derived previously:

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

We want to get $\langle x''|\hat{p}|x'\rangle$ out of this somehow, so let us Taylor expand both sides of the equation:

$$\langle x''|1+i\hat{p}x_0-\frac{1}{2}\hat{p}^2x_0^2+\dots|x'\rangle = \delta(x''-x')+x_0\delta'(x''-x')+\frac{1}{2}x_0^2\delta''(x''-x')+\dots$$

Now we note that the first term is easy to equate. For the x_0 term, we have that

$$\begin{aligned}x_0 i\,\langle x''|\hat{p}|x'\rangle &= \delta'(x''-x') \\ &= \frac{\partial}{\partial x''}\delta(x''-x') \\ &= -\frac{\partial}{\partial x'}\delta(x''-x')\end{aligned}$$

If we then multiply both sides by $-i$:

$$\begin{aligned}\langle x''|\hat{p}|x'\rangle &= -i\frac{\partial}{\partial x''} \\ &= -i\,\langle x''|x'\rangle \\ &= +i\,\langle x''|x'\rangle\end{aligned}$$

We can also write these as:

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

Or

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

This derives the properties that we know:

$$\begin{aligned}\langle x''|\,\hat{p} &= -i\frac{\partial}{\partial x''}\,\langle x''| \\ \hat{p}\,|x'\rangle &= +i\frac{\partial}{\partial x'}\,|x'\rangle\end{aligned}$$

If we look at the x_0^2 term, we have that

$$\begin{aligned}\langle x''|\hat{p}^2|x'\rangle &= -\delta''(x''-x') \\ &= -\frac{\partial^2}{\partial x'^2}\,\langle x''|x'\rangle \\ &= \frac{\partial^2}{\partial x''^2}\,\langle x''|x'\rangle\end{aligned}$$

Now let us ask what $\langle x|\hat{p}|\psi\rangle$ is. We have $\hat{p}$ acting on x:

$$
\begin{aligned}
&(\langle x|\,\hat{p})\,|\psi\rangle \\
&\qquad = -i\frac{\partial}{\partial x}\langle x|\psi\rangle \\
&\qquad = -i\frac{\partial}{\partial x}\psi(x)
\end{aligned}
$$

This is what we initially learn when we learn QM.

Suppose we now have $\hat{p}\,|\psi\rangle$. Let us now insert 1:

$$
\begin{aligned}
\hat{p}\,|\psi\rangle &= \mathbb{I}\hat{p}\,|\psi\rangle \\
&= \int dx\ |x\rangle\,\langle x|\,\hat{p}\,|\psi\rangle \\
&= \int dx\ |x\rangle\left(-i\frac{\partial}{\partial x}\psi\,(x)\right)
\end{aligned}
$$

Now if we take the commutation relation that we have for $\hat{p}$ and x, we can use the generalized uncertainty principle:

$$\sigma_x\sigma_p \geq \frac{1}{2}$$

3 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 it must be some unitary operator that does a time translation:

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

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

$$
\begin{aligned}
\langle\psi(t_0)|U^\dagger U|\psi(t_0)\rangle &= \langle\psi(t)|\psi(t)\rangle \\
&= 1
\end{aligned}
$$

It can be shown that

$$\frac{dU(t,t_0)}{dt}U^\dagger(t,t_0) = -iH$$

Where H is some Hermitian operator. Now for notation's sake, let us say that $t_0 = 0$, and drop the t_0.

To prove the above statement, let us note that

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

since the inside is $\mathbb{I}$. We can now use the product rule:

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

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

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

Where H is some Hermitian operator. Now suppose we multiply by U on both sides:

$$i\frac{d}{dt}[U]U^\dagger U = HU$$
$$i\frac{d}{dt}[U] = HU$$

Now let us multiply on the right by the ket vector $|\psi(t_0)\rangle$:

$$HU|\psi(t_0)\rangle = i\frac{\partial}{\partial t}\left(U|\psi(t_0)\rangle\right)$$
$$H|\psi(t)\rangle = i\frac{\partial}{\partial t}|\psi(t)\rangle$$

This is the Schrodinger equation, and we see that H must then be the Hamiltonian. We see that if we start with the basic assumption that states remain normalized, the Schrodinger equation naturally comes out.

Suppose that $H(t) = H(t_0) = H$, the Hamiltonian is time independent. In this case, we have a trivial solution, which we obtain via $U = e^{-iHt}$. One way to show that this solves our equation 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 eigenbasis:

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

Where $\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle$. Note that this equation is the time independent Schrodinger equation.

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

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

Where T is the time ordered product. For two operators:

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

Where Θ is the Heaviside step function, it is 1 if the argument is larger than 0, and 0 if the argument is less than 0. Note that we can also define the Heaviside step function via a delta function:

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

Note that in our use case, we have an exponential, which we have to Taylor expand, which then gives us the arguments to the time ordered product.

$$T\left[\exp\left(-i\int_{t_0}^{t} \hat{H}(t')\, dt'\right)\right] = T\left[\mathbb{I} - i\int_{t_0}^{t} \hat{H}(t')\, dt' + \frac{1}{2}\int_{t_0}^{t} \hat{H}(t')\, dt' \int_{t_0}^{t} \hat{H}(t'')\, dt'' + \dots\right]$$

Looking at the quadratic term:

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

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. The claim is 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

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

This is proof that this $\hat{U}$ is a solution of

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

Let us now consider the expectation value $\langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle A\rangle(t)$. First, we note that this is the same as

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \langle\psi(0)|\, U^{\dagger}(t)\hat{A}U(t)\, |\psi(0)\rangle$$

The original expectation value is the Schrodinger picture, the operator remains the same and the state moves in time. Now instead, consider $\hat{A}_H = U^{\dagger}\hat{A}U$, which turns the expectation value into

$$\langle\psi_0|\hat{A}_H(t)|\psi_0\rangle$$

This is the Heisenberg picture, the state remains the same and the operator changes over time. For simplicity, let us assume that $\hat{A}$ has no time dependence. What if we want to write a diffeq for the evolution of $\hat{A}_H$ over time? We can compute the derivative:

$$\begin{aligned}\dot{A}_H &= \frac{d}{dt}\hat{U}^{\dagger}(t)\hat{A}\hat{U}(t)\\ &= \dot{U}^{\dagger}(t)\hat{A}U(t) + U^{\dagger}(t)\hat{A}\dot{U}(t)\end{aligned}$$

Now using the fact that $\dot{U} = -iHU$ and $\dot{U}^{\dagger} = +iU^{\dagger}H$:

$$\dot{A}_H = +iU^{\dagger}HAU - iU^{\dagger}AHU$$

$$\begin{aligned}
&= iU^\dagger H U^\dagger U A U - iU^\dagger A U^\dagger U H U \\
&= -i\left[U^\dagger A U, U^\dagger H U\right] \\
&= -i\left[A_H, H_H\right]
\end{aligned}$$

This tells us that

$$\dot{A}_H = -i[A_H, H_H]$$

Where H_H is something that we have defined, and we can easily that $H_H = H$ when H is time-independent, since if $A = H$, then our derived value for $\dot{A}_H$ tells us that $\dot{H}_H = 0$. This tells us that we have

$$\dot{A}_H = -i[A_H, H]$$

This is the equation of motion in the Heisenberg picture.

Consider a 1D case of a particle. We have that $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}$, where $V(\hat{x})$. We have defined V as a function, and it acts on the operator $\hat{x}$. Using the Heisenberg equation of motion, we can find $\dot{x}_H$:

$$\dot{x}_H = -i\left[\hat{x}_H, \hat{x}\right]$$

Before we do this, let us compute $[x_H, p_H]$:

$$\begin{aligned}
[x_H, p_H] &= [U^\dagger x U, U^\dagger p U] \\
&= U^\dagger x U U^\dagger p U - U^\dagger p U U^\dagger x U \\
&= U^\dagger i U \\
&= i\mathbb{I}
\end{aligned}$$

We see that in the Schrodinger and Heisenberg pictures, our commutators are the same. Going back to the equation of motion, we have that $\hat{H} = \frac{p_H^2}{2m} + V(x_H)$. Thus the equation of motion is:

$$\begin{aligned}
\dot{x}_H &= -i[x_H, \frac{p_H^2}{2m}] \\
&= \frac{p_H}{m}
\end{aligned}$$

We see that we have the same structure that we did in classical mechanics.

Now let us consider the derivative of p_H:

$$\begin{aligned}
\dot{p}_H &= -i\left[p_H, H\right] \\
&= -i[p, V(x_H)] \\
&= -V'(x_H)
\end{aligned}$$

Where V' is the derivative with respect to its argument, and we then insert hats on top of the xs. Note that the derivative of potential is force. From this, we get Ehrenfest's theorem, which states that

$$\frac{d}{dt}\langle p\rangle = \langle \text{Force}\rangle$$

Moving to 3 dimensions, let us first consider the commutation relations:

$$[x_j, p_k] = i\delta_{jk}$$

We can write the Hamiltonian:

$$\hat{H} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + V(\hat{x}, \hat{y}, \hat{z})$$

Following the same logic as for the 1D case, we get that

$$\dot{x}_j = \frac{p_j}{m}$$

And similarly:

$$\dot{\boldsymbol{p}} = -\nabla(\boldsymbol{x})$$

Where once again, the gradient represents the gradient of the functional form of V, and then the replacement of $\boldsymbol{x}$ with $\hat{\boldsymbol{x}}$. Note that this is also equal to the 3D representation of the force. We can also write $\dot{\boldsymbol{p}} = m\ddot{\boldsymbol{x}}$:

$$m\ddot{\boldsymbol{x}} = \text{Force}(\boldsymbol{x})$$

We see that we have reduced this down to classical mechanics.

Let us look at an extremely simple system, the two level system. We have a single spin, and we apply an external magnetic field. It wants to align with the magnetic field, but it cannot, since that would mean a decrease in energy and there is nothing to take the energy away. Instead, the spin will precess.

Let us begin with the Hamiltonian:

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

Where $\boldsymbol{\mu} = g\mu_B \boldsymbol{S} = g\mu_B \frac{\boldsymbol{\sigma}}{2}$, where g is the g-factor, μ_B is the Bohr magneton. Thus we have that the Hamiltonian is

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

Suppose that the magnetic field was aligned in the $\hat{z}$ direction, $\boldsymbol{B} = B_0\hat{z}$. Let us call $\omega = g\mu_B B_0$. Thus we have that

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

Now let us see how this time evolves. We have our time evolution operator, $\hat{U} = e^{-i\hat{H}t}$:

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

Now note that σ_z in the Heisenberg picture will not change, since it commutes with the Hamiltonian. However, σ_x and σ_y do not commute with the σ_z in the Hamiltonian, and thus we will have precession. We can show this by looking at what σ_x^H is, which is $U^\dagger \sigma_x U$, which we have shown (in the homework) generates rotations. The same is true for σ_y^H. We can also do this by looking at the Heisenberg equation of motion for σ_x and σ_y, and solve those diffeqs. MISSED A LECTURE HERE

We introduced the harmonic oscillator and rewrote our scaled x and p operators in terms of a and $a^\dagger$, and we found that $\hat{H} = \omega\left(\hat{N} + \frac{1}{2}\right)$, $[\hat{a}, \hat{N}] = \hat{a}$, and $[\hat{a}^\dagger, N] = -\hat{a}^\dagger$. Let us find the eigenvectors of $\hat{N}$:

$$\hat{N}\left|n\right\rangle = n\left|n\right\rangle$$

Consider $\hat{a}\left|n\right\rangle$. Let us first assume that this is an eigenstate, and let us find its eigenvalue:

$$\begin{aligned}
\hat{N}\left(\hat{a}\left|n\right\rangle\right) &= \left[\hat{a}\hat{N} + (\hat{N}\hat{a} - \hat{a}\hat{N})\right]\left|n\right\rangle \\
&= [\hat{a}\hat{N} - \hat{a}]\left|n\right\rangle \\
&= \hat{a}(\hat{N} - 1)\left|n\right\rangle \\
&= \hat{a}(n-1)\left|n\right\rangle \\
&= (n-1)\hat{a}\left|n\right\rangle
\end{aligned}$$

Thus we have that $\hat{a}\left|n\right\rangle$ is an eigenstate of $\hat{N}$, with eigenvalue $n-1$.

Now suppose that $\left|n\right\rangle$ is normalized, $\langle n|n\rangle = 1$. Note that $\hat{a}\left|n\right\rangle$ is not normalized:

$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle = n$$

Since $\hat{a}^\dagger\hat{a} = \hat{N}$. From this, we know that we can write $\hat{a}\left|n\right\rangle$ as a normalization factor times the state $\left|n-1\right\rangle$ (since it has eigenvalue $n-1$) :

$$\hat{a}\left|n\right\rangle = \sqrt{n}\left|n-1\right\rangle$$

We can do the same thing with $\hat{a}^\dagger$:

$$\hat{a}^\dagger\left|n\right\rangle = \sqrt{n+1}\left|n+1\right\rangle$$

Note that the restriction on the values of n to positive integers comes from the fact that state functions cannot have negative norm. Consider

$$\langle n|\hat{a}^\dagger\hat{a}|n\rangle = n$$

Note that we immediately see that $n \geq 0$. Now we also note that this is also equal to $n\left\langle n-1|n-1\right\rangle$, since $\left|n-1\right\rangle$ is normalized. Note that if we take some positive integer value of n, then we can drop the state over and over again until we reach 0, at which point the chain will stop. And note that if we state with a non-integer n, then eventually we will reach $\langle n-1|n-1\rangle$ that is not normalizable. The argument is completely algebraic, we haven't said anything about the physics of the system.

Now let us write the time evolution operator for this system:

$$\hat{U}(t) = \exp\left(-i\omega(\hat{N} + \frac{1}{2})t\right)$$

This as written is not very useful, let's instead write it out in the diagonal form in its eigenbasis:

$$\hat{U}(t) = \sum_{n=0}^{\infty} |n\rangle \langle n| \, e^{-i\omega(n+\frac{1}{2})t}$$

Now how would we raise the vector $|0\rangle$ to $|n\rangle$:

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

Now consider the matrix elements. Suppose we wanted to compute $\langle n'|\hat{\tilde{x}}|n'\rangle$. Now to do this, lets express $\hat{\tilde{x}}$ in terms of $\hat{a}$ and $\hat{a}^{\dagger}$:

$$\begin{aligned}
\langle n'|\hat{\tilde{x}}|n'\rangle &= \frac{1}{\sqrt{2}} \langle n'|\hat{a} + \hat{a}^{\dagger}|n\rangle \\
&= \frac{1}{\sqrt{2}} \left[\langle n'|\hat{a}|n'\rangle + \langle n'|\hat{a}^{\dagger}|n'\rangle\right] \\
&= \sqrt{n}\delta_{n',n'-1} + \sqrt{n+1}\delta_{n',n'+1}
\end{aligned}$$

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 operator:

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

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

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

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

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

Suppose we now consider

$$\begin{aligned}
\int_{0}^{\infty} e^{-\beta\omega} \, d\omega \int_{-\infty}^{\infty} dt \, e^{i\omega t} \mathrm{Tr}\left[\hat{U}\left(t\right)\right] &= \sum_{n} \exp(-\beta E_n) \\
&= \mathrm{Tr}\left[e^{-\beta \hat{H}}\right] \\
&= Z(\beta)
\end{aligned}$$

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 get the partition function. Suppose we instead do the ω integral first:

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\,\left[\int_{0}^{\infty} d\omega\, e^{-\beta\omega}e^{-i\omega t}\right]\text{Tr}\left[\hat{U}\left(t\right)\right] = \int_{-\infty}^{\infty} dt\,\frac{1}{\beta - it}\text{Tr}\left[\hat{U}(t)\right]$$

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

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

We have a classical statistical mechanics result that has been 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

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

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

We still haven't reached the first page of Griffiths, the Schrodinger equation in position space. We have that

$$\hat{H}\left|\psi\right\rangle = i\frac{\partial}{\partial t}\left|\psi\right\rangle$$

And we have some Hamiltonian:

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

Now we can apply $\langle x|$ to both sides of the Schrodinger equation:

$$\begin{aligned}\langle x|\hat{H}|\psi\rangle &= \langle x|\, i\frac{\partial}{\partial t}\left|\psi\right\rangle \\ &= i\frac{\partial}{\partial t}\left\langle x|\psi\right\rangle \\ &= i\frac{\partial}{\partial t}\psi(x)\end{aligned}$$

Now looking at the left side, we have

$$\langle x|\frac{\hat{p}^2}{2m}|\psi\rangle + \langle x|V(\hat{x}|\psi\rangle)$$

Looking at the second term and applying $\mathbb{I}$:

$$\begin{aligned}\int dx'\,\langle x|V(\hat{x})|x'\rangle\,\langle x'|\psi\rangle &= \int dx' V(x)\delta(x - x')\psi(x') \\ &= V(x)\psi(x)\end{aligned}$$

And looking at the left term:

$$\langle x|\frac{\hat{p}^2}{2m}|\psi\rangle = \int dx'\,\langle x|\frac{\hat{p}^2}{2m}|x'\rangle\,\langle x'|\psi\rangle$$

$$= \int dx' \left(-\frac{\delta''(x-x')}{2m}\psi(x') \right)$$

We can now integrate this by parts twice, which introduces two minus signs so they cancel out:

$$\langle x|\frac{\hat{p}^2}{2m}|\psi\rangle = -\frac{1}{2m}\frac{\partial^2\psi}{\partial x}$$

Thus the Schrodinger equation is written as

$$-\frac{1}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi(x) = i\frac{\partial}{\partial t}\hat{H}(x,t)$$

And that is the Schrodinger equation that we first learned.

3.1 Propagators

Suppose we want to solve all time evolutions for all wavefunctions? We know that $|\psi(t)\rangle = \hat{U}(t,t')\,|\psi(t')\rangle$. Suppose we want to do this for a wavefunction rather than a state. We can apply the position bra:

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

We denote $\langle x|\hat{U}(t,t')|x'\rangle$ as $K(x,t;x',t')$ as the propagator:

$$\psi(x,t) = \int dx'\,K(x,t;x',t')\psi(x',t')$$

If we have a system at some position and time, and we later find it at some new position and time, the propagator denotes the QM amplitude of going from the old point to the new point.

There is another interpretation of this matrix element, in terms of Greens functions. We can rewrite the Schrodinger equation:

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

Suppose we denote the term in parentheses as an operator $\mathcal{O}$. We now *claim* that the propagator has the following property:

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

Subject to the condition that $K(x,t;x',t') = 0$ if $t < t'$. From this, K can be seen as the Greens function for the operator $\mathcal{O}$. Green's functions are related to their boundary conditions, and as such we have a retarded Green's functions and an advanced Greens function, based on whether we are going from the past to the future or from the future to the past.

To prove our claim, we will just plug it in. What we want to obtain is $\psi(x,t)\Theta(t-t')$:

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

Now suppose that we apply $\mathcal{O}$ to both sides of the equation:

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

We will show that it does satisfy our condition, and then wave our hands and claim that it is a unique solution. Looking at the left hand side, we will have to product rule because of the time derivative of the Θ function. Thus we have that

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

On the right hand side, we have

$$\begin{aligned}\int dx'\, \mathcal{O}K(x,t;x',t')\psi(x',t') &= \int dx'\, \left(-i\delta(x-x')\delta(t-t')\psi(x',t')\right)\\ &= -i\psi(x,t)\delta(t-t')\end{aligned}$$

Now we note that both sides are equal, and thus K must be a Green's function for $\mathcal{O}$.

3.2 Feynman Path Integral

Let us look at the simplest Hamiltonian for a system propagating in space in 3D:

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

Can we write down the Green's function for this system? We have the propagator:

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

Now inserting the identity in terms of $|p\rangle$:

$$\begin{aligned}K &= \langle\boldsymbol{x}|\int dp\ |p\rangle\langle p|\exp\left(-i\frac{\hat{\boldsymbol{p}}^2}{2m}(t-t')\right)\int dp'\ |p'\rangle\langle p'|\,|\boldsymbol{x}'\rangle\\ &= \int dp\int dp'\ \langle\boldsymbol{x}|\boldsymbol{p}\rangle\, e^{-i\frac{\hat{\boldsymbol{p}}^2}{2m}(t-t')}\,\langle\boldsymbol{p}'|\boldsymbol{x}'\rangle\,\delta^3(\boldsymbol{p}-\boldsymbol{p}')\\ &= \int\frac{d^3p}{(2\pi)^3}\exp\left(-\boldsymbol{p}(\boldsymbol{x}-\boldsymbol{x}')-\frac{\boldsymbol{p}^2}{2m}(t-t')\right)\end{aligned}$$

We can now complete the square in the exponent, then use the integral of a Gaussian, and we are left with

Might be the wrong expression, was hard to read:

$$K = \sqrt{\frac{m}{2\pi i(t-t')}}e^{i\left(\frac{m(x-x')}{2(t-t')}\right)}$$

Feynman, as a graduate student, rewrote QM using the action rather than the Hamiltonian, which is useful in relativistic cases, since the Hamiltonian is not invariant under frame changes, whereas the action is invariant.

Suppose we want to calculate $K(x,t;x',t')$. Starting at some point (x',t'), we have some path that leads to (x,t). We have some function $x(t)$ that does this path. He stated that the propagator can be written as

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

Where $S = \int_{t'}^{t} dt''\,\mathcal{L}(\dot{x}(t),x(t))$ is the action.

Suppose we have the Hamiltonian:

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

From this, we have that

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

Suppose we take our path, and we partition it into infinitely many time steps, Δt apart. What is the propagator between time t_j and t_{j-1}? We can write it out:

$$\langle x_j|\hat{U}(t_j,t_{j-1})|x_{j-1}\rangle$$

We can look at $\hat{U}$:

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

Now let us use Trotterization:

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

We now throw out the higher order terms, because who likes those. We can write out the propagator:

$$\langle x_j|\hat{U}(t_j,t_{j-1})|x_{j-1}\rangle = \int dp\ \langle x|\exp\left(-i\frac{p^2}{2m}\Delta t\right)|p\rangle\langle p|\exp\left(-iV\Delta t\right)|x'\rangle$$

Where we have inserted $\mathbb{I}$ in terms of p.

$$\begin{aligned}\langle x_j|\hat{U}(t_j,t_{j-1})|x_{j-1}\rangle &= \int dp\, e^{-i\frac{p^2}{2m}}e^{ip(x-x')}V(x')e^{iV\Delta t}\\ &= \int dp\, e^{-i\frac{p^2}{2m}\Delta t - ip\Delta x}e^{V(x)\Delta t}\end{aligned}$$

We can now complete the square, and we are left with a Gaussian integral, which gives a constant. Thus we are left with

$$\langle x_j|\hat{U}(t_j,t_{j-1})|x_{j-1}\rangle = \text{constant}\cdot e^{i(T-V)\Delta t}$$

$$= \text{constant} \cdot e^{i\mathcal{L}\Delta t}$$
$$= \text{constant} \cdot e^{iS}$$

This was for one time slice. Now we want to compute the propagator from the initial point to the ending point, across the entire path. We can split U up into n different Us, and then compute n integrals:

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

This is essentially going over all paths. Note that computing these on a computer is very difficult due to the sign problem, caused by the exponential terms that cancel out.

3.3 Gauge Potentials

MISSED A LECTURE ABOUT GAUGE TRANSFORMATIONS HERE Consider a rectangular box with dimensions L_x and L_y, with periodic boundary conditions. Note that these conditions are nice because they maintain translational invariance, which keeps momentum as a good quantum number.

Now we can generate a quantum number N_y, since $L_y k_y = 2\pi N_y$. Note that this has to be restricted to the range that keeps it inside the box, otherwise the shift will just repeat solutions. We can compute the degeneracy factor (the number of choices for k_y that respect the boundary conditions of the box), $N_d = \frac{L_y L_x m\omega_0}{2\pi} = \frac{Am\omega_0}{2\pi}$. This equation can't be right, because the left side is an integer, and the right side is a generic real number. However, we claim that this is close enough (good enough for government work).

4 Identical Particles

Suppose we have two particles, and let us assume that their properties are identical (mass, charge, etc). We have states of the form

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

This forms a generic basis for all states of two particles. For 3 particles, we simply tack on the systems:

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

Now suppose we swap particle 1 and particle 2, what happens? We might intuitively guess that we simply end up with $|b\rangle_1 \otimes |a\rangle_2$. However, when we have identical particles, the real world introduces constraints. Is $|b,a\rangle = |a,b\rangle$? Thinking classically, we would assume that we have a distinct configuration, but it evolves the same way as the previous configuration. From first principles, we can't tell if $|b,a\rangle = |a,b\rangle$, but nature tells us that they are the same, up to a possible phase:

$$|b,a\rangle = e^{i\theta}\,|a,b\rangle$$

Now the question is, what are the phases that are allowed? We know that if we swap twice, we expect to get the original state back, so $e^{i2\theta} = 1$. This argument is flawed, but let's just accept it for now. We thus have the cases where

$$|a,b\rangle \to +\,|b,a\rangle \quad \text{(Bosons)}$$

$$|a,b\rangle \to -|b,a\rangle \quad \text{(Fermions)}$$

Note that if we are working in 2D, these are not the only possible phases. If we think about swapping particles in 2D, we can consider the "clockwise" swap and the "counterclockwise" swap, which generates a distinction. This same behavior does not occur in 1D or 3D, and so we will ignore these for now.

Let us introduced an operator $P_{i,j} : |i,j\rangle \to e^{i\theta}|j,i\rangle$, and we note that $P_{i,j}^2 = 1$.

The Spin and Statistics theorem states that particles with integer spin are Bosons (photons, pions, deuteron nucleus, alpha particles, hydrogen atom), and particles with half-integer spin are Fermions (Electrons, muon, tau, neutrino, proton). This theorem is a result of QFT, where we impose causality, unitarity, and Lorentz invariance.

Consider a box of quantum coins, which has two energy levels, heads and tails, and we have two particles inside. Suppose we pull out one, and we find that it was heads. What is the probability that the other is also a heads? We can work out the probabilities in the classical case, and we have a 50% chance of getting another heads. Now suppose that we have bosons in the box. The possible states are HH, TT, and $\frac{HT+TH}{\sqrt{2}}$. If we now reach in an pull out a heads, then the probability that the second coin is also heads is $\frac{2}{3}$. We see that the bosons naturally hang around with other bosons.

Suppose we instead have a box with N quantum children (quantum daycare center), where all possible ratios of boys to girls must be equally likely. If we reach into the daycare center and pull out a quantum child that we measure to be a boy, classically, we would expect the ratio of boys to girls in the remaining $N-1$ children to be roughly 50/50. In the quantum case, it will turn out that $\frac{2}{3}$ of the remaining quantum children will be boys, and similarly for the case where we pull out a quantum girl.

Note that we never assumed there was any interactions between the identical particles, just by the existence of other particles, do we see this behavior.

Suppose we have a state, which depends on two particles. What are we swapping when we exchange the two? Are we exchanging just the spatial coordinates? Just the spin coordinates? It turns out that when we exchange two particles, we exchange **everything** about the two particles, position, spin, internal quantum numbers, etc.

If we have two particles, with a central potential between them (so orbital angular momentum is conserved), under exchange, we pick up a factor of $(-1)^L$.

Consider the case of two particles with internal spins and total angular momentum. We can write out the 4 possible states:

$$\begin{aligned} |s=0\rangle &= \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \\ |s=1\rangle &= |\uparrow\uparrow\rangle,\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right),\ |\downarrow\downarrow\rangle \end{aligned}$$

If we have two spin-$\frac{1}{2}$ particles, there are 5 quantum numbers to specify a state:

$$\psi = |n, L, m_L, S, m_s\rangle$$

Now what happens under exchange? Well since they are identical fermions, then we have to pick up a negative sign:

$$-\left|n, L, m_L, S, m_s\right\rangle$$

Suppose we know that L is even. Since the exchange goes as $(-1)^L$, we know that we don't pick up a sign from this. Thus we need the minus sign to come from the S, so it must be the antisymmetric case, so $S = 0$ $\left(|s=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)\right)$. Now when L is odd, then $S = 1$. We see that we have constraints on the quantum numbers in the state function when we pick up the negative sign under exchange.

4.1 Slater Determinants

Suppose we want to write out a set of basis states for 17 fermions, in such a way that the wavefunctions remain anti-symmetric. For the sake of argument, let us ignore spin and any other quantum numbers.

Let us work our way up from 2 particles to many particles.

We have two levels, $|\psi_a\rangle$ and $|\psi_b\rangle$. The wavefunction can be written as

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\psi_a(x_1)\psi_b(x_2) - \psi_a(x_2)\psi_b(x_1)\right)$$

Now what about for 3 particles, where we have $|\psi_a\rangle$, $|\psi_b\rangle$, and $|\psi_c\rangle$:

$$\psi(x_1, x_2, x_3) = \frac{1}{\sqrt{6}}\,\text{(The six one and two swap permutations of our 3 levels)}$$

Note that not all states can be written like this, superpositions of states of this form are not necessarily of this form. However, any many-body state can be written as a superposition of states of this form.

Now let us consider the case of many particles. How can we generalize this construction? We can use what is known as the Slater determinant:

$$|\psi\rangle_n = \frac{1}{\sqrt{n!}}\begin{bmatrix} |a\rangle^1 & |b\rangle^1 & |c\rangle^1 & \dots & |N\rangle^1 \\ |a\rangle^2 & |b\rangle^2 & |c\rangle^2 & \dots & |N\rangle^2 \\ \vdots & & & & \\ |a\rangle^n & |b\rangle^n & |c\rangle^n & \dots & |N\rangle^n \end{bmatrix}$$

Where $|a\rangle^1$ indicates that particle 1 is in state a. Using this as a variational ansatz is known as the Hartree-Fock method.

Consider a 1-dimensional system, where we have two particles. Note that we can always consider a center of mass frame for this system. Our wavefunction is based on plane waves:

$$\psi(x_1x, x_2) = A\left(e^{ikx_1}e^{-ikx_2} \pm e^{ikx_2}e^{-ikx_1}\right)$$

Where the plus is for Bosons, and the minus is for Fermions.

We can rewrite this:

$$\begin{aligned}\psi(x_1,x_2) &= A'\cos(k(x_1-x_2)) \quad \text{for Bosons}\\ &= A''\sin(k(x_1-x_2)) \quad \text{for Fermions}\end{aligned}$$

Now if we look at the probability distribution, $\psi^*\psi$, we get a $\cos^2$ for the Bosonic case, and a $\sin^2$ for the Fermionic case. Note that in the bosonic case, the probability is maximized when $x_1 - x_2 = 0$, and the opposite for the fermion case, the probability is 0 when $x_1 - x_2 = 0$.

Let us look at degeneracy pressure. Suppose we have a 3D box, and we toss in a bunch of noninteracting fermions. We will see that they exert a force on the walls of the box, simply via the properties of fermions. We will consider the thermodynamic limit, which is when the density is fixed and the volume of the box is large (lots of particles). We can write out the single particle Hamiltonian:

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

Let us now claim that the boundary conditions do not affect the system, and we will choose periodic boundary conditions.

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

$$\psi_1(x,y,z) = \text{const.}\left[e^{ik_x x}e^{ik_y y}e^{ik_z z}\right]$$

Let us now determine what values of k_x are allowable, based on the boundary conditions, $\psi(x+L_x,y,z) = \psi(x,y,z)$. We find that $k_x L_x = 2\pi n_x$, for any integer n_x, and similarly for k_y and k_z. Now let us begin by finding the number of states with energy less than some E_0, $N(E_0)$:

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

Where the d is a degeneracy factor, which takes into account spin. Now consider plotting all the allowed values of the quantum numbers, and looking at the number of points that fall within a sphere given by energy E_0. We will assume that E_0 is very large, so we can replace the sum with an integral. We know that $\Delta k_x = \frac{2\pi}{L_x}\Delta n_x$, and similarly for the other two directions. Thus we have the integral:

$$N(E_0) = L_x L_y L_z \cdot d\int \frac{d^3k}{(2\pi)^3}\Theta\left(E_0 - \frac{1}{2m}\left(k_x^2+k_y^2+k_z^2\right)\right)$$

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

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

$$= \frac{dVk_F^2}{6\pi^2}$$

Where k_F is the Fermi momentum, $k_F = \sqrt{2mE_0}$.

In general, in the thermodynamic limit:

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

Now suppose we fill the box with Fermmions, up to an energy, $\frac{k_F^2}{2m}$, we have $N(E_0)$ states filled:

$$N = V\frac{dk_F^3}{6\pi^2}$$

We can write this in terms of the number density:

$$n = \frac{N}{V} = d\frac{k_F^2}{6\pi^2}$$

Suppose we want to know how much energy to put into the system to kick out all of the Fermions:

$$\begin{aligned} E_{\text{total}} &= Vd\int_0^{k_F} \frac{dk}{2\pi^2}k^2\frac{k^2}{2m} \\ &= \frac{3}{5}Nd\frac{k_F^2}{2m} \end{aligned}$$

$$\begin{aligned} \epsilon &= \frac{E}{V} \\ &= \frac{3}{5}n\frac{k_F^2}{2m} \end{aligned}$$

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 the derivative, and we find the degeneracy pressure that we see in astronomy textbooks.

5 Statistical Mechanics

During the development of statmech, the concept of entropy was phenomenological, and Boltzmann realized that you could associate entropy with the number of classical microstates:

$$S = k\log W$$

Which in this class we will write as $S = \log W$. W is the number of classical microstates. This idea of the number of microstates is the basis for the microcanonical ensemble, which we will ignore in this class, because the notion of defining the number of states at a fixed energy is difficult. In QM, at most energies, there are no states, since the energies are quantized.

Let us ignore Boltzmann, Gibbs, and Maxwell, and instead start quantum mechanically.

We begin by looking back at the von Neumann entropy

$$S = -\mathrm{Tr}[\hat{\rho}\log\hat{\rho}]$$

Where $\hat{\rho}$ is the density matrix. Let us recall that the density matrix, in the eigenbasis, has diagonal elements that are the eigenvalues that represent the probability that the system is in the corresponding eigenstate.

Let us make an claim, that systems that are allowed to interact with the environment, will attempt to maximize their total entropy, subject to constraints. This is an empirical law, S is some measure of "disorder" in the system. We will claim that thermal equilibrium is when S is maximized subject to the constraint of fixed average energy (and possibly other constraints). This maximization is in terms of the density matrix for the system. Note that if we have an isolated system that is not in thermal equilibrium, and we let it evolve on its own, entropy will be conserved, since the entropy depends on the eigenvalues of $\hat{\rho}$, and unitary time evolution preserves the eigenvalues of the system. Thus a system that is isolated and not in thermal equilibrium will never reach thermal equilibrium.

Let us make an argument about why this is a sensible measure of entropy. First, we note that $S = 0$ when $\hat{\rho} = |\psi\rangle\langle\psi|$, that is, when the system is in one state only. When we have minimal randomness, we get 0 for the entropy. Secondly, suppose we have two systems that are uncorrelated, there is no entanglement. Is $S_{\text{total}} = S_1 + S_2$? We claim that this is true, S is extensive, it increases with the size of the system if we keep everything else the same.

Let us see that this is the case using the von Neumann definition. First, what is the total density matrix for the two systems:

$$\hat{\rho}_{\text{total}} = \hat{\rho}^1 \otimes \hat{\rho}^2$$

We assume that the systems have discrete states (because it's easier):

$$\begin{aligned} S^1 &= -\sum_j p_j \log p_j \\ S^2 &= -\sum_k p_k \log p_k \end{aligned}$$

We have eigenstates of the total system, $|j,k\rangle = |j\rangle^{(1)} \otimes |k\rangle^{(2)}$. What is the probability that we are in this state, p_{jk}? Intuitively, it will be the product of the probabilities, $p_{jk} = p_j p_k$. We can now write out the total entropy:

$$\begin{aligned} S_{\text{total}} &= -\mathrm{Tr}\left[\hat{\rho}_{\text{total}}\log\hat{\rho}_{\text{total}}\right] \\ &= -\sum_{jk} p_{jk}\log p_{jk} \\ &= -\sum_{jk} p_j p_k \log(p_j p_k) \\ &= -\sum_{jk} p_j p_k (\log(p_j) + \log(p_k)) \\ &= -\sum_{jk} p_j p_k \log p_j - \sum_{jk} p_j p_k \log p_k \\ &= -\sum_j p_j \log p_j - \sum_k p_k \log p_k \end{aligned}$$

$$= S_1 + S_2$$

What is the maximal entropy density matrix that we can have, if we keep the average energy $\langle E\rangle = \mathrm{Tr}[\hat{H}\hat{\rho}] = \sum_k E_k p_k$ fixed?

We can, via classical statistical mechanics, guess that the answer will be the Boltzmann distribution:

$$\begin{aligned}\hat{\rho} &= \frac{\exp(-\beta\hat{H})}{\mathrm{Tr}[\exp(-\beta\hat{H})]}\\ &= \frac{\sum_j |j\rangle\langle j|\exp(-\beta E_j)}{\sum_k \exp(-\beta E_k)}\end{aligned}$$

Where β is a lagrange multiplier that fixes $\langle E\rangle$.

To prove this, we assume that $\hat{\rho}_0$ is as above, and then we make slight variations, $\hat{\rho} = \hat{\rho}_0 + \delta\hat{\rho}$, and we will show that the first order shifts will not make a difference, and that we have a maximum.

However, we note that $\mathrm{Tr}[\delta\hat{\rho}]$ must be 0, and that it changes the average energy, so we have to do a Lagrange multiplier to fix $\langle E\rangle$.

This is a slightly daunting problem, as we have a $\delta\hat{\rho}$, and for generic $\delta\hat{\rho}$, the energy will change. This is why we introduce a lagrange multiplier, we have a constrained optimization. Let us call the multiplier $-\beta$. What we want to do is say that

$$\delta\left[-\beta\langle E\rangle + S\right] = 0$$

This will give the correct variation to maximize the entropy subject to the constraint. Note that this technically extremizes it, rather than maximimizes it, but thats good enough for government work.

Let us introduce a function $F = (\beta, \hat{\rho}) = \langle E\rangle - \frac{1}{\beta}S$. We can see that maximizing the previous equation, is the same as minimizing this equation. Note that when we minimize this, we will have the free energy. What do we want to minimize this with respect to? β is fixed, we want to vary $\hat{\rho}$. We want the variation in F to be 0:

$$\begin{aligned}\delta F &= 0\\ &= \delta\left[\mathrm{Tr}\left(\hat{H} + \frac{1}{\beta}\log(\hat{\rho})\hat{\rho}\right)\right]\end{aligned}$$

What we want to do is say that $\hat{\rho} = \hat{\rho}_0 + \delta\hat{\rho}$, and then show that this first order change to $\hat{\rho}$ will not affect our function.

When the smoke clears, we will obtain the answer

$$\hat{\rho} = Z^{-1}\exp\left(-\beta\hat{H}\right)$$

Where $Z = \mathrm{Tr}\left[\exp(-\beta\hat{H})\right]$.

Let us start the algebraic proof. First, we note that we can write $\hat{\rho}$ as

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

Where $\hat{U}$ is unitary. Now we note that we can write $\hat{U}$ as

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

Now let us look at $\delta\hat{\rho}$. This can consist of two parts:

$$\delta\hat{\rho} = \delta\hat{\rho}_d + i\left[\hat{\rho}_d, \delta G\right]$$

Essentially, we can either change the eigenvalues, or we can change the eigenvectors. The commutator comes in because changing the eigenvectors causes a change on both sides, with opposite signs.

Given this, we can write that

$$\delta F = \mathrm{Tr}[\delta\hat{\rho}\hat{H}] + \frac{1}{\beta}\mathrm{Tr}\left[(\hat{\rho}_0 + \delta\hat{\rho})\log(\hat{\rho}_0 + \delta\hat{\rho}) - \hat{\rho}_0\log\hat{\rho}_0\right]$$

Now our argument will be that we have two different types of variation, and in either case we will have no change. Thus, for any variation, we will have no change.

Suppose we vary G. In this case, the second term in δF will be 0, because the second term is the change in S, and S only cares about the eigenvalues. Thus, the change in S will be 0, if we only change the eigenvalues.

Now let us look at the effect of changing G on the first term, Tr $\left[\delta\hat{\rho}\hat{H}\right]$. Let us first suppose that the Hamiltonian is in the same basis as $\hat{\rho}_0$, that is, $\left[\hat{\rho}_{0_d}, \hat{H}\right] = 0$. Note that this is true if we look at our answer. Let us insert the definition of $\delta\hat{\rho}$ into our first term:

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

Where we used the cyclic property of the trace to rewrite the operator products, and then use our hypothsis about the commutation relation between $\hat{\rho}_{0_d}$ and $\hat{H}$.

Now let us look at variations in the eigenvalues. We can then write out δF as

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

Now, by construction, we can say that $[\delta\hat{\rho}_d, \hat{\rho}_d] = 0$. We can also rewrite the logarithm:

$$\begin{aligned}
\log(\hat{\rho}_d + \delta\hat{\rho}_d) &= \log\left[\hat{\rho}_d\left(1 + \hat{\rho}_d^{-1}\delta\hat{\rho}_d\right)\right] \\
&= \log(\hat{\rho}_d) + \log\left(1 + \hat{\rho}_d^{-1}\delta\hat{\rho}_d\right) \\
&= \hat{\rho}_d^{-1}\delta\hat{\rho}_d + \mathcal{O}\left(\delta\hat{\rho}^2\right)
\end{aligned}$$

Where we have used the fact that they commute to rewrite the logarithm, and then Taylor expanded.

Now looking back at δF, the second term can be rewritten via what we have now:

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

Now adding the first term back in:

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

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. Thus we have that δF is 0 for any choice of $\delta\hat{\rho}$. Thus we have that

$$\hat{H} - \frac{1}{\beta}\log(\hat{\rho}) + \text{const.} = 0$$

Which we can rewrite as

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

We can rewrite this as

$$\begin{aligned}\text{const}\hat{\rho} &= \exp\left(-\beta\hat{H}\right)\\ \hat{\rho} &= \frac{\exp\left(-\beta\hat{H}\right)}{\text{const.}}\end{aligned}$$

Now let us call the constant Z, and we realize that Z must be $\text{Tr}[\exp(-\beta\hat{H})]$, since the trace of $\hat{\rho}$ must be 1. Thus we have that

$$\hat{\rho} = \frac{\exp(-\beta\hat{H})}{\text{Tr}\left[-\beta\hat{H}\right]}$$

By arguing that the von Neumann entropy is the entropy, and finding the density matrix that maximizes it, we find the Boltzmann distribution.

We have shown that systems "want" to maximize entropy, when they are allowed to exchange energy with their surroundings.

We write the Lagrange multiplier as $\beta = \frac{1}{T}$, and have

$$\begin{aligned}Z(\beta) &= \text{Tr}\left[\exp(-\beta\hat{H})\right]\\ &= \sum_n e^{-\beta E_n}\end{aligned}$$

Where Z is known as the partition function. The total density matrix for the system is $\hat{\rho}(\beta) = \frac{\exp(-\beta\hat{H})}{Z}$.

Suppose we know Z. How can we find the energy? From quantum mechanics:

$$\begin{aligned}\langle E\rangle &= \text{Tr}\left[\hat{\rho}\hat{H}\right]\\ &= -\frac{\partial}{\partial\beta}\log\text{Tr}\left[e^{-\beta\hat{H}}\right]\\ &= -\frac{\partial}{\partial\beta}\log Z\end{aligned}$$

We can also compute it as

$$\langle E\rangle = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_m e^{-\beta E_m}}$$

Which allows us to see the previous derivation a little more clearly.

Let us now look at the entropy, or specifically the maximum entropy:

$$\begin{aligned}
S_{\text{max}} &= -\text{Tr}\left[\hat{\rho}_{\text{eq}}\log(\hat{\rho}_{\text{eq}})\right] \\
&= -\text{Tr}\left[\frac{e^{-\beta\hat{H}}}{Z}\log\left(\frac{\exp(-\beta\hat{H})}{Z}\right)\right] \\
&= -\text{Tr}\left[\hat{\rho}_{\text{eq}}\left[-\beta\hat{H} - \log Z\right]\right] \\
&= \beta\langle H\rangle + \log Z \\
&= \beta E + \log Z
\end{aligned}$$

Now let us consider the derivative of S with respect to E :

$$\begin{aligned}
\frac{\partial S}{\partial E} &= \beta + E\frac{\partial\beta}{\partial E} + \frac{\partial\log Z}{\partial\beta}\frac{\partial\beta}{\partial E} \\
&= \beta + E\frac{\partial\beta}{\partial E} - E\frac{\partial\beta}{\partial E} \\
&= \beta \\
&= \frac{1}{T}
\end{aligned}$$

Now recall that we can write the partition function as the exponential of the free energy:

$$Z = e^{-\beta F}$$

From this, we can rewrite the entropy:

$$\begin{aligned}
S &= \beta E + \log(e^{-\beta F}) \\
&= \beta(E - F)
\end{aligned}$$

This tells us that $F = E - \frac{1}{\beta}S$, or $F = E - TS$. Note that when we were doing the previous gory derivation, we had the same F show up. This is the Helmholtz free energy.

Now let us look at derivatives, holding certain things fixed. If we fix E, we can calculate T, S, and F. If we fix T, we can determing E, S, and F. If we instead fix S, we can find E, T, and F.

Let us rewrite our relation $-\frac{\partial\log Z}{\partial\beta} = E$. First, we note that $\frac{\partial(\beta F)}{\partial\beta} = E$, and thus we have that

$$F + \beta\frac{\partial F}{\partial\beta} = E$$

Now we note that $\beta\frac{\partial}{\partial\beta} = -T\frac{\partial}{\partial T}$:

$$F - T\frac{\partial F}{\partial T} = E$$

Now using the fact that $F = E - TS$:

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

Now let us look at the relationship between E and S. We claim that they are related by a Legendre transform. Legendre transforms are very common, for example, the transformation between a Hamiltonian and Lagrangian is just a Legendre transform. Take the Lagrangian in one dimension:

$$\mathcal{L}(q, \dot{q})$$

We can find the conjugate momentum, $p = \frac{\partial L}{\partial \dot{q}}$. The Hamiltonian is a function of the position and the conjugate momentum:

$$\hat{H} = \dot{q}p - \mathcal{L}$$

How do we get rid of the $\dot{q}$? We re-express $\dot{q}$ in terms of p:

$$\dot{q} = \frac{\partial H}{\partial p}$$

The relationship between $H = \dot{q}p - \mathcal{L}$ and $\mathcal{L} = \dot{q}p - H$ is a Legendre transformation.

Now let us do something similar for the free energy. We have that F is a function of T, and we can take the derivative with respect to T:

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

Looking at $E(S) = F + TS$, we see that this parallels the Lagrangian and the Hamiltonian:

$$\frac{\partial E}{\partial S} = \frac{1}{\frac{\partial S}{\partial E}} = T$$

We see that the free energy and energy contain the same information, and we can use the one that is easiest to use, just like how we can choose to use the Hamiltonian or the Lagrangian.

We have previously seen that

$$\begin{aligned} E &= -\frac{\partial}{\partial \beta}\log Z \\ &= \frac{\mathrm{Tr}\left[\hat{H}e^{-\beta\hat{H}}\right]}{\mathrm{Tr}\left[e^{-\beta\hat{H}}\right]} \end{aligned}$$

Where the first statement we have proven, and the second statement is obvious, we take the density matrix of the equilibrium state and then we take the trace with the $\hat{H}$ tacked on. Now how can we compute $\langle E^2\rangle$? We can, by the same logic as the previous case:

$$\begin{aligned} \langle E^2\rangle &= \frac{\mathrm{Tr}[\hat{H}^2 e^{-\beta\hat{H}}]}{\mathrm{Tr}\left[e^{-\beta\hat{H}}\right]} \\ &= \frac{\frac{\partial^2}{\partial\beta^2}Z}{Z} \end{aligned}$$

Now let us think about fluctuations in the energy, $\langle E^2\rangle - \langle E\rangle^2$. We expect this to be small, when compared to the energy.

First, let us try to get insight into why $\frac{1}{\beta} = T$.

Suppose we have two systems, which are isolated from each other and the rest of the world, and have the same temperature. What is the partition function for the combined system?

$$\begin{aligned} Z(\beta) &= \sum_{i,j} \exp\left(-\beta(E_i^{(1)} + E_j^{(2)})\right) \\ &= \sum_i \exp\left(-\beta E_i^{(1)}\right) \sum_j \exp\left(-\beta E_j^{(2)}\right) \\ &= Z_1(\beta) Z_2(\beta) \end{aligned}$$

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

$$F = F_1 + F_2$$

for the combined system.

Now consider two systems that are isolated from the outside world, but are in contact with each other. Let us assume that what happens far from that dividing wall don't matter, we have a finite correlation length. The only difference between this case and the previous case is that we have things going on near the contact barrier. If the volume is very big, then the things going on around the contact point cause a small change to the free energy:

$$F = F_1 + F_2 + \delta F$$

From here, we argue that in the large volume limit (thermodynamic limit), we can ignore this term, and write the free energy as

$$F = fV + \delta F$$

Where f is known as the free energy density, and δF is known as a finite volume effect, and we can ignore it.

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We have that the canonical ensemble has fixed N, T and V, and we maximize the entropy. In the microcanonical ensemble, we find the number of accessible states at fixed N, E, and V, and then we compute the entropy via $S = \log W$. In the grand canonical ensemble, we fix μ, T, and V. Whichever one we pick, they all agree in the thermodynamic limit. The chemical potential is the lagrange multiplier for particle number, but physically, it is the amount of energy it takes to add another particle to the system.

Let us introduce a grand partition function, $\mathcal{Z}$:

$$\mathcal{Z} = \mathrm{Tr}\left[\exp\left(-\beta\left(\hat{H} - \mu\hat{N}\right)\right)\right]$$

Where the trace is over the Hilbert space of all particles.

We can compute the derivative of the log of this partition function with respect to μ:

$$\frac{\partial \log \mathcal{Z}}{\partial \mu} = \beta \langle N \rangle$$

Taking the derivative with respect to β:

$$\frac{\partial \log \mathcal{Z}}{\partial \beta} = \langle E \rangle - \mu \langle N \rangle$$

We can also rewrite the grand partition function:

$$\begin{aligned}\mathcal{Z} &= \mathrm{Tr}\left[e^{\beta\mu N} e^{-\beta \hat{H}}\right] \\ &= \sum_n e^{\beta\mu N}\mathrm{Tr}\left[e^{-\beta\hat{H}}\right] \\ &= \sum e^{-\beta\mu N} Z_N(\beta)\end{aligned}$$

This first term, $e^{\beta\mu N}$ is known as the fugacity.

Now we note that if we let $\mu = i\alpha$, then our expression is a Fourier series, and we can extract the coefficient via:

$$Z_N(\beta) = \frac{1}{2\pi}\int_0^{2\pi} d\alpha \, Z\left(\beta, i\frac{\alpha}{\beta}\right) e^{i\alpha N}$$

So far we have been doing everything in equilibrium. Now let us consider quasistatic processes, which always stay in equilibrium. These, in a thermodynamic sense, are considered reversible, if we have a starting macrostate, and we run a quasistatic process to an ending state, we can run an inverse process that takes us back to the exact same starting macrostate. Note that these are impossible practically, since we cannot change things infinitely slowly, and we can't perfectly isolate our system, so heat can't get in or out.

We have thermodynamic variables, and they come in pairs, (T, S), which represent heat, (P, V), which represent mechanical work, and we have (μ, N), which represent energy related to particles. In principle, we can have any set of variables, one that "drives" a change, and another that "responds", such as magnetic field strength and magnetization.

Let us consider a simple example. Suppose we want to study an isothermal process, T is held constant. Since T is fixed, we then use S. For an adiabatic process (not adiabatic in the QM sense), $\delta Q = 0$, no heat is exchanged. In this case, since $\Delta Q = TdS$, then S is fixed, and we vary T. For isobaric processes, P is fixed, so we use V. For fixed V, we use P. For fixed N, we use μ, and vice versa. Depending on the nature of the process that we are studying, the relevant thermodynamical variables change.

There is a type of free energy associated with any combination of these variables. For simplicity, we drop μ and N, we implicitly fix N.

$$\begin{aligned}U(S, V) &= TdS - PdV \\ F(T, V) &= -SdT - PdV\end{aligned}$$

$$
\begin{aligned}
H(S,P) &= TdS + VdP \\
G(T,P) &= VdP - SdT
\end{aligned}
$$

We see that they are related via Legendre transformations:

$$
\begin{aligned}
F &= U - TS \qquad && \frac{\partial F}{\partial T}\mid_V = -S \\
U &= F + TS \qquad && \frac{\partial U}{\partial S}\mid_V = T \\
H &= U + PV \qquad && \frac{\partial H}{\partial P}|_S = V \\
U &= H - PV \qquad && \frac{\partial U}{\partial V}|_S = -P \\
G &= H - TS \qquad && \frac{\partial F}{\partial T}|_P = -S \\
H &= G + TS \qquad && \frac{\partial H}{\partial S}|_P = -T \\
G &= F + PV \qquad && \frac{\partial G}{\partial P}|_T = V \\
F &= G - PV \qquad && \frac{\partial F}{\partial V}|_T = -P
\end{aligned}
$$

Now if we introduce μ and N, we get grand free energies, more commonly known as grand potentials. Consider one example, $\Phi_G(T,V,\mu)$, which is the moral equivalent of the Helmholtz free energy:

$$\Phi_G(T,V,\mu) = -T\log(\mathcal{Z})$$

Where $\mathcal{Z}$ is the grand partition function:

$$
\begin{aligned}
\mathcal{Z} &= \mathrm{Tr}\left[e^{-\beta\left(\hat{H}-\mu\hat{N}\right)}\right] \\
&= e^{-\beta\Phi_G}
\end{aligned}
$$

We can write this as:

$$\Phi_G = F - \mu N$$

And $F = \Phi_G + \mu N$. this is a Legendre transformation, so

$$
\begin{aligned}
\frac{\partial \Phi_G}{\partial \mu}\mid_{T,V} &= -N \\
\frac{\partial F_G}{\partial N}\mid_{T,V} &= \mu
\end{aligned}
$$

Where we use F_G to denote that this is in the grand context. We have done this in the case of the Helmholtz free energy, but we could do the same thing for any of the other free energies. More generally, we can do this in general for other conserved quantities, $\hat{x}$, which is some quantity of interest, and it has some Lagrange multiplier:

$$\hat{H} \to \hat{H} - \lambda\hat{x}$$

and we can obtain the free energy via this change.

Using these free energies, we can take derivatives, and find equations of state, which express thermodynamic quantities in terms of other thermodynamic quantities.

Let us consider the notion of an equation of state. Everything that we need to know about a thermodynamic system is contained within Φ_G, but sometimes we don't want Φ_G in our expression, so we find equations of states, by taking a derivative of a free energy with respect to one variable. This expresses one thermodynamic identity in terms of others. The characteristic example of an equation of state is the equation of state for a classical ideal gas, $PV = NT$. How do we derive this? We take the free energy:

$$-P = \frac{\partial F}{\partial V} \bigg|_{T,N}$$

We see that this gives us $P(T,V,N)$. If this an ideal gas of classical particles, this tells us that $P = T\frac{N}{V}$.

Let us consider now 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, $\sum_{\text{species}} \mu_i dN_i$:

$$dU = TdS - PdV + \sum_{\text{species}} \mu_i dN_i + \sum_j \lambda_j dX_j$$

Where the last term is any other quantities that we care about, such as magnetization, isospin, and whatever else there is in our system. We derived this for the internal energy, and we can derive analogous expressions for the rest of the free energies, for example, the Helmholtz free energy:

$$dF = -SdT - PdV + \sum_i \mu_i dN_i + \sum_j \lambda_j dX_j$$

We can do the same thing for any other free energy or grand potential that we care about.

We can also combine these, such as looking at the change in products of thermodynamic quantities:

$$\begin{aligned} d(PV) &= PdV + VdP \\ &= dH - dU \\ &= dG - dF \end{aligned}$$

$$\begin{aligned} d(TS) &= dU - dF \\ &= dH - dG \end{aligned}$$

The relationships between the derivatives of thermodynamic quantities are known as Maxwell's relations. Let us consider a system with fixed N, and we have an internal energy with S and V fixed, $U(S,V)$. Consider $\frac{\partial^2 U}{\partial S \partial V}$:

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial}{\partial S}\frac{\partial U}{\partial V}$$

$$
\begin{aligned}
&= \frac{\partial}{\partial V}\frac{\partial U}{\partial S} \\
&= -\frac{\partial P}{\partial S}\Big|_V \\
&= \frac{\partial T}{\partial S}\Big|_S
\end{aligned}
$$

Thus we have that

$$-\frac{\partial P}{\partial S}\Big|_V = \frac{\partial T}{\partial S}\Big|_S$$

There are many other similar relations:

$$
\begin{aligned}
\frac{\partial T}{\partial P}\Big|_S &= \frac{\partial V}{\partial S}\Big|_P \\
\frac{\partial S}{\partial V}\Big|_T &= \frac{\partial P}{\partial T}\Big|_V \\
\frac{\partial S}{\partial P}\Big|_T &= \frac{\partial V}{\partial T}\Big|_P
\end{aligned}
$$

each of which comes from a different free energy.

We can do the same thing for grand potentials:

$$\frac{\partial^2 \Phi_G}{\partial \mu \partial V}\Big|_T \;\rightarrow\; -\frac{\partial P}{\partial \mu}\Big|_{T,V} = \frac{\partial N}{\partial V}\Big|_{T,\mu}$$

5.1 Carnot Knowledge

Let us now consider Carnot knowledge. Consider a heat bath, at temperature T_H, and another heat (cold?) bath at a colder temperature, T_C, $T_C < T_H$. Let us use this to do get mechanical work out of it. We want to get work out of heat flowing from the hot reservoir to the cold reservoir, and we want to do this reversibly, so we could invert it and pump heat from the cold reservoir into the hot reservoir.

Our question is, how efficient is this engine at obtaining work from the heat transfer?

If we plot the Carnot cycle on a T-S plot, the cycle is a perfect square, and we move around the square clockwise. The first process is an isothermal process, with entropy increasing. Work is done in order to do this, so the system is expanding. After this, we have an adiabatic process, where the temperature decreases, and the system continues to expand. After this, we want to get the system back to the starting point, so we do an isothermal compression, after which we do an adiabatic compression to get back to the starting point.

What is the net work done by this cycle? For the isothermal processes, we put heat in, from the hot bath to the cold bath:

$$
\begin{aligned}
\Delta Q_{A\to B} &= \int_{S_A}^{S_B} T_H \, dS \\
&= T_H(S_B - S_A) \\
\Delta Q_{C\to D} &= \int_{S_B}^{S_A} T_C \, dS
\end{aligned}
$$

$$= T_C(S_B - S_A)$$

Adding these two, we see that the change in heat is $\Delta Q = (S_B - S_A)(T_H - T_C)$.

Now let us consider the work done:

$$\begin{aligned} W &= \oint P\, dV \\ &= \oint (TdS - dU) \end{aligned}$$

Where we have used the fact that $dU = TdS - PdV$. Now we note that $\oint dU = 0$:

$$W = (T_H - T_C)(S_B - S_A)$$

Now what is the effiency? We could argue that it is a perfect machine, and it never loses any, so it is 100% efficient. However, the efficiency η is defined via:

$$\begin{aligned} \eta &= \frac{W}{Q_H} - \frac{(T_H - T_C)(S_B - S_A)}{T_H(S_B - SA)} \\ &= 1 - \frac{T_C}{T_H} \end{aligned}$$

This is the Carnot efficiency, and is the maximum possible efficiency (Via Carnot's thereom). The reason we define the efficiency this way is that we have only two heat baths, we can only control the heat that goes into the cold bath, but once the energy has entered into the cold bath, we can't access it, we don't have anything colder than that. To prove Carnot's theorem, we can think about having a Carnot engine that pumps the heat back up, and then think about what physics problems would be brought up if the one pumping from hot to cold was more efficient that the other Carnot engine.

Much of physics is done via intensive quantities, which are independent of the volume. For example, the number of particles in the system, is equal to a number density times the volume, $N = nV$. In this case, n is an intensive quantity (in the thermodynamic volume). We can say that $U = uV$, $S = sV$, $F = fV$, $\Phi_G = \phi_G V$. We also have quantities that are already intensive, such as μ, T, and P. Most of the time, physicists are interested in the intensive versions of these thermodynamic quantities.

We have $\Phi_G(T, \mu)$, and suppose we wanted to find the number density, n. We can do this via the derivative:

$$n = -\frac{\partial \Phi_G}{\partial \mu} \Big|_T$$

Similarly, we can also find the entropy density:

$$s = -\frac{\partial \Phi_G}{\partial T} \Big|_\mu$$

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

$$P = -\frac{\partial \Phi_G}{\partial V}\Big|_{\mu,T}$$

We note that this is just the intensive grand potential density, $\Phi_G = V\phi_G$.

We also state that $P = -\frac{\partial F}{\partial V}\Big|_{T,N}$, and we know that $F = Vf(T,n)$, which is the same as $Vf(T,\frac{N}{V})$. Thus, when we compute this derivative, we need ot use the chain rule:

$$\begin{aligned} P &= -\frac{\partial F}{\partial V}\Big|_{T,N} \\ &= -\left(f(T,n) - n\frac{\partial f}{\partial n}\right) \\ &= -\phi_G \end{aligned}$$

5.2 Thermodynamic Stability

Now let us consider thermodynamic stability. What is negative pressure? We generally think about pressure as a gas pushing against the boundaries of the volume, and as such, how can particles striking the wall cause the wall to pull into the system? We claim that in stable systems, negative pressure is "impossible", $P \geq 0$, and due to this, $\phi_G > 0$.

Consider a system with total volume V, and we divide it into two subsystems in thermal equilibrium, with volumes V_1 and V_2, such that $V_1 = V_2$. What is the number in this system? Suppose we have N particles, and we allow the particles and energy to move across the barrier between the systems.

The number density in each subsystem is given by:

$$n_1 = \frac{N_1}{V/2} \qquad n_2 = \frac{N_2}{V/2}$$

We have that $N_1 + N_2 = N$, and we can see that $n_2 = 2n - n_1$.

What is the total free energy of the system? Free energy is additive, so it must be $F_1 + F_2$:

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

Now let us change the densities slightly, make one side have slightly more, and the other slightly less:

$$\begin{aligned} n_1 &= n + \Delta \\ n_2 &= n - \Delta \end{aligned}$$

From this, we can rewrite the free energy:

$$F_{\text{Split}} = \frac{V}{2}\left(f(T,n+\Delta) + f(T,n-\Delta)\right)$$

When we drop the wall, the system will maximize entropy, and with particle number fix, it will minimize the free energy. Thus we have that $F_{\text{Split}} \geq Vf(T,n)$, the free energy of the equilibrated system is lower. This tells us that

$$[f(T,n+\Delta)+f(T,n-\Delta)-2f(T,n)] \geq 0$$

Where we discard the volume since it is always positive. From this we have that

$$\frac{f(T,n+\Delta)+f(T,n-\Delta)}{2} \geq f(T,n)$$

This is always true. What does this tell us about derivatives? This gives us information about the second derivative. If we study the $\Delta \to 0$ limit, we find that

$$\frac{\partial^2 f}{\partial n^2}\,|_T \geq 0$$

5.3 Ideal Gases

Let us now pivot to considering ideal gases, starting with the classical ideal gas. We assume that the system is dilute, we ignore the collisions between particles entirely, the particles have just kinetic energy, and we have no potential energy between particles. This does raise the issue of how the system equilibrates, but we say that collisions happen infrequently enough that we can ignore it, and that over long timescales, the system does equilibrate. Let us consider one species of particle, with no internal degrees of freedom, such as spin.

When is the classical model kosher? It is when the temperature is larger than any relevant quantum energies, $kL \gg 1$, where L is the size of the box, and k is the deBroglie thermal momentum, $k=\sqrt{mT}$. In the classical model, we claim that the canonical model is the easiest to use.

Let us look at one particle in a box. The partition function will be

$$\begin{aligned} Z_1(T,N) &= \frac{1}{h^3}\int d^3q\,d^3p\,\exp\left[-\beta\frac{p^2}{2m}\right] \\ &= \frac{V}{h^3}\int d^3p\,e^{-\beta p^2/2m} \\ &= \frac{V}{h^3}\,(2\pi mT)^{3/2} \end{aligned}$$

If we look at N particles, it is easy to show/see that it will be $Z_N = Z_1^N$. This is not actually true, as Gibbs found out, but we will ignore that for now.

Now let us look at equations of state. Starting with pressure:

$$\begin{aligned} -P &= T\frac{\partial \log Z}{\partial V} \\ &= T\frac{\partial \log(Z_1^N)}{\partial V} \\ &= T\frac{\partial}{\partial V}\left[\log\left(\frac{V^N}{V_0}\right)+\log\left(\frac{V_0}{h^3}\,(mT)^{3/2}\right)\right] \\ &= -TN\frac{\partial \log\left(\frac{V}{V_0}\right)}{\partial V} \end{aligned}$$

$$\begin{aligned}
&= -\frac{TN}{V} \\
&= -Tn
\end{aligned}$$

Thus we have recreated the ideal gas law, $P = nT$.

Now we can look at the total energy:

$$\begin{aligned}
U &= -\frac{\partial \log Z}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta}\left(\log\left(\frac{V}{h^3}m^{3N/2}\left(\frac{1}{\beta}\right)^{3N/2}\right)\right) \\
&= \frac{3N}{2}\frac{1}{\beta} \\
&= \frac{3}{2}NT
\end{aligned}$$

This is a result of the equipartition theorem, which states that 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.

5.4 Maxwell-Boltzmann Distribution

Let us now introduce the Maxwell distribution, also known as the Maxwell-Boltzmann distribution. Consider a box with many particles. Suppose the box has a little person inside, who can measure the individual momentum of particles in the box. What is the probability distribution in the box?

$$P(p_0) = \frac{\exp\left(-\beta p_0^2/2m\right)}{(2\pi mT)^{3/2}}$$

Where the denominator is for normalization, as the probability distribution must integrate out to 1.

This is a distribution in terms of momentum, but we generally write it in terms of speed:

$$P(v) = 4\pi\left(\frac{m}{2\pi T}\right)^{3/2} V^2 \exp\left[-\frac{1}{2}mv^2/T\right]$$

And it has the property that

$$\int dv\, P(v) = 1$$

Everything so far seems good, but we've made a profound error. When we defined entropy, we stated that it needed to be additive, (or extensive). It should be the case that the free energy should also be extensive, but we can show that it fails. We have that

$$Z(T,N,V) = (Z_1(T,V))^N$$

We can relate this to the free energy:

$$-\beta F = \log Z$$

$$\frac{F}{V} = -Tn\log\left(\frac{V}{h^3}\left(2\pi mT\right)^{3/2}\right)$$

We see that we have an issue, $\frac{F}{V} = f$ should be intensive, but we see that it depends on volume! Thus we have that F and S are not extensive (or equivalently, f and s are not intensive). Gibbs saw this, and noticed that something was wrong. Gibbs' logic was that we have a lot of particles in the box, and thus in effect, the particles are indistinguishable from one another, since they're all bouncing around. Therefore, we should count the configuration where particles are swapped as being the same configuration. If we make this argument, the factor of V disappears, and S and F become extensive. However, this creates a paradox. Suppose we have two species of particles, red and blue, which are identical other than their color, and place them in a box, on opposite sides of the box. We remove the divider, and let the system thermalize. We argue that the entropy has increased once the system has thermalized. However, if we listen to Gibbs, the entropy has not changed, since they are indistinguishable.

Classically, this doesn't make any sense. We however, can see that the solution to this problem is quantum mechanics.

Consider a 2 particle system, which has partition function Z_2. Before, we stated that

$$Z_2 = \left(Z_1(T,V)\right)^2$$

Suppose we named each of the particles:

$$Z_2 = Z_1^{(a)}Z_1^{(b)}$$

Suppose we don't distinguish between particles a and b. If we do this, and then switch a and b, we are double counting the configuration in phase space. Thus, we have that

$$Z_2 = \frac{1}{2}Z_1^2$$

Where the $\frac{1}{2}$ avoids the double counting. For the case of 3 particles, we expect to divide by 6, since there are 6 ways of interchanging the particles:

$$Z_3 = \frac{1}{6}Z_1^3$$

We can now generalize this:

$$Z_N = \frac{Z_1^N}{N!}$$

This was Gibbs' insight, he assumed the particles were indistinguishable, even though he didn't know about quantum mechanics. If we now compute write Z out:

$$\begin{aligned} Z_N &= \frac{1}{N!}\left(Z_1\right)^N \\ &= \frac{V^N}{N!}(2\pi mT)^{3N/2} \end{aligned}$$

Now recalling Stirling's approximation for $N!$:

$$N! \approx \sqrt{2\pi N}N^Ne^{-N} \times \mathcal{O}\left(e^{-1/2N}\right)$$

Now looking at $-\log(N!)$:

$$-\log(N!) = N\log\left(\frac{1}{N}\right) + N + \epsilon$$

where ϵ is some small quantity. Now we can go back and take the log of Z to find F:

$$\begin{aligned}\beta f V &= -\log Z \\ &= -N\log\left(\frac{V}{Nh^3}(2\pi mT)^{3/2} + 1 + \epsilon\right) \\ &= -N\log\left(\frac{V}{Nh^3}(2\pi mT)^{3/2} + 1 + \epsilon\right)\end{aligned}$$

From this, we find that

$$f = nT\log\left(\frac{nh^3}{(2\pi mT)^{3/2}} - 1\right) + \epsilon$$

We see that this is intensive, rather than the extensive quantity that was causing us trouble before. We see that assuming that the particles are indistinguishable solves Gibbs' paradox. Gibbs was right, the particles are indistinguishable, but he was right without knowing the reason, which is based on quantum mechanics.

We have seen that this solves the issue of f being extensive, and from this we can solve for the entropy:

$$f = u - Ts \to s = \frac{u-f}{T}$$

If we plug things in and mess around a bit, we find that

$$S = n\left(\frac{3}{2}\log\left(\frac{4\pi mu}{3h^3n}\right) + \frac{5}{2}\right)$$

Which is the Sackur-Tetrode formula.

Suppose we have a box, with a wall separating it into two parts, with equal volumes, $\frac{V}{2}$. 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. 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 entropy have we gained? Looking at the entropy of the separated system:

$$S_{\text{Separated}} = \frac{V}{2}\left[n\left(\frac{3}{2}\log\left(\frac{2\pi mT}{n^{2/3}h^2}\right)\right) + \frac{5}{2}\right] \times 2$$

$$= Vn\left[\frac{3}{2}\log\left(\frac{2\pi mT}{n^{2/3}h^2}\right)+\frac{5}{2}\right]$$

Which is exactly the same as a uniform distribution of 1 species of particle. Now if we look at the evolved system, we note that the densities of the two types of particle drop by a factor of 2, $n \to \frac{n}{2}$. If we do that, the n in the logarithm gives us a nonlinear change:

$$S_{\text{Mixed}} = Vn\left(\frac{3}{2}\log\left(\frac{2\pi mT}{n^{2/3}h^2}\right)+\frac{5}{2}+\log(2)\right)$$

This factor of $\log(2)$ is known as the Gibbs mixing entropy, and if we had 10 species of particles, then we would have $\log(10)$:

$$\Delta S = nV\log(N_{\text{species}})$$

We also have the concept of the specific heat, the energy per volume needed to raise the temperature:

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T}\Big|_n \\ &= \frac{3}{2}n \end{aligned}$$

5.5 Virial Expansion

Let us now consider nonideal gases. For an ideal gas, we have the equation of state:

$$P(n,T) = nT$$

This is a highly idealized situation, the particles are noninteracting. What if the particles do interact?

We know that if n is small, then there will be negligible interactions. We can expand out our equation of state for small n:

$$P(n,T) = T\left(n + B_2(T)n^2 + B_3(T)n^3 + \cdots\right)$$

This is known as the virial expansion. These coefficients can be determined experimentally, but thinking about this model, the second term, B_2 is related to two particle interactions, and B_3 is related to three particle interactions, and so on. This is known as a cluster expansion.

Let us look at a cluster expansion for B_2, for 1 species, and with no relevant internal degrees of freedom (no spin, vibration, etc):

$$\begin{aligned} B_2(T) &= V\left(\frac{1}{2}-\frac{Z_2}{Z_1^2}\right) \\ &= -2\pi\int_0^\infty dr\, r^2\left(e^{-\beta U(r)}-1\right) \end{aligned}$$

Where Z_2 is the partition function for two particles in a box, and Z_1 is the partition function for one particle in a box, and $U(r)$ is the potential between particles, and goes to 0 as $r \to \infty$. We can write out the expansion for B_3:

$$B_3(T) = V^2\left(\frac{2Z_2}{Z_1^2}\left(\frac{2Z_2}{Z_1^2}-1\right)-\frac{1}{3}\left(\frac{6Z_3}{Z_1^3}-1\right)\right)$$

Let us go through the derivation for $B_2(T)$. We begin with the grand partition function, $\mathcal{Z}$:

$$\begin{aligned}\mathcal{Z}_1 &= \sum_N \left(e^{\beta\mu}\right)^N Z_N \\ &= \sum_N \lambda^N Z_N\end{aligned}$$

Where $\lambda = e^{\beta\mu}$ is the fugacity. Let us expand in terms of the fugacity. Before we do that, we also know the relationship between the grand partition function and the grand potential:

$$\begin{aligned}\mathcal{Z} &= e^{-\beta\phi V} \\ &= e^{\beta VP}\end{aligned}$$

If this is true, then taking the log of both sides:

$$\ln \mathcal{Z} = VP\beta$$

Let us now do the fugacity expansion:

$$\begin{aligned}\mathcal{Z} &= \sum_N \lambda^N Z_N \\ &= (1+\lambda Z_1)\left(1+\frac{\lambda^2 Z_2}{1+\lambda Z_1}\right)\left(1+\frac{\lambda^3}{(1+\lambda Z_1)\left(1+\frac{\lambda^2 Z_2}{1+\lambda Z_1}\right)}+\cdots\right)\end{aligned}$$

Now let us truncate the expansion to what we have written down, and then take the log:

$$\ln \mathcal{Z} = \ln(1+\lambda Z_1)\left(1+\frac{\lambda^2 Z_2}{1+\lambda Z_1}\right)+\cdots$$

Where we have thrown out the third term because $\ln(1+x) \approx x$, and x in this case is of order λ^3, and so we toss that out. Now using this relation, $\ln(1+\lambda Z_1) = \lambda Z_1 - \frac{1}{2}\lambda^2 Z_1^2 + \ldots$, and similarly for the second term:

$$\ln \mathcal{Z} = \lambda Z_1 - \frac{1}{2}\lambda^2 Z_1^2 + \lambda^2 Z_2 + \mathcal{O}(\lambda^3)$$

From this, we have that

$$VP\beta = \lambda Z_1 + \lambda^2\left(Z_2 - \frac{1}{2}Z_1^2\right) + \mathcal{O}(\lambda^3)$$

Z_1 is the same as in the ideal gas case. We also note that based on the ideal gas law, $PV\beta = N$. Thus to lowest order in λ:

$$\lambda = \frac{N}{Z_1}$$

If we now insert this expression for λ, we find that

$$\beta PV = N - \left(\frac{N^2}{Z_1^2}\right)\left(\frac{1}{2}Z_1^2 - Z_2\right) + \mathcal{O}(\lambda^3)$$

Now solving for the pressure:

$$\begin{aligned} P &= T\left(\left(\frac{N}{V}\right) - \left(\frac{N}{V}\right)^2 \left(V\left(\frac{1}{2}Z_1^2 - Z_2\right)\right)\right) \\ &= T\left(n + n^2\left(V\left(\frac{1}{2} - \frac{Z_2}{Z_1^2}\right)\right) + \cdots\right) \end{aligned}$$

Now comparing this against the virial expansion, we see that we have the expected expression for $B_2(T)$. Note that in the ideal gas case, B_2 and all further terms are 0, since $Z_2 = \frac{Z_1^2}{2}$.

Let us now write out our Hamiltonian:

$$\hat{H} = \sum_i \frac{\boldsymbol{p}^2}{2m} + \sum_{ij} \frac{1}{2} V_{ij} + 3 \text{ and higher body forces}$$

For the case of B_2, we ignore the 3 and higher body forces. What is our potential? We assume it is some function $u\left(|q_i - q_j|\right)$. Now we can calculate our partition function:

$$\begin{aligned} Z_2 &= \frac{1}{2}\int d^3q_1\, d^3q_2\, d^3p_1\, d^3p_2\ \exp\left(-\beta\left[\frac{1}{2m}\left(p_1^2 + p_2^2\right) + u\left(|q_1 - q_2|\right)\right]\right) \\ &= \frac{1}{2}\left(\int d^3p_1\, e^{-\beta p_1^2/2m} \int d^3p_2 e^{-\beta p_2^2/2m}\right) \int d^3q_1\, d^3q_2 e^{-\beta u(|q_1 - q_2|)} \\ &= \frac{1}{2}\frac{Z_1^2}{V^2} \int d^3q_1\, d^3q_2\ e^{-\beta u(|q_1 - q_2|)} \end{aligned}$$

Now we note that $u(r)$ goes to 0, as $r \to \infty$, it is really important at short distances, and basically negligible at long distances. To exploit this, we can rewrite the exponential:

$$e^{-\beta u(|q_1 - q_2|)} = 1 + \left(e^{-\beta u(|q_1 - q_2|)} - 1\right)$$

Using that, we can do the integral:

$$\int d^3q_1\, d^3q_2\ e^{-\beta u(|q_1 - q_2|)} = \int d^3q_1\, d^3q_2\, 1 + \int d^3q_1\, d^3q_2\ \left(e^{-\beta u(|q_1 - q_2|)} - 1\right)$$

This first integral is just V_2. The second integral is difficult, we'd have to change of variables, to a relative coordinate and a difference integral. However, since we know the potential acts on microscopic distances, then we see that the difference integral quickly goes to 0, and thus we integrate to infinity. We define a variable $q = \frac{q_1 + q_2}{2}$, and a difference variable $r = q_1 - q_2$:

$$\int d^3q_1\, d^3q_2 e^{-\beta u} = V^2 + V\int d^3r\left(e^{-\beta u(r)} - 1\right)$$

Now we note that, via the polar Jacobian, $d^3r = 4\pi r^2 dr$:

$$= V^2 + V\int_0^\infty 4\pi r^2 dr\ \left(e^{-\beta u(r)} - 1\right)$$

Inserting this into the expression for Z_2, and then inserting that into the expression for B_2:

$$B_2 = -2\pi \int_0^\infty dr\, \left(e^{-\beta u(r)} - 1\right) r^2$$

Intuitively, this tells us that B_2 only gets a contribution from things that are within the interaction range of the potential. A positive B_2 means that we have a repulsive interaction, since it increases the pressure.

Let's do a simple example of this. Consider a hard sphere gas, where we model our atoms as hard spheres, that interact only when the spheres are colliding:

$$u(r) = \Theta\left(2R - r\right)$$

The closest that the centers of two spheres can get to each other is 2R. Thus, we have a repulsive force when two of the hard spheres touch. Let us compute what the B_2 coefficient is for this gas.

$$B_2 = -2\pi \int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right)$$

In this case, the integral turns into $2\pi \int_0^{2R} dr\, r^3$, which is equal to $\frac{16\pi R^3}{2}$. Thus, the pressure becomes:

$$P = nT\left(1 + \frac{16\pi R^3}{3} n + \cdots\right)$$

This is an excluded volume effect, and can be thought of as saying that part of the volume of the system is not available (see homework 8).

5.6 Quantum Ideal Gases

When do we have to worry about the quantum mechanics of a system mattering? We first define the thermal deBroglie wavelength, sometimes also known as just the thermal wavelength. For nonrelativistic gases, we say that the temperature scales with the kinetic energy:

$$\frac{p^2}{2m} \sim T \to p \sim \sqrt{mT}$$

We can define the thermal wavelength:

$$\lambda_{\text{th}} = \sqrt{\frac{2\pi}{mT}}$$

When is QM important? It is when $n\lambda_{\text{th}}^3 \sim 1$.

5.6.1 Ideal Bose Gas

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, ϵ_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. We can stick no particles in, and we have state $|0\rangle$. We can stick a single particle in, and we have $|1\rangle$. For 2 particles, since Bosons are indistinguishable, we have only 1, 2 particle state, $|2\rangle$, and we can go all the way up to $|\infty\rangle$. Now let us look at the respective energies, we have 0 for no particles, ϵ_i for 1 particle, $2\epsilon_i$ for 2 particles, and all the way up, for as many particles as we care about.

This is the energy spectrum of the harmonic oscillator, with the 0 point energy is removed.

So let us write out the grand partition function for the ith mode:

$$\begin{aligned}\mathcal{Z}_i &= \text{Tr}\left[e^{-\beta(\hat{H}-\mu N)}\right] \\ &= \sum_{N=0}^{\infty} \exp\left[-\beta(\epsilon_i-\mu)\right]^N \\ &= \frac{1}{1-\exp\left(-\beta\left(\epsilon_i-\mu\right)\right)}\end{aligned}$$

Now expanding this to all modes:

$$\mathcal{Z} = \prod_i \mathcal{Z}_i$$

Note that we used the geometric series, which only converges if $\epsilon_i - \mu$ is positive (where we assume that β is positive.) If ϵ_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 let us ask some simple questions. How many particles do we have in the ith mode, N_i? Or, instead, what is $P(N_i)$?

$$\begin{aligned}P(N_i) &= \frac{\exp\left(-\beta N_i\left(\epsilon_i-\mu\right)\right)}{\mathcal{Z}_i} \\ &= \exp\left(-\beta N_i(\epsilon_i-\mu)\right)\left(1-\exp\left(-\beta(\epsilon_i-\mu)\right)\right)\end{aligned}$$

Suppose we want to know, as a function of β and μ, on average, how many particles are in the ith mode:

$$N_i = \langle N_i\rangle$$

$$\begin{aligned} &= \sum_{N_i} P(N_i) N_i \\ &= \sum_{N} N_i e^{-\beta N_i(\epsilon_i - \mu)} \left(1 - e^{-\beta(\epsilon_i - \mu)}\right) \\ &= \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \end{aligned}$$

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:

$$\begin{aligned} N_i &= \frac{1}{(1 + \beta(\epsilon_i - \mu) + \cdots) - 1} \\ &\approx \frac{1}{\beta(\epsilon_i - \mu)} \end{aligned}$$

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.

5.6.2 Bose-Einstein Condensation

What is the maximum occupation if we have fixed temperature? Well, by the distribution, $\mu = 0$, 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. Let us consider U_i, the energy of the ith mode:

$$\begin{aligned} U_i &= \epsilon_i \langle N \rangle \\ &= \frac{\epsilon_i}{e^{\beta(\epsilon_i - \mu)} - 1} \end{aligned}$$

We can now look at the grand potential:

$$\begin{aligned} \beta\Phi_G &= \log \mathcal{Z}_i \\ &= T \log\left(1 - e^{-\beta(\epsilon_i - \mu)}\right) \\ &= U_i - \mu N_i - TS \end{aligned}$$

If we want to look at all modes, we can just sum over i:

$$\begin{aligned} E &= \sum_i E_i \\ S &= \sum_i S_i \\ N &= \sum_i N_i \end{aligned}$$

We can replace the summations with an integral:

$$\sum_i \to V \int \frac{d^3k}{(2\pi)^3}$$

Where we assume the thermodynamic limit. Let us focus on the total particle number.

The number density is given by

$$\begin{aligned} n &= \frac{\langle N\rangle}{V} \\ &= \int \frac{d^3k}{(2\pi)^3} \frac{1}{\exp\left(\beta\left(\frac{k^2}{2m}-\mu\right)\right)-1} \\ &= \int_0^\infty \frac{dk}{2\pi^2} \frac{k^2}{e^{\beta\left(\frac{k^2}{2m}-\mu\right)}-1} \end{aligned}$$

Now what is the highest density we can get?

$$n_{\text{max}} = \int_0^\infty \frac{dkk^2}{2\pi^2} \frac{1}{e^{\beta\frac{k^2}{2m}}-1}$$

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. One method is to rescale the integral, and then either doing it numerically, asking a graduate student, or asking mathematica. Let us do the factoring. Let us define $y = \frac{1}{\sqrt{2mT}}$. From this, $k = \sqrt{2mT}y$:

$$n_{\text{max}} = (2mT)^{3/2} \int_0^\infty dy \, \frac{y^2}{2\pi^2 \left(e^y\right) - 1}$$

We see that all the dimensionful quantities are out of the integral, and we can compute the integral however we'd like:

$$n_{\text{max}} = (2mT)^{3/2} \frac{\zeta\left(\frac{3}{2}\right)}{8\pi^{3/2}}$$

Where $\zeta(x)$ is the Riemann zeta function, and is defined as $\zeta(x) = \sum_{n=1}^\infty \frac{1}{n^x}$.

This just gets us a number, so we have that

$$n_{\text{max}} = (mT)^{3/2} (0.165869)$$

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.

The point at which we have the phase transition is n_{crit}:

$$n_{\text{crit}} = (mT)^{3/2} \frac{\zeta\left(\frac{3}{2}\right)}{(2\pi)^{3/2}}$$

Any density higher than n_{crit}, is the system in a BEC phase. An alternative way of thinking about it is fixing the density and increasing the temperature:

$$T_{\text{crit}} = \frac{2\pi}{\zeta\left(\frac{3}{2}\right)^{2/3}} \frac{n^{2/3}}{m}$$

Recall that the thermal wavelength was defined as

$$\lambda_{\text{Th}} = \sqrt{\frac{2\pi}{mT}}$$

One obvious question is, how do we relate this to the critical number density for the BEC phase transition? We can define a critical thermal wavelength:

$$\lambda_{\text{crit}} = \sqrt{\frac{2\pi}{mT_{\text{crit}}}}$$

Another way of doing this is to allow T to be whatever we want it to be, and write the thermal wavelength in terms of the critical number density:

$$\lambda_{\text{crit}} = \left(\frac{\zeta\left(\frac{3}{2}\right)}{n}\right)^{1/3}$$

Note that $\frac{1}{n^{1/3}}$ is roughly the average distance between particles. The critical thermal wavelength, is a number of order 1 times the average distance between particles. This is exactly what we would expect to happen. When the thermal wavelength is large enough to realize that there are other particles, quantum mechanics matters.

Let us look at the density of condensed particles, $n_0(T)$:

$$n_0(T) = \begin{cases} 0 & n < n_{\text{crit}} \\ n - n_{\text{crit}} & n > n_{\text{crit}} \end{cases}$$

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:

$$\begin{aligned} \frac{n_0}{n} &= \frac{n - n_{\text{crit}}}{n} \\ &= 1 - \frac{n_{\text{crit}}}{n} \end{aligned}$$

This number is always finite. This is a macroscopic quantum effect. Now let's do some dimensional analysis and toss back in the $\hbar$s. Taking a look at n_{crit}:

$$n_{\text{crit}} = \frac{\zeta\left(\frac{3}{2}\right)}{(2\pi)^{3/2}} (mT)^{3/2}$$

The first thing to do is to put back that k_B next to the temperature:

$$n_{\text{crit}} = \frac{\zeta\left(\frac{3}{2}\right)}{(2\pi)^{3/2}} (mk_BT)^{3/2}$$

Now we note that the density is 1 over length cubed, and the right side goes as momentum squared, and thus we need a factor of $\hbar^2$ in the denominator:

$$n_{\text{crit}} = \frac{k_B^{3/2}}{\hbar^2} \frac{\zeta\left(\frac{3}{2}\right)}{(2\pi)^{3/2}} (mT)^{3/2}$$

5.6.3 Classical Limit

Now let us see how we can get the classical ideal gas starting from here. Note that this isn't very hard to see, since when we developed the Bose gas, we had an energy spectrum that matched the harmonic oscillator, aside from the zero point motion. However, we have a problem. We previously had:

$$\langle N_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$$

If we take the high temperature limit:

$$\begin{aligned}\frac{1}{e^{\beta(\epsilon_i-\mu)} - 1} &\to \frac{1}{1 + \beta\left(\epsilon_i - \mu\right) + \cdots - 1} \\ &= \frac{1}{\beta(\epsilon_i - \mu)} \\ &\to \infty\end{aligned}$$

We see that we have a divergence. What have we messed up?

The subtlety is that, as the temperature changes, the chemical potential necessary to keep the density fixed changes. Thus, we cannot have μ fixed. What should we do instead?

Well, to get low density, we need μ to be large and negative. If we do this, then integral for the density will change:

$$\begin{aligned}n &= \frac{\langle N \rangle}{V} \\ &= \int \frac{d^3k}{(2\pi)^3} \frac{1}{\exp\left(\beta\left(\frac{k^2}{2m} - \mu\right)\right) - 1} \\ &\approx e^{\beta\mu} \int \frac{d^3k}{(2\pi)^3} e^{-\beta k^2/2m}\end{aligned}$$

Now we note that this prefactor is the fugacity, which we will denote ϕ. Thus, if we want finite densities, we should keep the fugacity low. It turns out that this is what we would have obtained had we started with the classical grand potential.

GOT COVID, MISSED A TON OF CLASSES HERE

5.6.4 Ideal Fermi Gases

We have that the occupation is given by

$$N(\epsilon, T, \mu) = \frac{1}{e^{\frac{\epsilon - \mu}{T}} + 1}$$

And we can compute the density:

$$n = g \int \frac{dA^3k}{(2\pi)^3} \frac{1}{e^{\frac{\frac{k^2}{2m} - \mu}{T}} + 1}$$

Where the g is the spin degeneracy.

What does the Fermi gas look like at low temperatures and high density. How should we think about this problem? We will assume that T is small, look at the Fermi surface, and have particle-hole excitations, particles leaving filled states near the Fermi surface.

We have an expansion in n_F

$$\Delta n_F = n_f\left(\frac{(\epsilon-\mu)}{T}\right) - \Theta\left(\mu-\epsilon\right)$$

This must integrate to 0.

We are working with fixed total n. We eventually want to write out the internal energy density:

$$\begin{aligned} u &= \frac{U}{V} \\ &= \frac{3}{5}n\epsilon_F\left(1+\frac{5}{12}\pi^2\left(\frac{T}{\epsilon_F}\right)^2+\cdots\right) \end{aligned}$$

From this, we will deduce that the heat capacity:

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_{N,V} \\ &= \frac{N\pi^3 T}{2\epsilon_F}\left(1+\dots\right) \end{aligned}$$

Before we go through the expansion, let us introduce a mathematical trick. Suppose we have a function $\Delta(x)$, such that $\int dx\,\Delta(x)x^n$ is finite for all non-negative integers. Qualitatively, this function falls off faster than any power law, it is "localized" in some sense. Suppose we want to compute $I(\lambda)$:

$$I(\lambda) = \int_{-\infty}^{\infty} dx\, f(x)\Delta\left(\frac{x-x_0}{\lambda}\right)$$

for small λ. Note that if λ goes to 0, we approach something that looks like a Dirac delta (it gets skinnier and skinnier), and thus $I(\lambda)$ will evaluate to about $f(x_0)$, times the area of the Δ function. Suppose we want to do this integral, we use the second most-used trick in our box, we Taylor expand. We want to Taylor expand f, since we will have powers of $x-x_0$, and we know that the integral of Δ function is convergent. Thus, we write out $f(x)$ as a Taylor series around x_0.

$$\begin{aligned} I(\lambda) &= \int_{-\infty}^{\infty} dx\, f(x)\Delta\left(\frac{x-x_0}{\lambda}\right) \\ &= \int_{-\infty}^{\infty} dx\,\Delta\left(\frac{x-x_0}{\lambda}\right)\left(f(x_0)+f'(x_0)(x-x_0)+\frac{1}{2}f''(x_0)\left(x-x_0\right)^2+\dots\right) \end{aligned}$$

To get this in terms of λ, we introduce a change of variables, $y=\frac{x-x_0}{\lambda}$, which turns $x-x_0$ into λy:

$$I(\lambda) = \int_{-\infty}^{\infty} dx\,\Delta(y)\left(f'(x_0)+\lambda f''(x_0)y+\frac{\lambda^2}{2}f'''(x_0)y^2+\dots\right)$$

This can then be split into separate integrals, each of which we can do easily:

$$I(\lambda)=\sum_{n=0}^{\infty}\frac{\lambda^{n+1}}{n!}\frac{\partial^n f}{\partial x^n}\Big|_{x=x_0}\int_{-\infty}^{\infty}dy\,y^n\Delta(y)$$

This series has an amusing feature, we can rewrite this:

$$I(\lambda)=\sum_{n=0}^{\infty}\frac{\lambda^{n+1}}{n!}\frac{\partial^n f}{\partial x^n}\Big|_{x=x_0}c_n$$

Where $c_n=\int_{-\infty}^{\infty}dy\,y^n\Delta(y)$. We are approximating Δ as a delta function, plus all higher derivatives of the delta function, we have replaced $\Delta(y)$ with $\sum_n c_n\frac{(-1)^n}{n!}\delta^{(n)}(y)$. This is a terrible approximation for $\Delta(y)$ (since the derivatives of the delta function have zero width, but Δ has finite width), but we have reproduced all the "moments" of Δ. If $f(x)$ is analytic, this provides a very good approximation of the integral, and is exact if we sum to infinity.

What we are doing is developing the Sommerfeld expansion for low temperatures. Recall that we are attempting to compute

$$\begin{aligned}n&=g\int d\left(\epsilon\right)n_F\left(\beta\left(\epsilon-\mu\right)\right)\\ u&=g\int d(\epsilon)\epsilon n_F(\beta\left(\epsilon-\mu\right))\end{aligned}$$

And we had that

$$n_F\left(\beta\left(\epsilon-\mu\right)\right)=\Theta(\mu-\epsilon)+\Delta n_F$$

Let us rewrite this:

$$\Delta n_F=n_F(x)-\Theta(x)$$

And we want to compute the moments, C_n:

$$\begin{aligned}C_0&=\int_{-\infty}^{\infty}dx\,\Delta n_F(x)\\ &=-\int_{-\infty}^{\infty}dx\,\Theta(-x)+\int_{-\infty}^{\infty}n_F(x)\\ &=-\int_{-\infty}^{0}(n_F(x)-1)+\int_{0}^{\infty}n_F(x)\\ &=-\int_{-\infty}^{0}dx\left(\frac{1}{e^x+1}-1\right)+\int_0^{\infty}dx\,n_F(x)\\ &=-\int_{-\infty}^{0}dx\left(\frac{1}{e^x+1}-\frac{e^x+1}{e^x+1}\right)+\int_0^{\infty}dx\,n_F(x)\\ &=-\int_{-\infty}^{0}dx\,\frac{1}{1+e^{-x}}+\int_0^{\infty}dx\,n_F(x)\\ &=0\end{aligned}$$

Where we note that the left integral, after a change of variables, is the exact same as the second integral, and thus C_0 is 0.

We can now compute the first order term:

$$\begin{aligned}
C_1 &= \int_{-\infty}^{\infty} dx\, x\Delta n_F(x) \\
&= 2\int_0^{\infty} dx\, \frac{x}{e^x+1} \\
&= \frac{\pi^2}{6}
\end{aligned}$$

Now let us see how to extract what we care about. We want u as a function of n in the end. We can write this as

$$u = n\left(\frac{u(T,\mu)}{n(T,\mu)}\right)$$

Let us now compute $u(T,\mu)$ and $n(T,\mu)$ to the lowest nontrivial order.

$$n = n_{T=0} + g\int_0^{\infty} d\epsilon\, d(\epsilon)\overbrace{\left(n_F\left(\frac{\epsilon-\mu}{T}\right) - \Theta(\mu-\epsilon)\right)}^{\Delta n_F}$$

Similarly:

$$u = g\int_0^{\infty} d\epsilon\, d(\epsilon)\epsilon\overbrace{\left(n_F\left(\frac{\epsilon-\mu}{T}\right) - \Theta(\mu-\epsilon)\right)}^{\Delta n_F}$$

Starting with n, we have an integral of a function times Δn_F. In this case, $T = \lambda$:

$$\begin{aligned}
\Delta n_F\left(\frac{\epsilon-\mu}{T}\right) &= g\int_0^{\infty} d\epsilon\, d(\epsilon)\left(n_F\left(\frac{\epsilon-\mu}{T}\right) - \Theta(\mu-\epsilon)\right) \\
&= gT^2C_1 d'(\epsilon)|_{\epsilon=\mu} + \mathcal{O}(T^4)
\end{aligned}$$

We can do the same thing for the energy:

$$\Delta u = gT^2C_1\left(\frac{d\epsilon d(\epsilon)}{d\epsilon}\right) + \mathcal{O}\left(T^4\right)$$

If we now compute the ratio, $\frac{u}{n}$, we have that

$$\begin{aligned}
\frac{u}{n} &= \frac{u_0 + T^2C_1\mu d'(\mu) + T^2C_1 d(\mu)}{n_0 + T^2C_1 d'(\mu)} + \mathcal{O}\left(T^4\right) \\
&= \frac{u_0 + T^2\left(C_1\mu d'(\mu) + C_1 d'(\mu)\right)}{n_0}\left(1 - \frac{T^2C_1 d'(\mu)}{n_0}\right)
\end{aligned}$$

If we do this out, we find that

$$\frac{u}{n} = \frac{3}{5}\epsilon_F + \frac{\epsilon_F\pi^2}{4}\left(\frac{T}{\epsilon_F}\right)^2$$

We have the first order corrections to our ratio.

We can compute the heat capacity:

$$\begin{aligned} C_V &= \frac{\partial U}{\partial T} \Big|_{N,V} \\ &= \frac{N\pi^2 T}{2\epsilon_F} \end{aligned}$$

5.7 Spin Models and Phase Transitions

Many systems form crystals, which means that there is some lattice structure, with sites, and atoms sitting at the lattice sites. We can think of spins at each one of the lattice sites, and thus we can associate a spin to each lattice site (even if we think about them connected to each other by springs, they still remain pretty much localized). From this, we see paramagnetism, which is spins aligning themselves to an external magnetic field. We can then also see ferromagnetism, where spins interact with their neighbors. At high temperatures, there is no structure for the spins, and as we cool past the Curie temperature, we see ferromagnetic structure.

5.7.1 Paramagnetism

For a single spin at a lattice site, the Hamiltonian is given by

$$\hat{H} = -\boldsymbol{m} \cdot \boldsymbol{B}$$

Where $\boldsymbol{m} = g\mu_B \boldsymbol{s}$, where g is the gyromagnetic factor, μ_B is the Bohr magneton, and $\boldsymbol{s}$ is the spin, which we will assume to be $\frac{1}{2}$.

Let us say that $\boldsymbol{B} = B\boldsymbol{z}$, which turns the total Hamiltonian into

$$\begin{aligned} \hat{H} &= \sum_{\text{sites}} -g\mu_B B s_z \\ &= \sum_{\text{sites}} \frac{1}{2} g\mu_B B \sigma_z \end{aligned}$$

Let us condense all the constant factors into $\tilde{b}$:

$$\hat{H} = \sum_i \tilde{b} \sigma_z^i$$

The probability that a spin will be up will be given by the Boltzmann factor:

$$P_\uparrow = \frac{e^{-\beta\tilde{b}}}{e^{-\beta\tilde{b}} + e^{\beta\tilde{b}}}$$

Similarly, the probability that it will be down:

$$P_\downarrow = 1 - P_\uparrow$$

Now what is the average value of the spin at site i:

$$\begin{aligned}\langle\sigma_z^i\rangle &= P_\uparrow - P_\downarrow\\ &= \frac{e^{-\beta\tilde{b}} - e^{\beta\tilde{b}}}{e^{-\beta\tilde{b}} + e^{\beta\tilde{b}}}\\ &= \tanh(\beta\tilde{b})\end{aligned}$$

Let us consider the expectation value of the magnetization:

$$\begin{aligned}\langle\boldsymbol{m}\rangle &= \hat{z}g\langle\sigma_z\rangle n_{\text{sites}}\\ &= \hat{z}\left(\frac{1}{2}g\mu_B n_{\text{sites}}\right)\tanh\left(\frac{1}{2}\frac{g\mu_B B}{T}\right)\end{aligned}$$

Note that at high temperatures, this goes to 0, as expected, there should be no net magnetization, since there is no magnetic structure.

Now consider a material, and we apply a magnetic field to it, we expect there to be some screening on each spin, since the magnetic field will cause the other spins to generate another force.

$$\boldsymbol{B} = \boldsymbol{H} + \boldsymbol{m}$$

Where $\boldsymbol{H}$ is the magnetic field that we can externally control.

If we assume that $|\boldsymbol{H}|$ is small, then

$$\boldsymbol{m} = \frac{\boldsymbol{H}}{H}\left(\frac{1}{2}g\mu_B n_{\text{sites}}\right)\tanh\left(\frac{1}{2}\mu_B g\frac{H}{T}\right)$$

We can talk about the susceptibility:

$$\begin{aligned}\chi_m &= \frac{\partial m}{\partial H}\Big|_{H=0}\\ &\approx \frac{\left(\frac{1}{2}g\mu_B\right)^2 n_{\text{sites}}}{T}\end{aligned}$$

5.7.2 Ferromagnetism

We can now introduce interactions between spins, starting with the simplest model, the Ising model. We assume that the spins on the lattice are all aligned with the z direction, with spins of ±1:

$$\hat{H} = \sum_{\text{nn}} J\sigma_i^{(z)}\sigma_j^{(z)}$$

If we cool down the system, we see ferromagnetic regions forming. This is analytically solvable in 1D, and 2D (worth a Nobel Prize), but not in 3D. After 2D, we have to do it numerically, via Monte Carlo methods.

We can also use a mean field theory, which is where we average over the neighbors to get an effective field that acts on a spin. This gets us the wrong answers, but the right qualitative results. We can then solve the 1D case analytically, which will not give us a phase transition.

At $T = 0$, if the system is ferromagnetic, we will get either all up spins, or all down spins. This breaks the symmetry that is in the Hamiltonian. This is known as spontaneous symmetry breaking, and is associated with critical behavior. In the anti-ferromagnetic case, we have two ground states still, with alternating neighboring spins, and they are equivalent up to a shift.

Consider a triangular lattice, intuitively, we cannot make this anti-align easily, and as such it is a frustrated anti-ferromagnetic system.

We will call $\langle\sigma\rangle$ an order parameter. There are three types of behaviors that we can have. The first is called crossover, where the system is all aligned at low temperature, and it smoothly because un-aligned. This does not happen in the Ising model. The second type is known as a second order phase transition, the alignment hits zero at some critical temperature, T_c. Finally, we have the first order transition, where the alignment instantly drops to zero as soon as we pass a critical point.

A lot of what we will do is looking at second order phase transitions, as those are quite interesting.

Let us begin by looking at the Ising model using a mean field theory, which will give us the wrong answer, but will give the right qualitative results. We have that

$$\hat{H} = -\frac{1}{2}J\sum_{i,j}\sigma_i\sigma_j - h\sigma$$

Where h is the strength of the external field. Note that the minus sign tells us that the particles want to align, it corresponds to lower energy states. If we had no minus sign, we have an anti-ferromagnetic system, it would be lower energy to have spins that alternate.

We will be most interested in the case where $h = 0$. What happens when we increase the temperature? As we increase the temperature, the energy gained via aligning the spins is fighting the change in entropy, since the system wants to minimize the free energy, $E - TS$. The energy is stored in the bonds between nearest neighbors, which is why we have the $\frac{1}{2}$, since we would be double-counting otherwise.

If the temperature is 0, and $h > 0$, then we will have all up spins, and if $h < 0$, then we have all down spins. What if $h = 0$ and $T \neq 0$? This is what we will try to solve.

We want to minimize the free energy:

$$F = U - TS$$

The energy U is pretty easy to compute, we can just look at all the bonds. We now choose an ansatz, we want a density matrix for the system ρ that minimizes the free energy. The simplest density matrix that encodes some information is one that says that each spin is independent, there is no relationship between the spins. This approximation is useful when h is large, and the temperature is low. In this case, the spins are all aligned, and local fluctuations don't really affect the neighbors.

However, in the case of second order phase transitions, as we approach the transition point, correlation lengths go to infinity, changes in a local spin can affect spins arbitrarily far away. This means that our approximation is terrible at the phase transition point. However, let us continue with this density matrix. The density matrix of each spin is a 2D matrix, since we have two spins, up and down. The density matrix for the total system is the product of all the density matrices:

$$\hat{\rho} = \prod_i \hat{\rho}_i$$

For our approximation, we will say that the local spin matrices will be the same:

$$\hat{\rho}_i = \hat{\rho}_0$$

This is our ansatz, our guess for the functional form. We can now try to compute $\langle H \rangle$, and try to find the value of $\hat{\rho}_0$ that gives the lowest value of $\langle H \rangle$. This is mean field theory. How do we compute S? Since each site has the same density matrix, it will be the number of sites times the entropy at one site:

$$S_0 = -P_\uparrow \log P_\uparrow - P_\downarrow \log P_\downarrow$$

We can define the average spin at a site:

$$\sigma_0 = P_\uparrow - P_\downarrow$$

We can replace $P_\uparrow$ with $\frac{1}{2}(\sigma_0 + 1)$, and $P_\downarrow = \frac{1}{2}(-\sigma_0 + 1)$. Let us now look at the expectation value of one of the particle pairs:

$$\langle H_{i,j} \rangle = -J \langle \sigma_i \sigma_j \rangle$$

Where i and j are nearest neighbors. By hypothesis, we have stated that there is no correlation between σ_i and σ_j, so this is the same as

$$\begin{aligned} \langle H_{i,j} \rangle &= -J \langle \sigma_0 \rangle^2 \\ &= -J\sigma_0^2 \end{aligned}$$

Instead of thinking about what is happening at each site, we are thinking about what is happening at the link between the sites.

$$\langle H \rangle = -h \sum_i \langle \sigma_0 \rangle - \sum_i \frac{J}{2} N_{nn} \langle \sigma_0 \rangle^2$$

Where the $\frac{1}{2}$ is to split the energy for each link across both sites, and where N_{nn} is the number of nearest neighbors, which depends on the form of the lattice. For a simple cubic lattice in 3D, $N_{nn} = 6$.

Now let us look at F:

$$\begin{aligned} F &= \langle H \rangle - TS \\ &= \sum_i \left(-h \langle \sigma_0 \rangle - \frac{N_{nn} J}{2} \langle \sigma_0 \rangle^2 + T \langle \rho_0 \log \rho_0 \rangle \right) \end{aligned}$$

We want to find the minimum value of this free energy. We want to find the point at which

$$\frac{\partial F}{\partial \rho} = 0$$

Where this is a functional derivative, but it boils down in this case to minimizing with respect to σ_0.

$$\frac{\partial F}{\partial \rho_0} = \overbrace{(-h - N_{nn} \langle \sigma \rangle J)}^{h_{MF}} \frac{\partial \sigma}{\partial \rho_0} + \frac{\partial \mathrm{Tr}\left[\rho_0 \log \rho_0\right]}{\partial \rho_0}$$

$$= 0$$

We denote the prefactor to be h_{MF}, for the mean field. If we do this, this seems very similar to the case of spins in an external field, which happens to be of strength h_{MF}. Now we claim to have already solved this problem, which we didn't do via minimization of the free energy, but by knowing the probability distribution. Thus we can reduce this to a problem that we have already solved, and we will just steal the answer that we had before, with noncoupled spins.

Previously, we had that $\langle\sigma\rangle = \tanh(\beta h)$, and thus using mean field theory, we claim that

$$\langle\sigma\rangle = \tanh\left(\beta\left(h + N_{nn}\langle\sigma\rangle J\right)\right)$$

This is a transcendental equation, and there is no analytic solution. At first, let us look at the case where $h = 0$:

$$\langle\sigma\rangle = \tanh\left(\left(JN_{nn}\langle\sigma\rangle\right)\beta\right)$$

We now define $\langle\tilde{\sigma}\rangle = JN_{nn}\langle\sigma\rangle$, which reduces the problem down to:

$$\tanh(\langle\sigma\rangle) = \frac{T\tilde{\sigma}}{JN_{nn}}$$

We still can't solve this, so how do we go about this. One method is to give it to a grad student, and another is to give it to Mathematica. Instead, let us consider a graphical solution, we have a line on the right side, and a tanh on the left side, so lets find where they cross.

If we have very high temperature, we see that we have 1 solution, at $\sigma = 0$, which is always a solution. If we cool the system, we see that the slope of the line starts decreasing, and if $T = JN_{nn}$, we see that the line becomes tangent to the tanh at the point 0. If we cool it down even further, we go from having 1 solution to 3 solutions. The 2 new solutions have lower F, and as such, are the approximate ground states. How does the system know which of the two solutions to pick (spontaneous symmetry breaking)? Well, it is based on h. If we start $h > 0$, then the system will be initially weighted towards the higher solution, and then we cool the system down, and then set $h = 0$, the system will pick the higher solution.

The critical point of the system is when $T = JN_{nn}$, the point at which we go from 1 solution to 3 solutions.

What happens if we plot $|\langle\sigma\rangle|$ as a function of T? We see that it starts at 1, and then goes to 0 at T_c, and then remains there as we increase T. This is a second order phase transition (the function is continuous, but the derivative is not). If we look at other models in the same universality class as this model (shares certain parameters or features), it turns out that we see similar behavior right around the transition point, T_c. We get locally non-analytic behavior, which is shared by the other models in the class. By non-analytic, we mean that we cannot compute a Taylor series expansion for the function at T_c. We will be able to relate the behavior to a critical exponent.

Let us look at a quantity that we can calculate, and look right near the critical point. Near this point, we expect $\langle\sigma\rangle$ to be near zero. We can then Taylor expand the tanh:

$$\frac{T\tilde{\sigma}}{JN_{nn}} = \tanh(\tilde{\sigma})$$

$$\sigma = \tanh\left(\frac{T_c}{T}\sigma\right)$$

$$\sigma \approx \frac{T_c}{T}\sigma - \frac{1}{2}\left(\frac{T_c}{T}\sigma\right)^3$$

Our claim is that this is legitimate when σ is small, and we claim that this is always true when we are in the vicinity of the critical point, on the right we are zero, which is small, and on the left we are almost zero, and getting closer to zero.

What happens to the left of the critical point when we have this approximation? What happens if we cool it down just a little bit?

Since we are not interested in the solution at $\sigma = 0$, we can divide by σ:

$$1 = \frac{T_c}{T} - \frac{1}{3}\left(\frac{T_c}{T}\right)^3 \sigma^2$$

This has the solution:

$$\sigma = \pm\sqrt{3\left(\frac{T}{T_c}\right)^2 - \left(\frac{T}{T_c}\right)^3}$$

We can write $T = T_c + (T - T_c)$, which allows us to rewrite, $\frac{T}{T_C} = 1 + \frac{T-T_c}{T_c}$. From this, we define $t = \frac{T-T_c}{T_c}$. We do this because t is now a dimensionless quantity, and is sometimes known as the reduced temperature. From this, we have that:

$$\left(\frac{T}{T_c}\right)^2 = 1 + 2t + \mathcal{O}\left(t^2\right)$$
$$\left(\frac{T}{T_c}\right)^3 = 1 + 3t + \mathcal{O}\left(t^3\right)$$

Inserting these, we have that:

$$\sigma = \pm\sqrt{-3t}$$

This might seem bad, since we want σ to be real, but its fine, since the temperature at which the magnetization occurs is when t is negative, since it is below the critical temperature. Also, we don't really care about the -3, since we just really care about behavior, not the scale:

$$|\sigma| \propto \text{const}\,(-t)^{1/2}$$

This is known as a critical exponent, and this is universal. Note that the constant is not universal, that varies. However, this exponent turns out to be universally *wrong* (if we are in dimensions less than 5). Note that $(-t)^{1/2}$ is non-analytic, the square root has no Taylor expansion around 0.

Let us now define what we mean by an order parameter. Definitionally, it is a parameter that is a measure of the order. Strictly, it is something that is nonzero in a symmetry-broken phase (system has less symmetry than the Hamiltonian that gave rise to it), and is zero in a symmetry-unbroken phase. In this case, σ is zero at high temperatures, equally likely to be up or down, and when cooled below the critical point, we have a nonzero σ. Note that the universality class of the model is based on the dimension of the order parameter, as well as the dimensions of our space.

5.7.3 Landau Theory

Let us define an order parameter ψ. In the case of the Ising model, $\psi = \sigma$. We have two different regimes, $t > 0$, and $t < 0$, and we have a bunch of quantities, C (the specific heat), ψ, and χ, the susceptibility (in this case, how quickly our system magnetizes). For $t < 0$:

- $C \propto t^{-\alpha}$
- $\psi = 0$
- $\chi \propto t^{-\sigma}$

And for $t > 0$:

- $C \propto (-t)^{-\alpha'}$
- $t \propto (-t)^{\beta}$
- $\chi \propto (-t)^{-\gamma'}$

We compute the case where $t < 0$, in mean field theory, that $\beta = \frac{1}{2}$.

To compute the susceptibility case, we use the definition of the susceptibility:

$$\chi = \frac{\partial \sigma}{\partial h} \Big|_{h=0}$$

We can compute this, using the fact that $\sigma = \tanh\left(\beta\left(h + JN_{nn}\sigma\right)\right)$.

The idea behind the universality of the phase transition is that we need long-range order as we cool, and this occurs due to long-range fluctuations, changes in the spins in one region will affect spins arbitrarily far away.

Let us define ψ as an order parameter, which is quasilocal, it is defined over a small but not too small region, i.e, not the magnetization of one spin, but not the magnetization over the entire sample. It must be large compared to the microscopic scales, but small compared to the macroscopic scales. How will we define the correlation length. Up until now, we have use $\langle \psi \rangle$ or $\langle \sigma \rangle$ to see how ordered the system is. However, let us consider $\langle \sigma_i \sigma_j \rangle$, which will, if there is correlation between σ_i and σ_j, not be the same as $\langle \sigma \rangle$. This is of the form:

$$\langle \sigma_i \sigma_j \rangle \sim \text{const } e^{-|\boldsymbol{r}_i - \boldsymbol{r}_j|/\xi}$$

And ξ is the correlation length.

We can define this for ψ:

$$\langle \left(\psi(x) - \langle \psi \rangle\right)\left(\psi(0) - \langle \psi \rangle\right) \rangle$$

The claim is that as we approach the critical temperature, ξ gets longer, it no longer drops off exponentially.

Our claim is that as $T \to T_c$, $\xi \to \infty$.

If we once again define $t = \frac{T - T_c}{T_c}$, the claim is that $\xi \sim t^{-\nu}$ in the disordered high T phase (in MFT, $\nu = \frac{1}{2}$), and $\xi \sim |-t|^{-\nu'}$ in the ordered low T phase (in MFT, $\nu' = \frac{1}{2}$).

Let us now begin Landau Theory. Let ψ be a generic order parameter. Let us assume that near the phase transition, ψ is small. Exploiting this, we do a Taylor series expansion in ψ. Let us also allow that ψ has spatial variations. Near the phase transition, we know that ψ will vary over long distance scales. This suggests that we do a derivative expansion, expanding in derivatives of ψ. Landau did the following:

$$F = \int d^D x f(\psi, \nabla\psi)$$

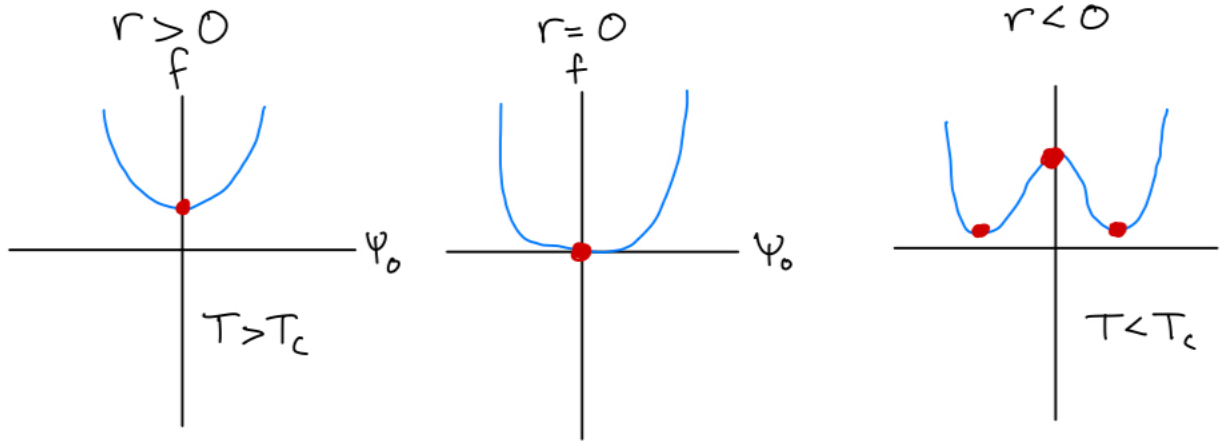
Where D is the spatial dimensionality. We let the free energy be:

$$f = a(T) + r(T)\psi^2 + s(T)\psi^4 + h(x)\psi + f(T)|\nabla\psi|^2$$

Where $f(T)$ is not the free energy, it is another function, and $h(x)$ is an external field.

We assume that a, r, s, and f are smooth functions of T. We can then assume that $h = 0$, and assume that $\psi(\boldsymbol{x}) = \psi_0$, a constant.

Now if $f(T) > 0$, then $s(T) > 0$, because if it were negative, we could lower the energy by increasing σ, but we assumed that σ is small, and thus it must be positive. Now what about $r(T)$? We don't care about $r(T)$, we can have 3 cases, $r > 0$, $r = 0$, and $r < 0$. We can plot these:



We can expand $r(T)$ as a Taylor series:

$$\begin{aligned} r(T) &= r(T_c) + (T - T_c)r'(T_c) \\ &= T_C\left(\frac{T - T_c}{T_c}\right)r' \\ &= ct \end{aligned}$$

where $c = r'(T_c)T_c$, and we have used the fact that $r(T_c) = 0$. When we use this an plug this into $f(T)$, we have two regimes, when $t > 0$:

$$\psi = 0$$

When $t < T_c$:

$$\psi = \pm\sqrt{\frac{4c}{3s(T_c)}(-t)}$$

Thus we see that $|\psi| \sim (-t)^{1/2}$, which is exactly the critical exponent that we got from mean field theory for the Ising model. This is the β critical exponent. We claim that if you compute α and γ, we will get the same answer as in MFT. Landau theory reduces to MFT when we assume that there is no external potential and there is no spatial variation.

Now what happens if we allow for spatial variation?

The technique that we will use to minimize F is the analogue of using the Euler-Lagrange equations to minimize the action. However, there is another subtlety, when we used Euler-Lagrange equations to minimize the action, we impose the boundary condition that the start and end points are held fixed. Here, we say that ψ goes to fixed values on the boundary of the volume.

We have that $\delta F = 0$:

$$\int d^D x f(\psi, \nabla\psi) = \int d^D x \left(\frac{\partial f}{\partial \psi} \delta\psi + \sum_i \frac{\partial f}{\partial \left(\partial_i \psi\right)} \delta \left(\partial_i \psi\right) \right)$$

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:

$$0 = \int d^D x \left[\left(\frac{\partial f}{\partial \psi} - \sum_i \delta_i \frac{\partial f}{\partial \left(\delta_i \psi\right)} \right) \delta\psi \right]$$

Now we use the same argument as in classical mechanics, in order for this to work for all $\delta\psi$, this implies that:

$$\frac{\partial f}{\partial \psi} - \sum_i \partial_i \frac{\partial f}{\partial \left(\partial_i \psi\right)} = 0$$

We can insert f, and we have that

$$\begin{aligned} -2f(T)\nabla^2\psi + 2r\psi + 4s(T)\psi^3 &= 0 \\ -\nabla^2\psi + \frac{r(T)}{f(T)}\psi + \frac{2s(T)}{f(T)}\psi^3 &= 0 \end{aligned}$$

This is nonlinear and has no analytic solution. To solve this, we will linearize it, $\psi = \psi_0 + \delta\psi$:

$$\frac{r(T)}{f(T)}\psi_0 + \frac{2s(T)}{f(T)}\psi_0^3 - \left(\nabla^2 + \frac{r(T)}{f(T)} + \frac{6s(T)}{f(T)}\psi_0^2 \right) \delta\psi + \mathcal{O}\left(\delta\psi^2\right) = 0$$

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

$$\left(-\nabla^2 + \frac{r(T)}{f(T)} + \frac{6s(T)}{f(T)}\psi_0^2 \right) \delta\psi = 0$$

This is Landau's equation.

In the high temperature phase, $\psi_0 = 0$, and thus the term proportional to ψ_0^2 is gone.

Now let us rewrite this via a constant:

$$\xi^{-2} = \frac{r(T)}{f\left(T\right)} + \frac{6s\left(T\right)}{f\left(T\right)}\psi_0^2$$

Which turns the equation into:

$$\left(-\nabla^2 - \xi^{-2}(T)\right)\delta\psi = 0$$

Recall that the critical point occurs when $r = 0$, and thus the ξ^{-2} term will go to zero. In one dimension, solving this is easy, we have an exponential (the grad turns into a single derivative squared, and thus we have an exponential solution). Let us work in 3 dimensions. Let us assume that the volume is very large. We assume spherical symmetry, and the ∇^2 becomes $\frac{1}{r^2}\partial_r r^2 \partial_r$. When we use this, we have that the solution becomes

$$\text{const}\frac{e^{-r/\xi}}{r}$$

More explicitly:

$$\text{const}\frac{\exp\left(-|\boldsymbol{r}-\boldsymbol{r}_0|\right)/\xi}{|\boldsymbol{r}-\boldsymbol{r}_0|}$$

Now we claim that we have a critical exponent for ξ:

$$\begin{aligned}\xi\left(t\right) &\sim |t|^{-\nu} \text{ for } t > 0\\ \xi(t) &\sim |t|^{-\nu'} \text{ for } t < 0\end{aligned}$$

Where $\nu = \nu' = \frac{1}{2}$.

Let us start by looking at the high temperature phase, with no symmetry breaking, $T > T_c$, $T > 0$. In this phase, we have that

$$\xi^{-2} = \frac{2r\left(T\right)}{f\left(T\right)}$$

Now let us assume that we have smooth variables:

$$\begin{aligned}f(t) &= f(0) + f'(t)\\ r(T) &= \underbrace{r(T_c)}_{\text{zero}} + r'(T_c)(T - T_c) + \mathcal{O}\left((T-T_c)^2\right)\end{aligned}$$

Now using these:

$$\begin{aligned}\frac{r(T)}{f(T)} &= t\frac{T_c r'(T_c)}{f(T_c)}\\ &= \text{const}\cdot t + \mathcal{O}(t^2)\end{aligned}$$

Once we have this, we can write out ξ^{-2}:

$$\begin{aligned}\xi^{-2} &= \frac{2r(t)}{f(t)}\\ &= t\left(\frac{2T_C r'(T_c)}{f(T_c)}\right)\\ &\to \xi = \text{const}\cdot t^{-1/2}\end{aligned}$$

We can do the same calculation for the symmetry-broken phase, and we will get the the correct critical exponent.

We see that we have long-distance effects coming from just nearest-neighbor interactions, and they are infinite range, they propogate indefinitely.

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 the critical dimensions. The upper critical dimension states that mean field theory or Landau theory is accurate if $D >$ UCD. For the Ising model, the UCD $= 4$, starting with 5 dimensions gives us the right critical exponents. Exactly at the critical dimension, we are almost right, there are logarithmic corrections that are necessary.

There is also the lower critical dimension. If $D <$ LCD, there is no phase transition, no spontaneous symmetry breaking. The LCD for the Ising model is 2, so in 1 dimension, we will not get a phase transition, and MFT will give the wrong result.

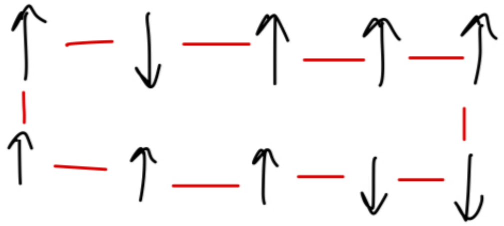
5.7.4 1-D Ising Model

Let us prove that spontaneous symmetry breaking in the 1D case is impossible.

First, let us think about the 2D case. We have two symmetry-broken states, how does the system pick which one? 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.

Let us attempt to solve the Ising model in 1 dimension, 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. The argument is that in the thermodynamic limit, the chain becomes very large, and the details of the boundary condition do not matter.



Our first mathematical trick is to focus on the links between the spins, rather than the spins themselves. We have that

$$H = H_0 - H\sigma$$
$$H_0 = \sum_{\langle i,i+1\rangle} J\sigma_i\sigma_{i+1}$$

Note that this trick only works in 1 dimension, since we cannot do the $\langle i, i+1 \rangle$ trick when we have more neighbors.

Let us first work with $h = 0$. We do this because we could carry the h term all the way across, but its just a pain. Let us consider

$$e^{-\beta H_0} = \exp\left[-\beta J\left(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_4 \ldots \sigma_{N-1}\sigma_N + \sigma_N\sigma_1\right)\right]$$

Now let us write this as a product of exponentials:

$$e^{-\beta H_0} = \exp\left[-\beta J\sigma_1\sigma_2\right]\exp\left[-\beta J\sigma_2\sigma_3\right]\ldots\exp\left[-\beta J\sigma_N\sigma_1\right]$$

Now let us consider what $\exp\left[-\beta J\sigma_1\sigma_2\right]$ looks like. If we know what σ_1 and σ_2 are, then this is a number, but if we don't, there are 4 possibilities for $\sigma_1\sigma_2$. Thus, we think about this as a matrix, the transfer matrix t_{12}:

$$t_{12} = \begin{bmatrix} e^{-\beta J} & e^{\beta J} \\ e^{\beta J} & e^{-\beta J} \end{bmatrix}$$

We see that if we look at the first two terms in the product, we are multiplying matrices, $A_{ij}B_{jk} = (AB)_{ik}$. Note that we can think of this in braket notation, $T_{\sigma_1\sigma_2} = \langle\sigma_1|t|\sigma_2\rangle$. Let us now look at the partition function:

$$\begin{aligned} Z\left(\beta\right) &= \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} e^{-\beta H} \\ &= \sum_{\sigma_1\ldots\sigma_N} \langle\sigma_1|t|\sigma_2\rangle\langle\sigma_2|t|\sigma_3\rangle\ldots\langle\sigma_N|t|\sigma_1\rangle \end{aligned}$$

Let us now rewrite this:

$$Z(\beta) = \sum_{\sigma_1}\langle\sigma_1|\,t\sum_{\sigma_2}|\sigma_2\rangle\langle\sigma_2|\,t\sum_{\sigma_3}|\sigma_3\rangle\langle\sigma_3|\,t\cdots\sum_{\sigma_N}|\sigma_N\rangle\langle\sigma_N|\,t\,|\sigma_1\rangle$$

We have done the opposite of what we normally do, we have extracted the identity, rather than inserting it.

$$\begin{aligned} Z(\beta) &= \sum_{\sigma_1}\langle\sigma_1|t^N|\sigma_1\rangle \\ &= \mathrm{Tr}\left[T^N\left(\beta\right)\right] \end{aligned}$$

Now let us reinsert the external field, which changes the transfer matrix:

$$t = \begin{bmatrix} e^{-\beta J}e^{-\beta h} & e^{\beta J} \\ e^{\beta J} & e^{-\beta J}e^{-\beta h} \end{bmatrix}$$

We can diagonalize this in order to get something that is easy to exponentiate:

$$Z\left(\beta, h\right) = \lambda_+^N + \lambda_-^N$$

Where λ_+ and λ_- are the eigenvalues of t.

Suppose we wanted to know the average value of a spin. First, we note that if we differentiate $e^{-\beta\left(H_0-h\sum\sigma_i\right)}$ with respect to h, we pull the σ down and we get exactly what we need for computing the average value:

$$\langle\sigma\rangle=-\frac{1}{N}\frac{\partial\log Z}{\partial h}$$

When we go through the math for this, we find that

$$\langle\sigma\rangle=\frac{\sinh\left(\beta h\right)}{\sqrt{\cosh^2\left(\beta h\right)-2e^{-2\beta J}\sinh\left(2\beta h\right)}}$$

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, there is a caveat, the case where $T\to 0$. In this case, $\beta\to\infty$, and we have that :

$$\langle\sigma\rangle\to\lim_{\beta\to\infty,h\to 0}\tanh\left(\beta h\right)$$

We have a double limit, but we take $h\to 0$ before we increase the temperature. If we do this, we see that if $h>0$, we have $+1$, and if we have $h<0$, we have -1. We get spontaneous symmetry breaking only if the temperature is exactly 0.

This should be intuitively obvious, if we have a section of the chain that is more up than down, but capped with a down spin. This section of the chain cannot propagate its information, and the same argument holds for the case where we take into account more neighbors. The only time we have the symmetry-broken states is if we start with all the spins up or down in the first place, which is if $T=0$.

In general, what do the critical exponents depend on? They will depend on things like the dimension of space, the symmetry of the problem, and the nature of the order parameter (is it a vector, etc).

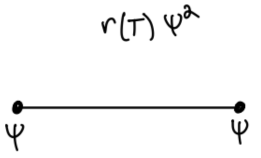
5.7.5 The Renormalization Group

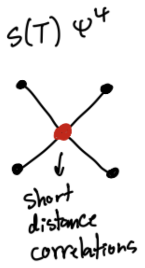
When we think about what we did with Ginsburg-Landau theory, the correlation lengths approach infinity. The information about the microscopic parts of the system is encoded in the parameters. If we change the scale at which we are looking at the system, how do the parameters change? The way the coefficients change as we change the scale at which we are loking at the problem, is the renormalization group approach. We can do an expansion in the number of spatial dimensions (which sounds insane), but if we keep enough terms, we can get the correct critical exponents for dimensionalities that were lower than the upper critical dimension. This was one of the most important developments in statistical mechanics in the mid to late twentieth century.

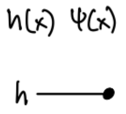
Let us attempt to motivate the renormalization group. Consider the free energy density:

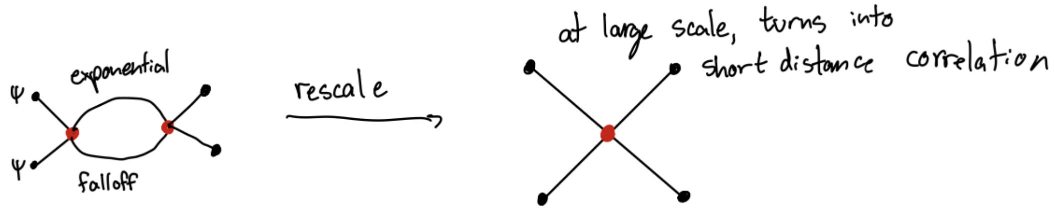
$$r\left(T\right)\psi^2+s\left(T\right)\psi^4+h\left(x\right)\psi\left(x\right)+f\left(T\right)\mid\nabla\psi\mid^2$$

We can represent these terms graphically, using a cousin to Feynman diagrams:









The argument is that we can rescale these diagrams, and note that whether we consider things to be long or short distance varies as we scale. Thus, we can change the coefficients of the theory by rescaling, and that is the essence of the renormalization group.

Why does this rescaling make a difference?

Suppose we could compute the ratio between the case where we consider it to be a long range interaction and the case where we consider it to be a short range interaction. This ratio could either be ∞, finite, or 0. If the ratio goes to ∞, we have a failure of MFT, since the long range corrections are going to ∞. If the ratio goes to 0 as the scale gets big, then MFT works. If it is finite, MFT sort of works, but we will get logarithmic corrections. We claim that this analysis explains why the success of MFT depends on the dimensionality of the space. This is because when we draw our diagrams, we are integrating, which is dependent on the dimensionality of the space.

If we formulate this mathematically, we can get significant insights. One amazing result is that the critical exponents are not independent. Due to scaling, the following can be deduced:

$$\alpha + 2\beta + \gamma - 2 = 0$$
$$\frac{2-\alpha}{d} - \nu = 0$$

The behavior of the second relation is true for the dimension $d \leq 4$. This makes sense, as ν is related to the correlation length.

5.7.6 First Order Phase Transitions

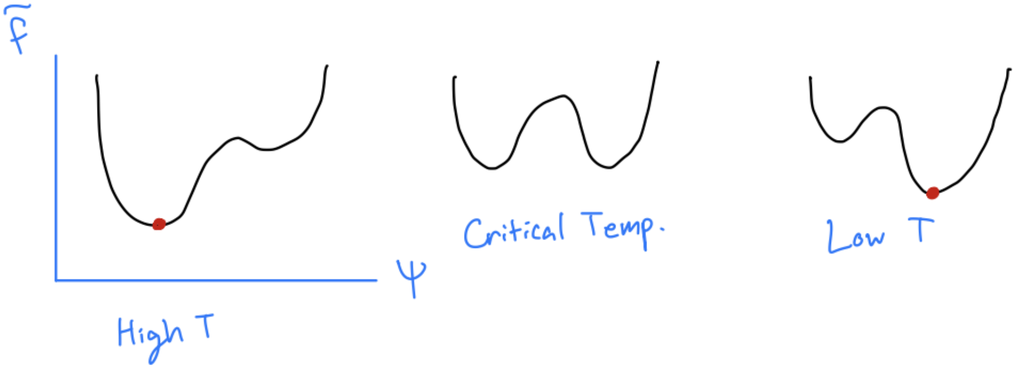
When we introduced second order phase transitions, we were working with spin systems. These are still possible when we allow particles to move, but instead of using the free energy density, we use the thermodynamic potential. Let us look at first order transitions using the same spin system scheme, since we don't have to worry about pressure or chemical potential. However, it is easy to generalize.

Let us introduce the free energy as a function of the order parameter. Let us say that we have some relevant order parameter, 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.

Another feature of the second order case is that everything is local in the order parameter phase, as we transition between phases, the change in the order parameter is smooth, not continuous, but smooth.

What happens in the first order case?

We claim that it looks like this:



In the second order case, we can tell when we are about to cross phases, since the correlation lengths will increase. However, in the first order case, we don't actually know that there is a phase transition, even though there is a new global minima.

At high temperatures, we have that u is large, and s is large, and at low temperatures, we have that u is small, and s is small. This means that not only is the free energy density discontinuous, the energy density is as well. This means that we have a latent heat, we get to the temperature of the transition, but we have to keep putting energy into the system before the temperature can continue rising.

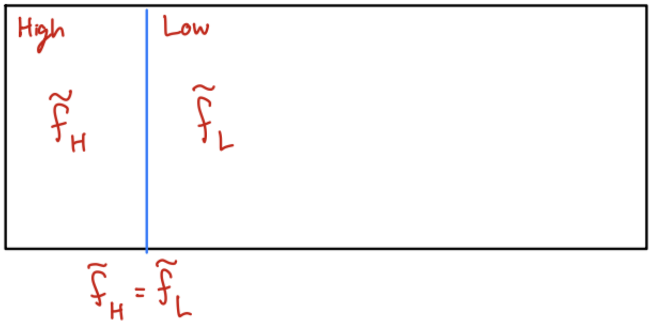
At the critical temperature:

$$u_H - T_C s_H = u_L - T_C s_L$$

The free energies are equal at both minima. The latent heat is defined as $u_H - u_L$, which gives us the relation:

$$u_H - u_L = T_C s_H - s_L$$

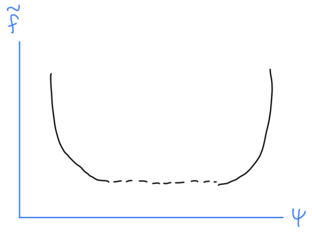
What phase are we in when we first reach the phase transition? When we enter and leave, we are all in one phase, but what about in between? This is where our assumption of homogeneity breaks down, we are in both phases at once:

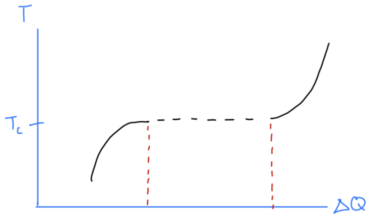


Consider the boundary between the two phases. This won't be exactly a straight line, there will be some interpolation between the two phases. There will be a surface tension along the boundary. We will want to minimize the surface tension across the boundary, which means we minimize the area. Why are we allowed to ignore the surface? Because the boundary is small compared to the bulk, the volume of the box goes as L^3, while the boundary area goes as L^2, and thus is irrelevant in the thermodynamic limit:

$$\frac{\tilde{f}_{\text{interface}}}{\tilde{f}_{\text{bulk}}} \sim \frac{1}{L}$$

In reality however, the theoretical plots that we drew assuming homogeneity are not correct, in reality, we have something that looks like these:





We can see clearly in the second plot the latent heat of the transition.

Recall that we have the relationship

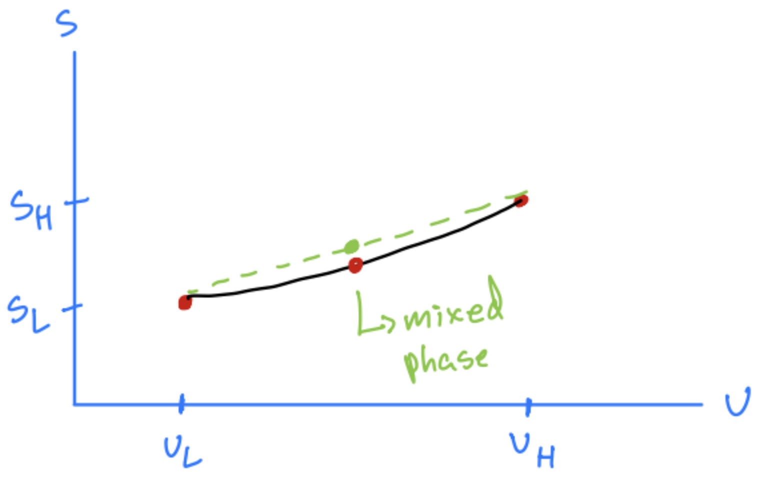
$$\frac{\partial s}{\partial u} = \frac{1}{T}$$

s is maximized at fixed u, and we claim that

$$\frac{\partial^2 s}{\partial u^2} \leq 0$$

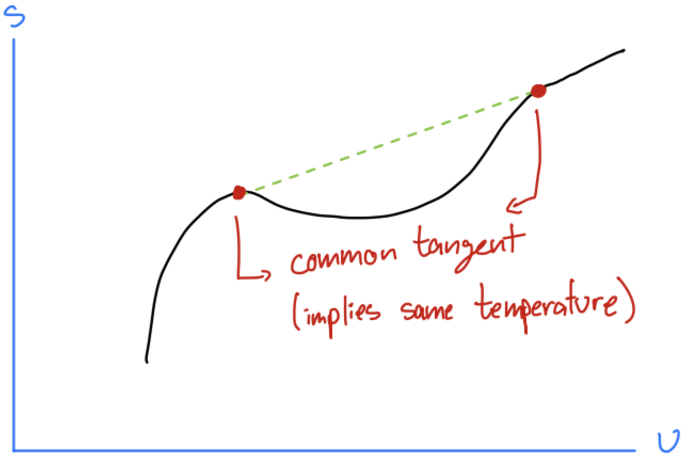
We claim that this must be true because if not, the system will gain entropy by dividing.

Suppose we are given that $s(u)$ looks like this:



For the mixed phase, it is entropically favorable for the system to take the point along the straight line between the two points, rather than along the curve, by breaking the system into two pieces.

Now consider the following case:

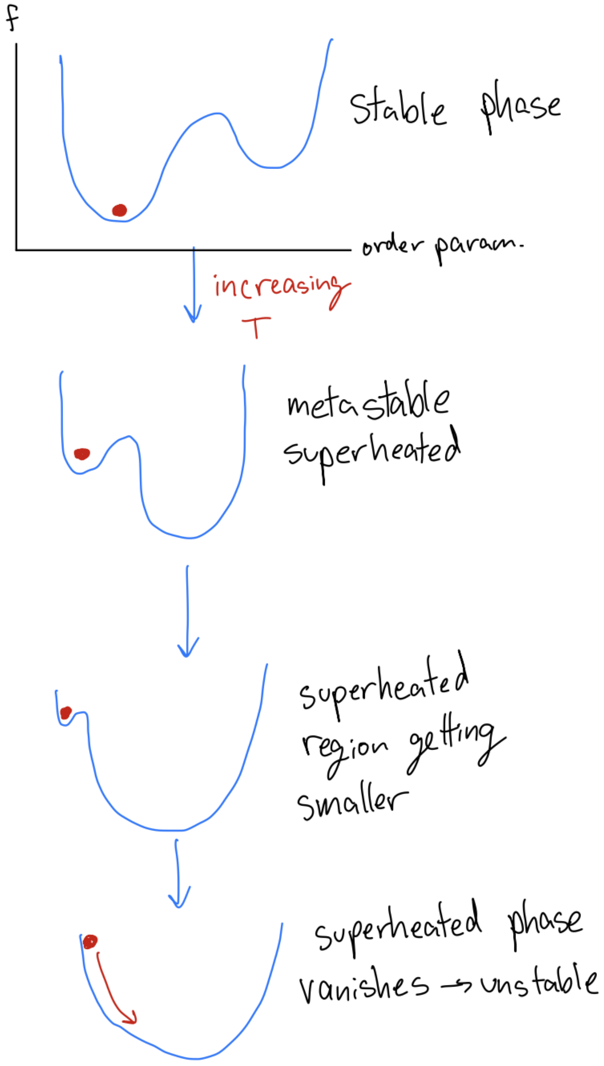


We see that we have a common tangent, and since the temperature is the derivative, they share the same temperature. Anywhere in between these two points, it is entropically favorable to split the system.

A situation is metastable if it is globally favorable to go into a mixed phase, but there are no local fluctuations that can allow the system to go into the mixed phase. The top metastable point is supercooling, we have cooled the system past the metastable point, but the system has not shifted phases yet. The bottom metastable point is the superheating point, we heat the system past the phase transition. Note that the metastable region is given from the supercooling point to the inflection point, and similarly for the superheating point and the inflection point. Past the inflection point, the system becomes locally unstable, so small fluctuations will drive us into the mixed phase.

Now consider the x-intercept of the tangent line. We claim that this will get us the free energy density at the critical point.

Also note that the locally unstable region past both metastable points are not experimentally obtainable, any fluctuation will allow us to get a more entropically favorable state.



What happens when we have a "bubble" of a certain phase that nucleates? The bubble can either shrink or grow, and that depends on the surface tension, σ. This is the free energy per unit area at the interface. Note that we assume that this is the only relevant term, the interface will be more complicated than just a sharp boundary, but for now let us assume that it is sharp. We have two phases, phase 1, with free energy f_1, and phase 2, with free energy f_2, with $f_1 \neq f_2$ (if $f_1 = f_2$, then we're at the phase transition and we're not superheated or supercooled). Let us say that $f_2 < f_1$, and the system is in phase 1, we are in a metastable state. We have two essential parameters that govern the behavior of this system. The first is σ, and the second is $\Delta f_B = f_1 - f_2$. This is a bulk free energy.

What happens if a small bubble of phase 2 forms? What is the free energy of the bubble? It depends on s, Δf_B, R (the size of the bubble), and the shape of the bubble (since that messes with the surface area to volume ratio).

Assume there are some dynamics, and the bubble forms a sphere shape (it has the best surface area to volume ratio, that's why bubbles are bubble shaped). What is the total free energy of the bubble ΔF, relative to the system remaining in phase 1?

$$\Delta f = -V\Delta f_B + A\sigma$$

Where V is the volume of the bubble. and A is the surface area. Given our assumptions:

$$\Delta f = -\frac{4\pi}{3}R^3\Delta f_B + 4\pi R^2\sigma$$

Now to find the critical bubble size, we just take a derivative:

$$\frac{d\Delta F}{dR} = 0$$

What we find is that

$$0 = 4\pi\left(2\sigma R - R^3\Delta f_B\right)$$

Which gives us that

$$R_{\text{crit}} = \frac{2\sigma}{\Delta f_B}$$

Anytime we have a bubble bigger than this, it will grow. Anything smaller than this will shrink.

Note that the production of these bubbles comes from random fluctuations in the system. For example, given a room, there is a possibility that all the oxygen molecules in the room will suddenly shift and be packed into one corner of the room. This probability is so vanishingly small that we never worry about it, but it is still possible. Similarly, large bubbles can be formed via the result of fluctuations in our systems, but what matters is the probability at which they occur, and by extension the time scale for how long you would have to wait for a bubble above the critical size to occur. For this reason, we can have metastable systems that do not transition phases for long periods of time, simply due to the fact that the critical size for bubbles is much larger than the fluctuations in the system, and thus it will take extremely long periods of time for the system to shift phases. Some examples include glass, as well as nitroglycerin (liquid until you give it a strong fluctuation, after which it reacts…violently).