

Statistical Physics

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Fundamentals of statistical mechanics

Microcanonical ensemble. Entropy, temperature and pressure. Laws of thermodynamics. Example of paramagnetism. Boltzmann distribution and canonical ensemble. Partition function. Free energy. Specific heats. Chemical Potential. Grand Canonical Ensemble. [5]

Classical gases

Density of states and the classical limit. Ideal gas. Maxwell distribution. Equipartition of energy. Diatomic gas. Interacting gases. Virial expansion. Van der Waals equation of state. Basic kinetic theory. [3]

Quantum gases

Density of states. Planck distribution and black body radiation. Debye model of phonons in solids. Bose-Einstein distribution. Ideal Bose gas and Bose-Einstein condensation. Fermi-Dirac distribution. Ideal Fermi gas. Pauli paramagnetism. [8]

Thermodynamics

Thermodynamic temperature scale. Heat and work. Carnot cycle. Applications of laws of thermodynamics. Thermodynamic potentials. Maxwell relations. [4]

Phase transitions

Liquid-gas transitions. Critical point and critical exponents. Ising model. Mean field theory. First and second order phase transitions. Symmetries and order parameters. [4]

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Properties	Microcanonical Ensemble	Canonical Ensemble	Grand Canonical Ensemble
Partition Function $Z = \sum Z_n$	/	$Z = \sum_n e^{-\beta E_n}$	$Z = \sum_n e^{-\beta(E_n - \mu N_n)}$
Probability	$\frac{1}{\Omega(E)}$	$p = \frac{Z_n}{Z}$	$p = \frac{Z_n}{Z}$
Energy	E	$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z = \sum_n \frac{E_n e^{-\beta E_n}}{Z}$	$\langle E \rangle = -\frac{\partial}{\partial \beta} \log Z + \frac{\mu}{\beta} \frac{\partial}{\partial \mu} \log Z$
Change in Energy	0	$(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2} \log Z = k_B T^2 C_V$	$\langle E^2 \rangle - \langle E \rangle^2$
Number of Particles	N	N	$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z$
Change in N	0	0	$\Delta N^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \log Z$
Entropy ($S = -k_B \sum_n p(n) \log p(n)$)	$S = k_B \log \Omega(E)$	$S = k_B \frac{\partial}{\partial T} (T \log Z) = -\frac{\partial F}{\partial T} _V$	$S = k_B \frac{\partial}{\partial T} (T \log Z)$
Temperature	$\frac{1}{T} = \frac{\partial S}{\partial E}$	Same as left	Same as left
Heat Capacity C, C_V, C_p	$C = \frac{\partial E}{\partial T}, C_V = \frac{\partial E}{\partial T} _V, C_p = \frac{\partial E}{\partial T} _p$	Same as left	Same as left
Pressure	$p = T \frac{\partial S}{\partial V}$	$p = T \frac{\partial S}{\partial V} = -\frac{\partial F}{\partial V} _T$	$p = T \frac{\partial S}{\partial V} = -\frac{\partial F}{\partial V} _{T,N}$
Helmoltz Free Energy	/	$F = E - TS = -k_B T \log Z$	$F = E - TS$
Gibbs Free Energy	/	$G = F + pV$	$G = F + pV$
First law of Thermodynamics	$dE = 0$	$dE = TdS - pdV$	$dE = TdS - pdV + \mu dN$

0.1 Introduction

Sorry guys, I had to get all the definitions out of the way, and that was what we were essentially doing for the first part of this course. Just a few more twirks:

0.2 Grand Canonical Potential

We define $\Phi = E - TS - \mu N = F - \mu N$ as the grand canonical potential. It is defined like this so that

$$\Phi = - \left(\frac{\partial \log Z}{\partial \beta} \right)_{\mu, V} - kT \frac{\partial}{\partial T} (\log Z)_{\mu, V} = -kT \log Z$$

So $Z = e^{-\beta\Phi}$.

0.3 Extensive and Intensive Quantities

Definition. An *extensive quantity* is one that scales proportionally to the size of the system. An *intensive quantity* is independent of the size of the system.

Now $F = E - TS$ is extensive so $F(T, \lambda V, \lambda N) = \lambda F(T, V, N)$. Similarly Φ is extensive so $\Phi(T, \lambda V, \mu) = \lambda \Phi(T, V, \mu)$.

We differentiate the second equation with respect to λ to reach:

$$\Phi(T, V, \mu) = V \frac{\partial \Phi}{\partial V}(T, V, \mu) = -pV$$

1 Classical Gases

1.1 The Classical Partition Function

Classically we can specify the states of the system by a point in phase space, the space of positions and momentum. This creates an equivalence between integral over phase space and summing over states.

For a single particle, we have the energy/hamiltonian as $h = \frac{\mathbf{p}^2}{2m} + V(\mathbf{q})$ where \mathbf{q} is the position. This motivates the single particle partition function:

$$Z_1 = \frac{1}{h^3} \int d^3\mathbf{q} d^3\mathbf{p} e^{-\beta H(\mathbf{p}, \mathbf{q})}$$

1.2 Ideal Gas

We have N particles in volume V . We assume the gas is made up of ideal non-interacting particles and thus they have no internal structure. Thus $H = \frac{p^2}{2m}$.

$$\begin{aligned} Z_1(V, T) &= \frac{1}{(2\pi\hbar)^3} \int d^3p d^3q e^{-\beta p^2/2m} \\ &= \frac{V}{(2\pi\hbar)^3} \int d^3p e^{-\beta p^2/2m} \\ &= V \left(\frac{mkT}{2\pi\hbar^2} \right) = \frac{V}{\lambda^3} \end{aligned}$$

where $\lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}}$, the thermal de Broglie wavelength. For N particles, we thus have:

$$Z = Z_1^N$$

And thus we have:

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{\partial}{\partial V} (kT \log Z)_T = \frac{NkT}{V}$$

1.2.1 Equipartition of Energy

$$\langle E \rangle = - \left(\frac{\partial \log Z}{\partial \beta} \right)_V = \frac{3}{2} NkT = 3N \left(\frac{1}{2} kT \right)$$

So each degree of freedom of gas has $\frac{1}{2}kT$. The heat capacity is $C_v = \left(\frac{\partial E}{\partial T} \right) = \frac{3}{2} Nk$.

1.2.2 Entropy

$Z = Z_1^N$ is not right! We overcounted because each particle is indistinguishable, so we really need to divide by $N!$. If we do, we have entropy:

$$S = Nk \left[\log \left(\frac{V}{N\lambda^3} \right) + \frac{5}{2} \right]$$

Which scales correctly as an extensive quantity. But if we do not include the $N!$, which is the classical way of doing it, the entropy is non-extensive! This is the classical *Gibbs' Paradox*.

1.3 Grand Canonical Ensemble

Therefore the grand canonical ensemble has:

$$\mathbb{Z} = \sum e^{\beta\mu N} Z = \sum \frac{1}{N!} \left(\frac{e^{\beta\mu V}}{\lambda^3} \right)^N = e^{\frac{e^{\beta\mu V}}{\lambda^3}}$$

The average number of particles is:

$$N = \frac{1}{\beta} \left(\frac{\partial \log \mathbb{Z}}{\partial \mu} \right)_{V, T} = \frac{e^{\beta\mu V}}{\lambda^3}$$

So we get that $\mu = kT \log \frac{\lambda^3 N}{V}$. Since for a classical gas, the de broglie wavelength λ is much smaller than the interparticle spacing $\frac{V}{N}^{\frac{1}{3}}$, the chemical potential is negative. now we have

$$\Delta N^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \log Z = N$$

So the fluctuations doesn't matter if we have a lot of particles. Now recall $\Phi = -kT \log Z$, and $pV = -\Phi$. This means that $pV = kT \frac{e^{\beta \mu} V}{\lambda^3} = NkT$.

1.4 Maxwell Distribution

What is the distribution of particle speeds in a gas? Probability of a given particle being in a region of phase space of volume $d^3q d^3p$ centered on (q, p) is $C d^3p d^3q e^{-\frac{\beta p^2}{2m}}$. The probability that the momentum is within d^3p of f is:

$$C V d^3p e^{-\frac{\beta p^2}{2m}} = C V m^3 \sin \theta d\theta d\phi v^2 dv e^{-\frac{mv^2}{2kT}}$$

We integrate over θ, ϕ and get that:

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}}$$

This is teh famous *Maxwell Distribution*

1.5 Diatomic Gas

We model a diatomic molecule as 2 point masses attached by a massless spring. [As you can see, physics is but increasingly more complicated harmonic oscillators] The motion of molecule can be decomposed into three types:

- The translation of the center of mass.
- Rotations about center of mass.
- Vibrations along axis of symmetry.

We assume these are independent. The partition function is:

$$Z_1 = Z_{trans} Z_{vib} Z_{rot}$$

And we know that $Z_{trans} \propto (kT)^{\frac{3}{2}}$ from above. So we focus on rotations and vibrations.

1.5.1 Rotations

We put our molecule in the polar coordinates. :

$$L_{rot} = \frac{I}{2} (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2)$$

The momenta is $|p_\theta = \frac{\partial L}{\partial \dot{\theta}} = I\dot{\theta}$ and $p_\phi = I \sin^2 \theta \dot{\phi}$, so the hamiltonian is:

$$H_{rot} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta}$$

Now thus:

$$Z_{rot} = \frac{1}{(2\pi\hbar)^2} \int d\theta d\phi dp_\theta dp_\phi e^{-\beta H_{rot}} = \frac{2IkT}{\hbar^2}$$

Thus $E_{rot} = kT$. And thus if vibrations are negligible then:

$$Z_1 \propto (kT)^{\frac{5}{2}} \quad E = \frac{5}{2}NkT \quad C_v = \frac{5}{2}Nk$$

1.5.2 Vibrations

We treat this as a harmonic oscillator, with mass m and frequency ω . If we write s as the displacement from equilibrium, then:

$$H_{vib} = \frac{p_s^2}{2m} + \frac{1}{2}m\omega^2 s^2$$

$$\text{So } Z_{vib} = \frac{1}{2\pi\hbar} \int dS dp + s e^{-\beta H_{vib}} = \frac{kT}{\hbar\omega}$$

So if we consider the total amount of energy, we have:

$$E = \frac{7}{2}NkT \quad C_v = \frac{7}{2}Nk$$

The experiment for H_2 showed that this prediction worked only for 2,000K and above. For temperatures between 200K and 2,000K, vibrations freeze out, and below 200K, rotations freeze out. Why? This is because of quantization of energy (which was only discovered in the 20th Century).

1.6 Interacting Gas

For real gases, particles do interact: it is just that their interactions are negligible when $\frac{N}{V}$ is small. So we expand:

$$\frac{p}{kT} = \frac{N}{V} + B_2(T) \frac{N^2}{V^2} + B_3(T) \frac{N^3}{V^3} + \dots$$

Now we want to know these interaction terms, and thus we look at the potential energy between two neutral atoms.

Larger r In this situation, since p_1 has an electric field $E \propto \frac{p_1}{r^3}$, and this induces a dipole in atom 2, $p_2 \propto E$. This gives a potential energy $\propto -p_2 E \propto -\frac{1}{r^6}$. This is the *Van der Waals interaction*.

Small r There is a huge repulsion force coming from the the Pauli exclusion principle. We will use the *hardcore* potential:

$$U(r) = \begin{cases} \infty & r < r_0 \\ -u_o(\frac{r_0}{r})^6 & r > r_0 \end{cases}$$

The Hamiltonian of the gas is:

$$H = \sum \frac{p_i^2}{2m} + \sum_{i>j} U(r_{ij})$$

Therefore, the partition function is:

$$\begin{aligned} Z(N, V, T) &= \frac{1}{N!(2\pi\hbar)^{3N}} \int \prod_{i=1}^N d^3p_i d^3r_i e^{-\beta H} \\ &= \frac{1}{N!(2\pi\hbar)^{3N}} \int \prod_{i=1}^N d^3p_i e^{-\beta p_i^2/2m} \int d^3r_i e^{-\beta \sum_{j<k} u(r_{jk})} \\ &= \frac{1}{N!\lambda^{3N}} \int \prod d^3r_i e^{-\beta \sum_{j<k} U(r_{jk})} \end{aligned}$$

Now we define the Mayer f -function as $f(r) = e^{-\beta U(r)} - 1$. Then letting $f_{ij} = f(r_{ij})$ we have:

$$Z = \frac{1}{N!\lambda^{3N}} \int \prod d^3r_i \prod_{j<k} (1+f_{jk}) = \frac{1}{N!\lambda^{3N}} \int \prod d^3r_i (1 + \sum_{j<k} f_{jk} + \sum_{j<k} \sum_{l<m} f_{jk} f_{lm})$$

The first term is just V^N . Each of the second term is the same, and is $V^{N-1} I$. The sum gives $\frac{1}{2}N(N-1) \approx \frac{1}{2}N^2$ terms like this, so:

$$\begin{aligned} Z &= \frac{V^N}{N!\lambda^{3N}} (1 + \frac{N^2}{2V} I + \dots) \\ &\approx \frac{V^N}{N!\lambda^{3N}} (1 + \frac{N}{2V} I + \dots)^N \\ &= Z_{ideal} (1 + \frac{N}{2V} I + \dots)^N \end{aligned}$$

Therefore, $F = F_{ideal} - NkT \log(1 + \frac{N}{2V} I + \dots)$. Now we want to expand the log. This expansion is valid when $\frac{NI}{2V} \ll 1$. As $I \propto r_0^3$, where r_0 is the radius of an atom, this is valid when:

$$\frac{N}{V} < \frac{1}{r_0^3}$$

Or when the density of the gas is much less the density of the atom, which means we need to assume it is a gas.

Thus

$$p = \frac{NkT}{V} (1 - \frac{NI}{2V})$$

So $B_2(T) = -\frac{1}{2}I$. For the hardcore repulsion,:

$$\begin{aligned} I &= \int_0^{r_0} d^3r (-1) + \int_{r_0}^{\infty} d^3r (e^{\beta u_0(r_0/r)^6} - 1) \\ &\approx -\frac{4}{3}\pi r_0^3 + \frac{4\pi u_0}{kT} \int_{r_0}^{\infty} dr \frac{r_0^6}{r^4} = \frac{4\pi r_0^3}{3} \left(\frac{u_0}{kT} - 1 \right) \end{aligned}$$

Here we use the high temperature limit $\beta u_0 \ll 1$ and expanded the exponential to its first order. Thus:

$$\frac{pV}{NkT} \approx 1 - \frac{N}{V} \left(\frac{a}{kT} - b \right)$$

where $a = \frac{2\pi r_0^3 u_0}{3}$, and $B = \frac{2\pi r_0^3}{3}$. Then:

$$p = \frac{NkT}{V - bN} - a \frac{N^2}{V^2}$$

The second term is due to the long-distance attractive force, and the reduced denominator is due to the fact that we are modeling the particles as hard sphere, so the actual volume is $V - bN$, at least heuristically. Why is the excluded volume half of the volume of the actual sphere? Denote Ω as the volume of one atom, then the total configuration space volume available to N atoms is:

$$\frac{1}{N!} V(V - \Omega)(V - 2\Omega) \dots \approx \frac{1}{N!} V^N \left(1 - \frac{N\Omega}{V} + \dots\right) = \frac{1}{N!} \left(V - \frac{N\Omega}{2}\right)^N$$

And that is where the half comes from.

2 Quantum Gases

2.1 Density of States

Consider ideal gas in cubic box with sides of length L , so $V = L^3$.

Consider single particle wavefunctions $\psi(x) = \frac{1}{\sqrt{V}} e^{ik \cdot x}$, $k_i = \frac{2\pi n_i}{L}$. The one particle energy is $E_n = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2 \hbar^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$. The one particle partition function is:

$$Z_1 = \sum_n e^{-\beta E_n} \quad \beta E_n \sim \frac{\lambda^2}{L^2} n^2 \quad \lambda = \sqrt{\frac{2\pi \hbar^2}{mkT}}$$

Now for $\lambda \ll L$, we have very small gaps between energy levels, so we approximately sum by an integral:

$$\sum_n \approx \int d^3 n = \frac{V}{(2\pi)^3} \int d^3 k = \frac{4\pi V}{(2\pi)^3} \int_0^\infty dk k^2$$

We change variables to $E = \frac{\hbar^2 k^2}{2m}$. Then:

$$\sum \approx \frac{4\pi V}{(2\pi)^3} \int_0^\infty \left(\frac{m^2}{\hbar^2} dE\right) \sqrt{\frac{2mE}{\hbar^2}} = \int_0^\infty dE g(E)$$

where $g(E) = \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$. The relation between E and k is called a dispersion relation. For a relativistic particle, $E = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$, and we can write $g(E) = \frac{VE}{2\pi^3 \hbar^3 c^3} \sqrt{E^2 - m^2 c^4}$. And for massless particles:

$$g(E) = \frac{VE^2}{2\pi^2 \hbar^3 c^3}$$

Note. On the test, if a dispersion-type relation is given, such as $E = h\sqrt{k}$ where $|k| \propto \sqrt{n_1^2 + n_2^2 + n_3^2}$ or in terms of ω , try the following methods:

- Write $\sum_n \approx \int d^3 n$, work out a relationship between n_i and k_i , and then k_i with k , and then k with E .
- If the relationship is hard to find, or k is not even in the question, as in a harmonic oscillator, find out how many states are there below a fixed energy level E through integral approximation. Then take the derivative.

2.2 Photons

A gas of photons in equilibrium at time T in a box with an infinitesimally small hole is called *blackbody radiation*. Photons have $E = \hbar\omega$, $\omega = \frac{2\pi c}{\lambda} = kc$, and their interactions are negligible. We have two polarization states so the number of single photon states with frequency between w and $w + dw$ is $g(w)dw = \frac{Vw^2}{\pi^2 c^3} dw$.

Note. Note that photons are *not conserved*. There are absorbed/emitted by walls of box, so we must sum over all photon numbers even in canonical ensemble.

So how do we do this? Consider a system of non-interacting particles with 1-particle states $|i\rangle$ energies ϵ_i . We label $\{n_1, \dots\}$ as general accessible states with n_i is the number of particles in $|i\rangle$. Then the energy is $\sum n_i \epsilon_i$. The canonical ensemble now gives:

$$Z = \sum_{\{n_k\}} e^{-\beta \sum_j n_j \epsilon_j} = \prod_i \frac{1}{1 - e^{-\beta \epsilon_i}}$$

Thus for photons we have:

$$\log Z = -\frac{V}{\pi^2 c^3} \int_0^\infty dw w^2 \log(1 - e^{-\beta \hbar w})$$

Now the average number of particles in $|i\rangle$ is:

$$\langle n_i \rangle = \sum_{\{n_k\}} n_i p(\{n_k\}) = \sum_{\{n_k\}} \frac{n_i e^{-\beta \sum_j n_j \epsilon_j}}{Z} = \frac{1}{e^{\beta \epsilon_i} - 1}$$

Then $n(w)dw = \frac{g(w)dw}{e^{\beta \hbar w} - 1}$, So $E(w)dw = \frac{V \hbar}{\pi^2 c^3} \frac{w^3}{e^{\beta \hbar w} - 1} dw$. This is called Planck's distribution. Now set $x = \beta \hbar w$, then we have:

$$E = \frac{V(kT)^4}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{x^3 dx}{e^x - 1}$$

The energy density is then:

$$\mathbb{E} = \frac{\pi^2 k^4}{15 \hbar^3 c^3} T^4$$

Let $S(k)$ be the set of all photons with wavevector with angle θ with normal to hole. Photons in $S(k)$ reach hole within time dt have $\theta \in [0, \frac{\pi}{2}]$ and sweep out volume $c \cos \theta dt A$, where A is the area for the hole. And thus they are a fraction $\frac{c \cos \theta dt A}{V}$ of $S(k)$. Let $E(|k|)d^3k$ be the total energy in $S(k)$. The total energy leaving hole in time t is:

$$\int_0^{\frac{\pi}{2}} \frac{c \cos \theta}{V} dt A E(|\mathbf{k}|) = \frac{cA}{4V} dt E$$

The energy flux is energy per unit area leaving hole is thus $\frac{c}{4} \epsilon = \sigma T^4$, where σ is the Stefan-Boltzmann constant. This applies to *any* blackbody. We can calculate some other interesting quantities:

$$F = \frac{-V \pi^2 k^4}{45 \hbar^3 c^3} T^4 \quad p = \frac{4\sigma}{3c} T^4 \quad S = \frac{16V\sigma}{2c} T^3 \quad C_v = \frac{16V\sigma}{c} T^3$$

Now the classical limit is when $\hbar\omega \ll kT$ so $\frac{1}{e^{\beta\hbar\omega}-1} \approx \frac{1}{\beta\hbar\omega}$. Then:

$$E(w)dw \approx \frac{Vw^2}{\pi^2c^3}kTdw$$

which is the Rayleigh-Jones law. Equipartition of energy gives $\frac{1}{2}kT$ per degree of freedom, so:

$$H = \frac{p^2}{2m} + \frac{1}{2}mw^2q^2 = \frac{1}{2}kT + \frac{1}{2}kT = kT$$

2.3 Phonons and Debye Model

The vibrations of crystal lattice are sound waves in crystal. The phonon is the equivalent of photons for sound. The phonon energy is $\hbar\omega$ and the dispersion relation is investigated in the AQM course. For $|k|a \ll 1$, then $\omega \approx |k|c_s$, where c_s is the speed of sound. Now another difference with photons is that ω cannot be arbitrary large; there exists a minimum possible wavelength set by atomic spacing, and we call that frequency ω_D for Debye.

Phonons have 3 polarizations: 2 transverse ones where $c_s = c_T$ and 1 longitudinal, $c_s = c_L$. Then we can repeat the argument for photons are reach that for $|k|a \ll 1$:

$$g(w)dw = \frac{Vw^2}{2\pi^2} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) dw = \frac{3V\omega^2}{2\pi^2c_s^3} d\omega$$

where $\frac{3}{c_s^3} = \frac{2}{c_T^3} + \frac{1}{c_L^3}$. Now the Debye model assumes that the equation above is valid even is $|k|a \sim 1$. Now knowing the maximum frequency, the total number of states are:

$$\int_0^{\omega_D} g(w)dw = \frac{V\omega_D^2}{2\pi^2c_s^3}$$

We call each state a *normal mode*. Now we claim that:

Claim. There are $3N$ normal modes.

Proof. Let $\mathbf{X} = \begin{pmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \\ \dots \\ \mathbf{x}_n \end{pmatrix}$, where \mathbf{x}_i is the position of atom i . Then the Lagrangian is:

$$L = \frac{1}{2}m \cdot \dot{\mathbf{X}} - V(\mathbf{X})$$

Assume V is minimized at $\mathbf{X} = \mathbf{X}_0$. Let $\delta\mathbf{X} = \mathbf{X} - \mathbf{X}_0$. Then we have:

$$L = \frac{1}{2}m\delta\dot{\mathbf{X}}^2 - V_0 - \frac{1}{2}\delta\mathbf{X}^T V \delta\mathbf{X} + \dots$$

Now the equation of motion gives $m\delta\ddot{\mathbf{X}} = -V\delta\mathbf{X}$, and we use the ansatz of $\mathbf{X} = \Re(e^{-i\omega t}\mathbf{Q})$. Then we have:

$$V\mathbf{Q} = m\omega^2\mathbf{Q}$$

where V is a $3N \times 3N$ symmetric matrix, so V has $3N$ eigenvalues. □

Then the equality gives that:

$$\omega_D = \frac{6\pi^2 N^{\frac{1}{3}}}{V} \bar{c}_s$$

Define $T_D = \frac{\hbar\omega_D}{k}$ as the Debye temperature. The highest frequency phonons are existed for $T \gtrsim T_D$. Now We compute the partition function:

$$\log Z = - \int_0^{\omega_0} d\omega g(\omega) \log(1 - e^{-\beta\hbar\omega})$$

So we can calculate that:

$$E = \frac{3V(kT)^4}{2\pi^2(\hbar\bar{c}_s)^3} \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1}$$

In the high temperature limit, we can expand $\frac{x^3}{e^x - 1}$ to be about x^2 , and thus $E \approx \frac{3Vk^4T}{2\pi^3(\hbar\bar{c}_sT_0)^3}$ and so $E \propto T$ so $C_v = 3Nk$ is constant. This is called *Dulong-Petit law*. For low temperature, we replace the upper limit in integral by infinity and get that:

$$C_v = \frac{12Nk\pi^4}{5} \left(\frac{T}{T_D} \right)^3$$

And this also agrees with experiment, unlike the Einstein model in the first example sheet.

Note.

$$\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15} = \Gamma(3)\zeta(4)$$

This may seem surprising, but a substitution or $r = e^{-x}$ would bring you to the more familiar form of Riemann's zeta function.

Therefore, this works well for most solids (except metals, which have free electrons forming essentially another gas).

Wait, wait, wait. Didn't we make wrong assumptions from the start? This should work in low temperatures, because our assumptions are true in low frequency regions, but why is it true in high temperatures? This is because we used equipartition of energy! This ensures that the C_v flats out at high temperatures.

2.4 Quantum Ideal Gas

Previously we took a brute force $\frac{1}{N!}$ factor to account for the indistinguishability of states. But that is in fact not quite true!

Note. By now, you probably understand that the purpose of this course is to see how wrong humans are.

Let's assume we have bosons, and we have 2 particles. The possible states are $|i\rangle |i\rangle$ and $\frac{1}{\sqrt{2}}(|i\rangle |j\rangle + |j\rangle |i\rangle)$, So the partition function is:

$$Z = \sum e^{-\beta 2\epsilon_i} + \frac{1}{2} \sum_{i \neq j} e^{-\beta(\epsilon_i + \epsilon_j)}$$

But we also have:

$$\frac{Z_1^2}{2!} = \frac{1}{2} \sum e^{-\beta 2\epsilon_i} + \frac{1}{2} \sum_{i \neq j} e^{-\beta(\epsilon_i + \epsilon_j)}$$

See the difference? Therefore the $N!$ thing is only true if the probability of 2 particles occupying same state is negligible. This is true if $\langle n_i \rangle \ll 1$ for all i where n_i is the number of particles in $|i\rangle$. This is also true for fermions. But we know how to calculate $\langle n_i \rangle$:

$$\langle n_i \rangle = \frac{-1}{\beta} \frac{\partial \log Z}{\partial \epsilon_i} = \frac{N}{Z_1} e^{-\beta \epsilon_i} \ll 1$$

For monatomic gas, we have $Z_1 = \frac{V}{\lambda^3}$, so we need $\lambda \ll \left(\frac{V}{N}\right)^{\frac{1}{3}}$. This is same as the classical assumption, and it is true at high temperature.

2.4.1 Diatomic Gas

We repeat the same derivation *again*.

$$H = H_{trans} + H_{rot} + H_{vib} \quad Z_1 = Z_{trans} Z_{rot} Z_{vib}$$

2.4.1.1 Translation

The translation H is same as the classical derivation, so $Z_{trans} = \frac{V}{\lambda^3}$. Of course, we also need the $\lambda \ll \left(\frac{V}{N}\right)^{\frac{1}{3}}$ assumption here.

2.4.1.2 Rotation

From quantum mechanics, we know that $H_{rot} = \frac{J^2}{2I}$, where J is the angular momentum. It has energy levels $\hbar^2 j(j+1)$, with degeneracy $2j+1$. Thus, our partition function is:

$$Z_{rot} = \sum (2j+1) e^{-\beta \hbar^2 j(j+1)/2I}$$

When we have high temperatures ($kt \gg \frac{\hbar^2}{2I}$), we approximately have:

$$Z_{rot} \approx \int_0^\infty dx (2x+1) e^{-\beta \hbar^2 x(x+1)/2I} = \frac{2I}{\beta \hbar^2}$$

which is the classical result. But when we have low temperature, all modes except $j=0$ are unimportant, so $Z_{rot} \approx 1$. This is what we meant by the rotational modes "freezing out".

2.4.1.3 Vibrations

We can see H_{vib} as a harmonic oscillator, so $E_n = \hbar\omega(n + \frac{1}{2})$, thus:

$$Z_{vib} = \frac{1}{2 \sinh \frac{\beta \hbar \omega}{2}}$$

When we have high temperatures ($kT \gg \hbar\omega/2$), we have $Z_{vib} \approx \frac{1}{\beta \hbar \omega}$ and when we have low temperatures, $Z_{vib} \approx e^{-\beta \hbar \omega / 2}$, and $E_{vib} = \frac{\hbar \omega}{2}$. So this is independent of T and the vibrational modes "freeze out".

2.5 Bosons

Now what if the approximation $\lambda \ll \left(\frac{V}{N}\right)^{\frac{1}{3}}$ is not true here? If we still assume that there are no interactions between particles, then there is only one effect that is important: quantum statistics.

Bosons They have integer spin, and its state is symmetric with respect to the interchange of 2 particles.

Fermions They have integer $+\frac{1}{2}$ spin, and its state is antisymmetric wrt the interchange of 2 particles.

2.5.1 Bose-Einstein Distribution

For Bosons, we assume single particle states $|r\rangle$, energy \mathcal{E}_r , $n_r = \#$ of particles in $|r\rangle$. Then the particles are indistinguishable, so the state of the system is specified by $\{n_1, n_2, \dots\}$ with energy $\sum_r n_r \epsilon_r$. Evaluating this in canonical ensemble is hard, so we use the grand canonical ensemble instead. Now:

$$Z = \sum_{\{n_r\}} e^{-\beta \sum_s n_s (\epsilon_s - \mu)} = \prod_s Z_s$$

where $Z_s = \sum_{n_s=0}^{\infty} e^{-\beta(\epsilon_s - \mu)n_s} = \frac{1}{1 - e^{-\beta(\epsilon_s - \mu)}}$. For convergence we need $\mu < \epsilon_s$ for all s , so from the ground state energy we need $\mu < 0$. Then calculating $\langle n_r \rangle$ we have:

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

Which is the BE distribution. Now we define the fugacity as $z = e^{\beta\mu}$. For a monatomic non-relativistic particle, we have:

$$g(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E^{\frac{1}{2}}$$

And thus we have:

$$pV = \frac{1}{\beta} \log Z = -\frac{1}{\beta} \int_0^{\infty} dE g(E) \log(1 - ze^{-\beta E}) = \frac{2}{3} \int_0^{\infty} dE \frac{g(E)E}{z^{-1}e^{\beta E} - 1} = \frac{2}{3} E$$

Now we can't really obtain closed-forms of the integrals for N and E . In the high-temperature limit, we have:

$$\frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \int_0^{\infty} \frac{dE E^{\frac{1}{2}}}{z^{-1}e^{\beta E} - 1}$$

Taking $x = \beta E$:

$$\begin{aligned} &= \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{z}{\beta^{3/2}} \int_0^{\infty} dx \sqrt{x} e^{-x} (1 + ze^{-x} + o(z^2)) \\ &= \frac{z}{\lambda^3} \left(1 + \frac{z}{2\sqrt{2}} + O(z^2)\right) \end{aligned}$$

Thus to leading order $z = \frac{\lambda^3 N}{V}$. We assumed z is small, so and this condition is equivalent to the classical $\lambda \ll \left(\frac{V}{N}\right)^{\frac{1}{3}}$ assumption. Now we can similarly evaluate $\frac{E}{V}$:

$$\frac{E}{V} = \frac{3z}{2\lambda^3\beta} \left(1 + \frac{z}{4\sqrt{2}} + O(z^2)\right)$$

Now we can eliminate z using the $\frac{N}{V}$ relation to get that:

$$pV = \frac{2}{3}E = NkT \left(1 - \frac{1}{4\sqrt{2}} \frac{\lambda^3 N}{V} + O\left(\frac{\lambda^3 N^2}{V}\right)\right)$$

2.5.2 Bose-Einstein Condensation

Since at high temperature we have $z \rightarrow 0$, at low temperature, we guess that $z \rightarrow 1$. Then:

$$\frac{N}{V} = \frac{1}{4\pi^2} \left(\frac{2mkT}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{dx x^{\frac{1}{2}}}{z^{-1}e^x - 1} = \frac{1}{\lambda^3} g_{\frac{3}{2}}(z)$$

where

$$\begin{aligned} g_n(z) &= \frac{1}{\Gamma(n)} \int_0^\infty \frac{dx x^{n-1}}{z^{-1}e^x - 1} \\ &= \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{z x^{n-1} e^{-x}}{1 - z e^{-x}} \\ &= \frac{z}{\Gamma(n)} \int_0^\infty dx x^{n-1} e^{-x} \sum_{m=0}^\infty z^m e^{-mx} \\ &= \frac{1}{\Gamma(n)} \sum_{m=1}^\infty z^m \int_0^\infty dx x^{n-1} e^{-mx} \\ &= \frac{1}{\Gamma(n)} \sum_{m=1}^\infty \frac{z^m}{m^n} \int_0^\infty du u^{n-1} e^{-u} = \sum_{m=1}^\infty \frac{z^m}{m^n} \end{aligned}$$

Thus this is a monotonically increasing function of z , and thus $g_{3/2}(z) = \lambda^3 \frac{N}{V}$. As $\lambda \propto T^{-\frac{1}{2}}$ then if $T \downarrow$ so $g \uparrow$ so $z \uparrow$ so we reach $z = 1$ at some temperature $T = T_c$. Then since $g_n(1) = S(n)$ where S is the Riemann zeta function we have:

$$T_c = \frac{2\pi\hbar^2}{km} \left(\frac{N}{S(\frac{3}{2})V}\right)^{\frac{2}{3}}$$

So we have :

$$\frac{T_c}{T} = \left(\frac{\lambda^3 N}{S(\frac{3}{2})V}\right)^{\frac{2}{3}}$$

What happens if t is reduced below T_c ? Then we see that g is still increasing and since λ and V are constant, N must decrease! But this is non-sensical. The problem is with $\sum \approx \frac{V(2m)^{\frac{3}{2}}}{4\pi^2\hbar^2} \int_0^\infty dE E^{\frac{1}{2}}$, which the right hand side neglects the ground state. The number of particles in this state is $n_0 = \frac{z}{1-z}$ increases without bound as $z \rightarrow 1$.

Now redo calculation including that:

$$N = \frac{V}{\lambda^3} g_{3/2}(z) + \frac{z}{1-z}$$

Then we have:

$$\frac{n_0}{N} = 1 - \frac{V}{N\lambda^3} \zeta\left(\frac{3}{2}\right) = 1 - \frac{T}{T_c}^{\frac{3}{2}}$$

Now $pV = \frac{2}{3}E - \frac{1}{\beta} \log(1-z)$ from ground state and we can verify that:

$$\frac{E}{V} = \frac{3kT}{2\lambda^3} g_{5/2}(z)$$

And thus substituting in, and noting that $\log(1-Z)$ is of order $\log(N)$ for $1-Z \propto \frac{1}{N}$ while the first term $E \propto N$, we drop the ground state term and thus have:

$$p = \frac{kT}{\lambda^3} S\left(\frac{5}{2}\right) \propto T^{\frac{5}{2}}$$

using the energy formula we can also get that:

$$\frac{C_v}{V} = \frac{15k}{4\lambda^3} g_{5/2}(z) + \frac{3kT}{2\lambda^3} g'_{5/2}(z) \left(\frac{\partial z}{\partial T} \right)_{V,N}$$

Then for $T < T_c$, $z \approx 1$, so we have $\frac{C_v}{V} = \frac{15k}{4\lambda^3} S\left(\frac{5}{2}\right) \propto T^{\frac{3}{2}}$. For $T > T_c$, z is determined by $g_{3/2}(z)$. We investigate this as $z \rightarrow 1$.

Now $g'_{3/2}(z) = \frac{1}{2}g_{1/2}(z)$, and $g_{1/2}(z)$ diverges:

$$\begin{aligned} g_{1/2}(z) &= \frac{1}{\Gamma(\frac{1}{2})} \int_0^\epsilon \frac{x^{-1/2}}{z^{-1}(1+x) - 1} + \text{finite terms} \\ &= \frac{z}{\Gamma(\frac{1}{2})} \int_+^\epsilon 0 \frac{dx x^{-\frac{1}{2}}}{1-z+x} + \dots \\ &= \frac{2z}{\Gamma(\frac{1}{2})\sqrt{1-z}} \int_0^{\sqrt{1-z}} \frac{du}{1+u^2} + \dots \end{aligned}$$

Thus $g'_{3/2}(z) = \frac{\pi}{\Gamma(\frac{1}{2})\sqrt{1-z}} + \text{finite terms}$. Therefore we have $g_{3/2}(z) = g_{3/2}(1) + A\sqrt{1-z} + \dots$. Then inverting the equation above for $g_{3/2}(z)$, and noting that $g_{3/2}(z) = \frac{\lambda^3 N}{V}$ gives:

$$z \approx 1 - \frac{1}{A^2} \left(\zeta(3/2) - \frac{N\lambda^3}{V} \right)^2 = 1 - \frac{\zeta(3/2)^2}{A^2} \left(\frac{T}{T_c}^{\frac{3}{2}} - 1 \right)^2 \approx 1 - B \left(\frac{T - T_c}{T_c} \right)^2$$

Then substituting this into the equation we have for C_v , and throwing all the constants together:

$$C_v = \frac{15Vk}{4\lambda^3} g_{5/2}(z) - b \left(\frac{T - T_c}{T_c} \right)$$

2.6 Fermions

Now fermions obey the *Pauli Exclusion Principle*: no two fermions can stay in the same state. Then in the grand canonical ensemble, the partition function is easy: each state is either occupied or not. Thus, for each energy E_r , we have $Z_r = 1 + e^{-\beta(E_r - \mu)}$, and $Z = \prod Z_r$. Then we can compute the average number of particles in each state r as:

$$n_r = \frac{1}{e^{\beta(E_r - \mu)} + 1}$$

This is called the *Fermi-Dirac* distribution. Note the absence of convergence issues.

2.7 Ideal Fermi Gas

As fermions have half-integer spin, they have degeneracies when we are counting states: For a spin s fermion, the number of degeneracies are $g_s = 2s + 1$. Thus, the density of states become:

$$g(E) = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E^{\frac{1}{2}}$$

Going through the same procedure as the Bose-Einstein distribution, we have:

$$N = \int dE \frac{g(E)}{z^{-1}e^{\beta E} + 1} \quad E = \int dE \frac{Eg(E)}{z^{-1}e^{\beta E} + 1} \quad pV = \frac{2}{3}E$$

And for $z \ll 1$, we can find, through our old friend of Taylor expansion, that:

$$pV = NkT \left(1 + \frac{\lambda^3 N}{4\sqrt{2}g_s V} + \dots \right)$$

2.7.1 Fermi Gas at $T = 0$

At $T = 0$, unlike the Bose-Einstein distribution, fermions cannot collapse all into one state. They still have to successively fill out the lowest energy state, and the highest filled energy is called the *Fermi Energy*, $E_F = \mu$. To understand this, we see that at $T = 0$, we must have:

$$N = \int_0^{E_F} dE g(E) = \frac{g_s V}{6\pi^2} \left(9 \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} E_F^{\frac{3}{2}}$$

An inversion tells us:

$$E_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{g_s V} \right)^{\frac{2}{3}}$$

Similarly, we can see that $E = \frac{3}{5}NE_F$ and $pV = \frac{2}{5}NE_F$, so even at zero temperature, fermi gas exerts pressure, which is called *degeneracy pressure*.

2.7.2 Fermi Gas in low temperatures

Note. There is some hand-waving in this section.

To investigate low temperature dynamics, since we understand $T = 0$ well, it would be sensible to expand in derivatives of T and look at perturbations. To do this, we impose a condition $\frac{dN}{dT} = 0$, so that particles are conserved. We *claim* that this implies $\frac{d\mu}{dT}|_{T=0} = 0$, so we just take $\mu = E_F$. Then we expand $\frac{dN}{dT}$ explicitly:

$$\frac{dN}{dT} = \int_0^\infty dE g(E) \frac{d}{dT} \left(\frac{1}{e^{\beta(E-E_F)} + 1} \right) \approx g(E_F) \int_0^\infty dE \frac{\partial}{\partial T} \left(\frac{1}{e^{\beta(E-E_F)} + 1} \right)$$

Now what we did here is to assume that when temperatures are really low, only fermions with energy near $g(E_F)$ can participate in the physics, so we expanded the integral in the vicinity of E_F . Continuing doing this gives:

$$\frac{dN}{dT} \approx g(E_F) \int_0^\infty dE \left(\frac{E - E_F}{kT^2} \right) \frac{1}{4 \cosh^2(\beta(E - E_F)/2)} \approx 0$$

As $E - E_F$ is odd around E_F but \cosh is even. So we are *kind of* okay. Then we do the same thing to the heat capacity, this time including a term in the taylor expansion of E around E_F :

$$C_V \approx \int_0^\infty dE \left[E_F g(E_F) + \frac{3}{2} g(E_F) (E - E_F) \right] \frac{\partial}{\partial T} \left(\frac{1}{e^{\beta(E-E_F)} + 1} \right)$$

The first term in the bracket goes to 0 because of odd/even arguments, but the second term stays. Writing $x = \beta(E - E_F)$ we have:

$$C_V \approx \frac{3}{2} g(E_F) T \int_{-\infty}^\infty dx \frac{x^2}{4 \cosh^2(x/2)}$$

Thus $C_V \propto T$, which is actually correct. [This is quite surprising given how much handwaving we did]

2.8 Pauli Paramagnetism

We now try to describe a cloud of electrons in some background magnetic field. For this, each electron picks up an extra term $\mu_B s B$, where s is the spin of that particular electron, and $\mu_B = |e|\hbar/2mc$ is the Bohr Magneton. So:

$$\frac{N_\uparrow}{V} = \int_0^\infty \frac{E^{1/2}}{E^{\beta(E+\mu_B B-\mu)} + 1} = \frac{1}{\lambda^3} f_{3/2}(ze^{\beta\mu_B B})$$

$$\frac{N_\downarrow}{V} = \int_0^\infty \frac{E^{1/2}}{E^{\beta(E-\mu_B B+\mu)} + 1} = \frac{1}{\lambda^3} f_{3/2}(ze^{-\beta\mu_B B})$$

Where $f_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{z^{-1}e^x + 1}$. Now we are interested in calculating the *magnetization*, which is how energy responds to a magnetic field, or $m = \frac{\partial E}{\partial B}$. Then by the formula of $E = \mu_B B s$, we know that:

$$M = \mu_b (N_\uparrow - N_\downarrow) = \frac{\mu_B V}{\lambda^3} [f_{3/2}(ze^{\beta\mu_B B}) - f_{3/2}(ze^{-\beta\mu_B B})]$$

When temperatures are high and magnetic fields are large, $f_{3/2}(z) \approx z$, so:

$$M \approx \frac{2\mu_B V}{\lambda^3} \sinh(\beta\mu_B B)$$

We also define the *magnetic susceptibility*, which is $\chi = \frac{\partial^2 E}{\partial B^2}$, and evaluating this in the limit as $B \rightarrow 0$ and $T \rightarrow \infty$, we have:

$$\chi|_{T=0} = \frac{N\mu_B^2}{kT}$$

In the low temperature limit, the fermi energy becomes important, and using the our dodgy expansion around E_F we can evaluate this to be:

$$M \approx \mu_B^2 g(E_F) B$$

Where $g(E_F)$ is a function of fermi energy that is not particularly important. In this limit, the magnetic susceptibility becomes a constant and no longer obeys Curie's law. This $\frac{1}{T}$ behavior is called Curie's law.

3 Classical Thermodynamics

Wait? But I thought this course is about *statistical physics*. Well, the teaching committee somehow found room for thermodynamics, so here we are.

3.1 Temperature, Zeroth and First Law of Thermodynamics

We start by some definitions:

Definition. A wall is *adiabatic* if it does not let anything pass, including heat. Then the systems separated by the wall are *insulated*. If the walls can pass heat, they are called *diathermal walls* and the two systems are in *thermal contact*. A system that has been left for a long while is in *equilibrium*.

Now we get these definitions out of the way, and state the zeroth law:

Law (Zeroth Law of Thermodynamics). If system A and system B are in equilibrium with a third system C , then A and B are in equilibrium.

This allows us to define a temperature. Since A and C , are in equilibrium, we have $V_3 = f_{AC}(p_A, V_A, p_C)$, while B and C are in equilibrium so $V_3 = f_{BC}(p_B, V_B, p_C)$ for some functions f_{BC} and f_{AC} as the knowledge of all other variables would give a fixed volume at equilibrium. This gives the equality:

$$f_{AC}(p_A, V_A, p_C) = f_{BC}(p_B, V_B, p_C)$$

Now we invoke the zeroth law and say this implies $f_{AB}(p_A, p_B, V_A, V_B) = 0$. But this is independent from p_C ! Thus, we must have:

$$\theta(p_B, v_B) = \theta(p_A, V_A)$$

This θ is the temperature we want.

Law (First Law of Thermodynamics). The amount of work required to change an isolated system from state 1 to state 2 is independent of how the work is performed.

Equivalently, when systems are not isolated, we have:

$$\Delta E = Q + W$$

Where W is the amount of work done, and Q the amount of *heat* transferred. We also have:

$$dW = -pdV$$

Where the sign convention is chosen such that if you are squeezing the gas, work done *on* the gas is positive.

Note. Note the difference between E and Q , W . E is a function of state, but Q and W are not. That means it makes sense to talk about dE as a total derivative, but dQ and dW are just small and are *not* exact differentials. Thus it is customary to assign them new notation, but why bother? Just note this for the rest of this section.

3.1.1 Quasi-Static Processes

From now on, we would assume that all the heat and work done are done *very gently*: The system is always in equilibrium at any given point in the process. This is called a *Quasi-static process*. Then we can use the differential form of the equations above in full force, as seen below.

3.2 Second Law of Thermodynamics, or Why we all dieTM

Definition. Remember a process is a procedure for changing a system's state from (p_1, V_1) to (p_2, V_2) . A *reversible* process is one that can be done backwards with no change in energy.

We now state the famous second law of thermodynamics:

Law (Second Law of Thermodynamics, Kelvin). No process is possible whose sole effect is to extract heat from a hot reservoir and turn it completely into work.

An equivalent formulation is done by Clausius:

Law (Second Law of Thermodynamics, Clausius). No process is possible whose sole effect is the transfer of heat from a colder to a hotter body.

3.2.1 Carnot Process and Theory

We first define a Carnot process:

Definition. A *Carnot process* is a process that involves the following steps:

- Isothermal expansion from A to B at $T = T_H$.
- Adiabatic expansion from B to C , making the temperature drop from T_H to T_C .
- Isothermal contraction from C to D at $T = T_C$.
- Adiabatic Contraction from D to A , making the temperature rise from T_C to T_H again.

What is so special about this process?

Theorem (Carnot's Theorem). Of all engines operating between 2 heat reservoirs, a reversible engine is most efficient. All such engines have the same efficiency $\eta(T_H, T_C)$.

Proof. Consider another engine Ivor. Use it to drive the Carnot cycle in reverse, meaning Ivor takes Q'_H energy from hot and deposits Q'_C energy to cold. Then the total extracted heat is $Q'_H - Q_H \geq 0$ from Clausius' inequality. And we have $Q'_H - Q_H = Q'_C - Q_C$. Then

$$\eta_{Ivor} = 1 - \frac{Q'_C}{Q'_H} = 1 - \frac{Q'_H - Q_H + Q_C}{Q'_H} = \frac{Q_H - Q_C}{Q'_H} \leq 1 - \frac{Q_C}{Q_H}$$

So the carnot cycle is the most efficient cycle possible, and if Ivor is reversible we can reverse the inequality and thus they are equal. So we are done. \square

This tells us that Carnot is the best!

3.2.2 Thermodynamic Temperature Scale

We can use $\eta(T_H, T_C)$ to define T . Let there be 3 heat reservoirs $T_1 > T_2 > T_3$ and two carnot engines between the three reservoirs. Let the second engine take the same amount of heat from T_2 as the first engine deposits. Then we have:

$$Q_3 = Q_1(1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3)) = Q_1(1 - \eta(T_1, T_3))$$

Where the second equality is achieved by considering one equivalent carnot engine between T_1 and T_3 . Now then:

$$1 - \eta(T_1, T_3) = (1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3))$$

Let $f(T_1) = 1 - \eta(T_1, \bar{T}_2)$ and $g(T_3) = 1 - \eta(\bar{T}_2, T_3)$ for some fixed \bar{T}_2 . Then $1 - \eta(T_1, T_3) = f(T_1)g(T_3)$. Then we substitute in our original equation:

$$f(T_1)g(T_3) = f(T_1)g(T_2)f(T_2)g(T_3)$$

So we have $g(T_2)f(T_2) = 1$ for all T_2 . Now we define T such that $f(T) \propto \frac{1}{T}$ and this defines T up to a constant of propotionality, adn we fix this by saying the triple point of water has $T = 273.16K$.

3.2.3 Entropy

For the carnot cycle, with the temperature now defined above, we have:

$$\eta = 1 - \frac{Q_c}{Q_H} = 1 - \frac{T_c}{T_H} \Rightarrow \frac{Q_H}{T_H} = \frac{Q_c}{T_c}$$

Definiting $Q_1 = Q_H, Q_2 = -Q_c, T_1 = T_H, T_2 = T_C$, we have $\sum \frac{Q_i}{T_i} = 0$ where Q_i now all represent heat absorbed. We could generalize this argument and say that:

$$\oint \frac{dQ}{T} = 0$$

For any reversible cycle. Now we define:

$$S(A) = \int_0^A \frac{dQ}{T}$$

where 0 is some fixed reference state and the integral is calculated along any reversible path $0 \rightarrow A$. For infinitesimal reversible change $TdS = dQ$, $-pdV = dW$, so we have:

$$dE = TdS - pdV$$

Since this is a relation between functions of state, it must hold for any infinitesimal change, whether reversible or not! More interestingly, this definition is the same, up to a constant, of the one defined as $k \log(\Sigma(E, V))$. Now if we consider a reversible process from A to B , and an irreversible one, we can similarly show that:

$$\oint \frac{dQ}{T} \leq 0$$

for any cycle. This is called Clausius inequality. And thus if we consider an irreversible process and a reversible one joined to form a cycle from A to B , the contribution from A is:

$$S(A) - S(B) = \int_1 \frac{dQ}{T} \leq 0$$

Which is the second law of thermodynamics.

3.3 Thermodynamic Potentials and Relations

3.3.1 Enthalpy

Now we have already met F , the Helmholtz free energy, and G , the Gibbs free energy. Why not add a H into the mix?

$$H = E + pV$$

This governs systems at fixed energy and pressure as $dH = Tds + Vdp$. The objects E, F, G and H are called *thermodynamic potentials*.

3.3.2 Maxwell's Relations

The following relations really are just mathematical tricks, but they give some far-from-trivial physical results:

$$\frac{\partial T}{\partial V}|_S = -\frac{\partial p}{\partial S}|_V \quad \frac{\partial S}{\partial V}|_T = \frac{\partial p}{\partial T}|_T \quad \frac{\partial S}{\partial p}|_T = -\frac{\partial V}{\partial T}|_p \quad \frac{\partial T}{\partial p}|_S = \frac{\partial V}{\partial S}|_p$$

If one expand each equality out in terms of its original definitions, then the equalities are trivial as partial derivatives commute. They are useful as they relate measurable quantities to ones that are much harder to do so, such as entropy.

3.4 Third Law of Thermodynamics

The third law is not often talked about as it really doesn't give much insight. It is:

Law.

$$\lim_{T \rightarrow 0} S(T) = 0$$

For any system's entropy S .

An immediate consequence of the third law is that heat capacities must also tend to zero as $T \rightarrow 0$. This is because:

$$S(B) - S(A) = \int_A^B dT \frac{C_v}{T}$$

Therefore since the entropy at $T = 0$ is finite, so the integral must converge when $A = 0$, So $C_V \rightarrow T^n$ where $n \geq 1$.

4 Phase Transitions

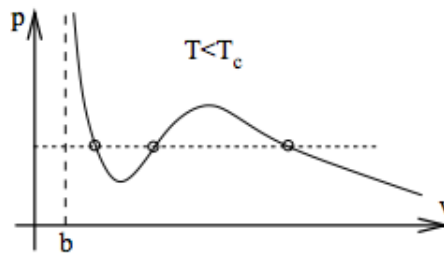
Well we have already seen one at the Bose-Einstein condensate, but now we would talk about more exciting ones, like the liquid-gas transition!

4.1 Liquid-Gas Transition

Now we go back to our van de waals equation:

$$p = \frac{kT}{v - b} - \frac{a}{v^2}$$

where $v = \frac{V}{N}$ is the volume per particle. Then, at low enough T , we would see the following curve:



This is weird. At a specific pressure p here, we have three different choices of volumes. What?

Left The leftmost solution has v only slightly bigger than b , but b is the closest that atoms can get, so this describes a *liquid*.

Middle This is unphysical.

Right This is our normal gaseous state.

Now knowing that at the same pressure liquid can coexist with gas, we will investigate liquid-gas equilibria, which require $\mu_{liquid} = \mu_{gas}$. But how do we achieve this?

4.1.1 Maxwell's Construction

Of course, more hand-waving!. The infinitesimal change in the chemical potential is:

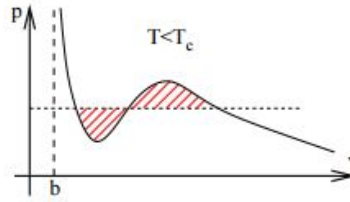
$$d\mu = \left. \frac{\partial \mu}{\partial p} \right|_T dp$$

And then we know from the "extensive variable" argument that $G = \mu N$, and thus $\frac{\partial \mu}{\partial p} = \frac{1}{N} \left. \frac{\partial G}{\partial p} \right|_{N,T} = \frac{V}{N}$. Thus:

$$\mu(p, T) = \mu_{liquid} + \int_{p_{liquid}}^p dp' \frac{V(p', T)}{N}$$

Graphically equality means the integral has to vanish, which means the two shaded areas below must have equal area.

Then for each T with T low enough, we can determine the pressure at which liquid and gas states are in equilibrium: these are called *coexistence curves*. These negative parabola curves on the $p-v$ plane curves turn the isothermal curves into straight lines within the region enclosed, as the density can take any value within this region due to equilibrium.

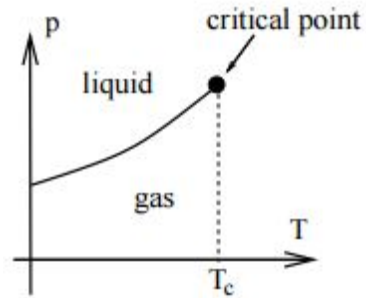


4.1.2 Clausius-Clapeyron Equation

If we choose to plot stuff in the $p-T$ plane, the coexistence region becomes a line, and T_c is defined as the point where the isothermal ceases to have the two kinks as illustrated above. Now on this line, $G_{liquid} = G_{gas}$ from the chemical potential, and thus using the differential form we can reach that:

$$\frac{dp}{dT} + \frac{S_{gas} - S_{liquid}}{V_{gas} - V_{liquid}} \quad L = T(S_{gas} - S_{liquid})$$

where L is defined as the latent heat. This is the *Clausius-Clapeyron Equation*. We can solve this approximately by using a lot of handwaving steps, but let's not.



4.1.3 The Critical Point and Law of Corresponding States

Now where is the critical point? We see that p is a cubic of v and thus the critical point occurs when the curve can be written as some $p_c(v - v_c)^3 = 0$. Solving gives:

$$kT_c = \frac{8a}{27b} \quad v_c = 3b \quad p_c = \frac{a}{27b}$$

Now knowing these give us a dimensionless quantity that does not depend on the gas itself:

$$\frac{p_c v_c}{kT_c} = \frac{3}{8} = 0.375$$

This is called the universal compressibility ratio. That means the coexistence curves for all gases, drawn in a correct way, should look all the same. And this is confirmed in experiments!

4.1.4 Critical Exponents

We then write the van de waal's equation in a new form:

$$\bar{p} = \frac{8}{3} \frac{\bar{T}}{\bar{v} - \frac{1}{3}} - \frac{3}{\bar{v}^2}$$

where $\bar{p} = \frac{p}{p_c}$ and similarly for the others. For $T < T_c$, we know that there are two solutions:

$$\bar{p} = \frac{8\bar{T}}{3\bar{v}_{liquid} - 1} - \frac{3}{\bar{v}_{liquid}^2}$$

And similarly for \bar{v}_{gas} . Thus, solving for \bar{T} gives:

$$\bar{T} \approx 1 - \frac{1}{16}(\bar{v}_{gas} - \bar{v}_{liquid})^2$$

Using the fact that the equation is symmetric so near the critical point, we have $\bar{v}_{gas} = 1 + \frac{\epsilon}{2}$ while $\bar{v}_{liquid} = 1 - \frac{\epsilon}{2}$. Thus:

$$v_{gas} - v_{liquid} \sim (T_c - T)^{\frac{1}{2}}$$

We also know that at the critical point we have $\frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0$, thus $p - p_c \sim (v - v_c)^3$.

If we define *compressibility* as $\kappa = -\frac{1}{v} \frac{\partial v}{\partial p}|_T$, then we know that:

$$\kappa \sim (T - T_c)^{-1}$$

Using the same result as above. Well, are these results right? Sadly no. The correct answers, should be respectively, in the order that we derived them:

$$\beta \approx 0.32, \delta \approx 4.8, \gamma \approx -1.2$$

I mean our results weren't that off, but they were incorrect due to the inappropriateness of the van de waal's equation in this scenario.

4.2 Ising Model

4.2.1 Introduction

The ising model is a simple but non-trivial system that shows a lot of interesting physics. Now it consists of N sites in a d -dimensional lattice. On each lattice site lives a quantum spin that can sit spin up or spin down. The eigenvalue of the spin is 1 if up and -1 if down. And these spins sit in a magnetic field with $E_B = -B \sum s_i$, so the spin up states have an energy advantage. This system also includes an interaction term, so:

$$E = -J \sum s_i s_j - B \sum s_i$$

Where the interaction sum is only summed over all closest neighborhood pairs. If $J > 0$, then the spins would like to be aligned and such a system is a ferromagnet, while for $J < 0$ the thing is called an *anti-ferromagnet*. We would assume $J > 0$ for the rest of our course. Then we start working in the canonical ensemble, with the interest on average magnetization: $m = \frac{1}{N} \frac{\partial \log Z}{\partial B}$.

4.2.2 Mean Field Theory

Now we want to know Z , but Z is a sum and we can't really do the sum in most of the cases. We would develop an approximate theory called *mean field theory*. We assume the deviations of spins from the average m is small over the sum of i, j :

$$s_i s_j = (s_i - m)(s_j - m) + m(s_j + s_i - 2m) + m^2 \approx m(s_j + s_i - 2m) + m^2$$

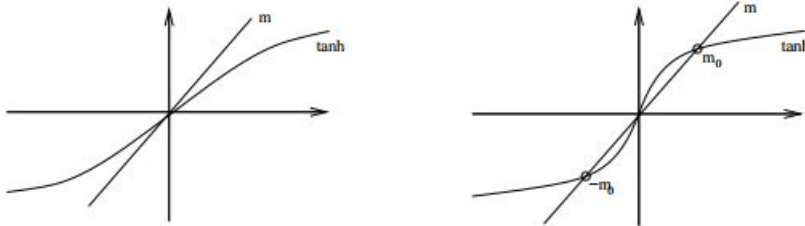
The energy can then be described as:

$$E_{mf} \approx \frac{1}{2} J N q m^2 - (J q m + B) \sum_i s_i$$

This reduces to a two state system where there is no interaction and each spin feels the effect of an effective magnetic field of $B + J q m$. Then:

$$Z = e^{-\frac{1}{2} \beta J N q m^2} s^N \cosh^N(\beta B_{eff})$$

Then we still need to find m , so we use the formula above to see that $m = \tanh(\beta B + \beta J q m)$. Then we solve graphically:



4.2.2.1 $B = 0$

Under $B = 0$, we graph $y = m$ and $y = \tanh(\beta J q m)$ and see that for $J q \beta < 1$ the only solution is $m = 0$ (graph on the left), and there is no average magnetization of the system. For $J q \beta > 1$, there are three solutions, but the middle one is unstable. The other two are possible and show magnetization becomes important at low T (high β).

4.2.2.2 $B \neq 0$

We can do a similar analysis and reach the following summary:

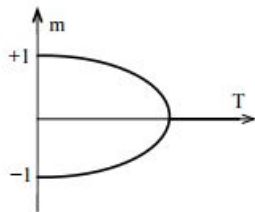


Figure 46: Magnetization with $B = 0$ and the phase transtion

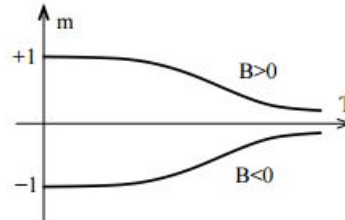


Figure 47: Magnetization at $B \neq 0$.

4.2.3 Critical Exponents

For the $B = 0$ case, we similarly have a phase transition, and we similarly do a critical exponent analysis *again*. The steps are boring Taylor expansions of the equations above, so here are the results:

$$m \sim (T - T_c)^{\frac{1}{2}} \quad m \sim B^{\frac{1}{3}} \quad \chi \sim (T - T_c)^{-1}$$

where $\chi = N \frac{\partial m}{\partial B} |_{T_c}$, and the second result is taken by sitting at T_c and moving from $B > 0$ to $B = 0$.

Hmm, these results look suspiciously similar to the ones in the liquid-gas transition. What are the correct results? They are:

$$m \sim (T - T_c)^{0.32} \quad m \sim B^{4.8} \quad \chi \sim (T - T_c)^{-1.2}$$

For $d = 3$, the Ising model in 3 dimensions. Wait, wait, wait, aren't these just the same expressions as the ones we have seen for the van de waal's equation? Yes! At critical points all systems lose memory of what the system actually is and behaves the same way. To see more of this, cf Part III *conformal field theory*.

Note. On the notes and in lectures, we derived some exact results for the 1D and 2D Ising models. However, not only is this part *uninteresting* (understatement), it has never been tested before and is not explicitly contained in the schedules. Moreover, I see no probability of this actually being tested due to the lack of actual "calculatable" material. Thus I would only present the important results.

4.3 Exact Results for Ising Model

4.3.1 1D

The partition function is:

$$Z = \lambda_+^N + \lambda_-^N \quad \lambda_{\pm} = e^{\beta J} \cosh \beta B \pm \sqrt{e^{2\beta J} \cosh^2 \beta B - 2 \sinh 2\beta J}$$

4.3.2 2D at low temperatures

The partition function is:

$$Z = 2e^{2N\beta J} \left(1 + Ne^{-8\beta J} + 2Ne^{-12\beta J} + \frac{1}{2}(N^2 + 9N)e^{-16\beta J} + \dots \right)$$

4.3.3 2D at high temperatures

The partition function is:

$$Z = 2^N (\cosh \beta J)^{2N} \left(1 + N(\tanh \beta J)^4 + 2N(\tanh \beta J)^6 + \frac{1}{2}(N^2 + 9N)(\tanh \beta J)^8 + \dots \right)$$

4.3.4 Kramers-Wannier Duality

Do the 2D results look similar in low T and high T ? Yup. They are the same if we exchange $e^{-2\beta J}$ and $\tanh \beta J$, and this symmetry is the *Kramers-Wannier duality*.

This means knowing the thermodynamics at one temperature gives you the other one immediately. A consequence of this is that we can use it to compute the exact critical temperature, as it must happen at the special self-dual point $\beta = \bar{\beta}$ if we assume there is just one phase transition. The temperature turns out to be $2.269J$.

4.4 Landau Theory

4.4.1 Introduction

The Landau Theory starts by considering the free energy under the mean field approximation. This gives:

$$F = \frac{1}{2}JNqm^2 - \frac{N}{\beta} \log(2 \cosh \beta B_{eff})$$

Now we start treating F as a function of m , where m is now called an *order parameter*. What does this mean?

- We extend our viewpoint from the equilibrium state to a class of states with constant m .
- m provides order. As in, non-zero m gives order to the spin.
- In general theory, we pick an *order parameter* so that it is 0 above the critical temperature of the phase transition and is non-zero below that. It is not always obvious which parameter we want to pick, however.

The general theory is well beyond this course, and we only look at some specific applications in some specific scenarios.

4.4.2 Second Order Phase Transitions

We now expand the free energy in powers of m . Assume a symmetry of $m \rightarrow -m$ so it cannot take odd powers:

$$F(T; m) = F_0(T) + a(T)m^2 + b(T)m^4 + \dots$$

And for the rest of this discussion, we assume that $b(T) > 0$ for all T , or otherwise we would need to consider the m^6 term.

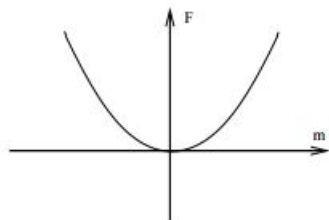


Figure 51: Free energy when $a(T) > 0$

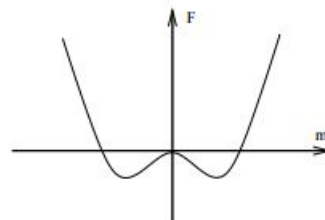


Figure 52: Free energy when $a(T) < 0$

Now, as in the specific Ising model, for $T > T_c$, we have $a(T) > 0$, and for $T < T_c$ we have $a(T) < 0$. [One could check this by noting that $a(T) = \frac{Njq}{2}(1 - Jq\beta)$] And thus truncating the free energy at m^4 , we know the equilibrium free energy is:

$$F(T) = \begin{cases} F_0(T) & T > T_c \\ F_0(T) - \frac{a^2}{2b}T & T < T_c \end{cases}$$

Then we look at what happens at $T = T_c$. The free energy is continuous and one can check to see that the first partial derivative of F , S , is also continuous, but the second derivative is not. That means the heat capacity $C = T \frac{\partial S}{\partial T}$ changes discontinuously at $T = T_c$.

Note. If you want to calculate equilibrium values, substitute the equilibrium value of m into the equation above and use that. Don't use the Taylor expansion as m changes with T .

We then can easily calculate critical exponents, as near $T = T_c$, we write $b(T) \approx b_0$ and $a(T) \approx a_0(T - T_c)$ to get that:

$$m_0 \sim (T_c - T)^{\frac{1}{2}}$$

which is the same as before.

4.4.3 First Order Phase Transitions

Now consider an expansion in which odd powers exist:

$$F(T; m) = F_0(T) + \alpha(T)m + a(T)m^2 + \gamma(T)m^3 + b(T)m^4 + \dots$$

Again we assume $b(T) > 0$ for all T , and for low T , in the specific example of the Ising model, we have:

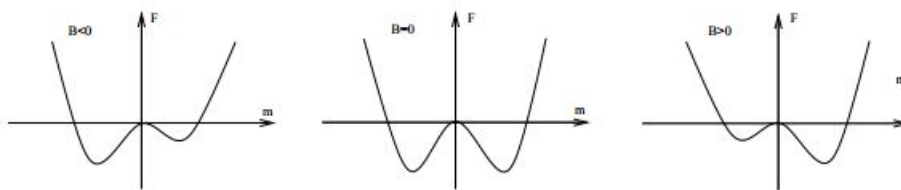


Figure 53: The free energy of the Ising model for $B < 0$, $B = 0$ and $B > 0$.

Here we can have a first order phase transition when $\alpha(T)$ and $\gamma(T)$ changes sign and the true ground state flips from $m < 0$ to $m > 0$. In the Ising model shown above, the behavior is induced by changing B .

At very high temperature we once again have a parabola looking graph but this time shifted due to the $\alpha(T)$ term, and the transition happens when the second ground state (thus the *meta-stable state*) disappears, and these meta-stable states correspond with the ones we talked about in the Van de Waal's model.