Ph12c Class Notes

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Chapter 1

Week 1

1.1 Tuesday 31 Mar 2015

Random Walk Let the step length be l, probability of right step p and probability of left step q. Want to calculate probability of finding drunk a distance of $x = ml$ away from the origin after N total steps.

Stirling's Approximation $N! \approx \sqrt{2\pi N} N^N e^{-N}$. $\ln N! \approx N \ln N - N$.

Poisson Distribution Consider the Binomial distribution with $n_r << N, p << 1$, where n_r is the number of steps taken to the right. Then using first order approximations, $(1-p)^{N-n_r} \approx e^{-pN}$.

Upper limits for null experiments Let zero events be observed in a time interval. Pick a confidence level $1-\alpha$. Then the $1-\alpha$ confidence level for the event rate given that zero events are observed in the time interval T is the non-zero rate $\dot{N}$ such that $P_{\dot{N}}(0 \text{ events in T}) = \alpha$.

1.2 Tuesday 31 Mar 2015 Recitation

Quantum states and phase space A quantum state in phase space occupies a volume of around $\hbar$.

1.3 Thursday 2 Apr 2015

Interval distribution between Poisson events Consider radioactive decay with the mean number of decays in a small time interval Δt as $\mu = \dot{N}\Delta t, \mu << 1$. Then the probability of getting a single event in that time interval is:

$$P_\mu(1) = \frac{\mu^1 e^{-\mu}}{1!} \approx \mu$$

to first order, and the probability of obtaining zero events is just $1-\mu$. Then the probability of having m consecutive time steps with zero events followed by one event is:

$$(1-\mu)^m \mu$$

and the total time elapsed before the event occurs is $m\Delta t$. Note that time is a continuous variable. Then we define the probability of obtaining a time interval between t and $t+\Delta t$ to be:

$$P(t)\Delta t$$

where $P(t)$ is a probability density. Then we equate this to the previously obtained result:

$$\begin{aligned} P(t)\Delta t &\approx (1-\mu)^{t/\Delta t}\mu \\ \implies P(t) &\approx \dot{N}(1-\mu)^{t/\Delta t} \\ \implies P(t) &\approx \dot{N}e^{-\mu t/\Delta t} \end{aligned}$$

Taking the limit as $\Delta t \to 0$,

$$P(t) = \dot{N} e^{-\dot{N}t}$$

Note that the interval distribution is an exponential.

Gaussian approximation to the binomial Consider a random walk with a large number of time steps N but the probability of taking a step in each direction being close to $\frac{1}{2}$ so that $n_r \approx n_l$. Then $n_r - n_l$ is small. Define $m = n_r - n_l$. Now expand the binomial distribution in terms of $\frac{m}{N} << 1$.

Rewrite the Binomial distribution in terms of m:

$$n_r = \frac{N+m}{2}$$
$$n_l = \frac{N-m}{2}$$

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!} p^{\left(\frac{N+m}{2}\right)} q^{\left(\frac{N-m}{2}\right)} \equiv g(N,m) p^{\left(\frac{N+m}{2}\right)} q^{\left(\frac{N-m}{2}\right)}$$

where we define the function g accordingly. It will be more efficient to examine the logarithm of g, since we can use the Stirling approximation for $\ln N!$

$$\ln N! \approx \frac{1}{2}\ln 2\pi + (N + \frac{1}{2}) \ln N - N$$

Furthermore, noting that m is small compared to N,

$$\ln \frac{N \pm m}{2} \approx \ln N \pm \frac{m}{N} - \frac{m^2}{2N^2} - \ln 2$$

to second order. After simplifying:

$$g(N,m) = \sqrt{\frac{2}{\pi N}} 2^N e^{-m^2/2N}$$

Noting that $p \approx q \approx \frac{1}{2}$, the factor behind the g-term is just approximately 2^{-N}. Then we have that:

$$P_N(m) = \sqrt{\frac{2}{\pi N}} e^{-m^2/2N}$$

Note that m has even parity, hence we can define $s = \frac{m}{2}$, which will be an integer. Then:

$$P_N(s) = \sqrt{\frac{2}{\pi N}} e^{-2s^2/N}$$

In the limit where $s \to 0$, we can introduce the probability density with $\sigma^2 \equiv \frac{N}{4}$:

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}$$

Average or Mean values Consider the average value of n_r:

$$\begin{aligned}
\langle n_r \rangle &= \sum_{n_r=0}^{N} \binom{N}{n_r} p^{n_r} q^{N-n_r} n_r \\
&= p\frac{\partial}{\partial p} \sum_{n_r} \binom{N}{n_r} p^{n_r} q^{N-n_r} \\
&= p\frac{\partial}{\partial p}(p+q)^N \\
&= Np(p+q)^{N-1} \\
&= Np, \quad \text{p+q has to be unity}
\end{aligned}$$

$$\begin{aligned}
\langle n_r^2 \rangle &= \sum_{n_r=0}^{N} \binom{N}{n_r} p^{n_r} q^{N-n_r} n_r^2 \\
&= p\frac{\partial}{\partial p}\left[p\frac{\partial}{\partial p} \sum_{n_r} \binom{N}{n_r} p^{n_r} q^{N-n_r}\right] \\
&= p\frac{\partial}{\partial p}\left[p\frac{\partial}{\partial p}(p+q)^N\right] \\
&= p\frac{\partial}{\partial p}\left[Np(p+q)^{N-1}\right] \\
&= p\left[N(p+q)^{N-1} + Np(N-1)(p+q)^{N-2}\right] \\
&= Np + N(N-1)p^2 \\
&= Np(1+(N-1)p) \\
&= Np(1-p+Np) \\
&= Npq + N^2p^2 \\
\implies Var(n_r) &= Npq
\end{aligned}$$

Chapter 2

Week 2

2.1 Tuesday 7 April 2015

Basic Postulate of Statistical Mechanics An isolated system in "equilibrium" is equally likely to be in any of its "accessible" states. Equilibrium: when the probability of finding the system in a given accessible state is independent of time. "Accessible" state: those allowed by constraints imposed on the system.

Derivation of Thermodynamics Consider the states of some closed system with a large number of particles.

Quantum 3D Square well Recall the energy of quantum states:

$$E = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

Configuration Set of states specified by the quantum numbers (or other numbers).

Ensembles Set of all possible configurations consistent with external constraints.

Spin-1/2 system Consider N total spin-1/2 particles in the system, each with magnetic moment m. Then define:

$$N = n_+ + n_-$$
$$s = \frac{n_+ - n_-}{2}, \quad \text{spin excess}$$

with n_+ being the number of states aligned with the external magnetic field B. Then the energy of the system (alignment with the field is low energy) is:

$$E_{tot} = -2smB$$

Then the number of states corresponding n_+ out of N spins is:

$$g(N, n_+) = \frac{N!}{(n_+)!(N-n_+)!} \approx \left(\frac{2}{\pi N}\right)^{1/2} 2^N e^{-2s^2/N}$$

Combination of two systems Consider two systems with initial energies E_1^i, E_2^i brought into thermal contact. Define $E = E_1 + E_2$ =constant. By conservation of energy, we expect that the sum of the system spin excesses $s = s_1 + s_2$ will be constant. We want to find the total number of accessible states in the combined system.

$$g^{tot}(N, s) = \sum_{s_1=-N/2}^{N/2} g(N_1, s_1) g(N_2, s - s_1)$$

which we can simplify to obtain:

$$g^{tot}(N,s) = \sum_{s_1=-N/2}^{N/2} \left(\frac{4}{\pi^2 N_1 N_2}\right)^{1/2} 2^N \exp\left(-\frac{2s_1^2}{N_1} - \frac{2(s-s_1)^2}{N_2}\right)$$

But we note that the most probable configuration will dominate the sum. We want to find s_1, which we call s_m, such that $\frac{2s_1^2}{N_1} + \frac{2(s-s_1)^2}{N_2}$ is minimised. Applying the first derivative condition, we require that:

$$s_m = \frac{N_1 s}{N}$$

which gives:

$$\exp\left(-\frac{2s_m^2}{N_1} - \frac{2(s-s_m)^2}{N_2}\right) = \exp\left(\frac{-2s^2}{N}\right)$$

Hence we write:

$$g^{tot}(N,s) \approx \left(\frac{4}{\pi^2 N_1 N_2}\right)^{1/2} 2^N \exp\left(\frac{-2s^2}{N}\right)$$

Note that we can see how much this term dominates the other terms by looking at the ratio:

$$f = \frac{g(N_1, s_m+\delta s) g(N_2, s-s_m-\delta s)}{g(N_1, s_m) g(N_2, s-s_m)} = \exp\left(-\frac{2\delta s^2 N}{N_1 N_2}\right)$$

Notice that this ratio vanishes very rapidly as δs increases when N is large.

Approximating exponentials Note that $e^{-x} = 10^{-x/\ln 10}$.

2.2 Recitation 07 Apr 2015

Rotations and Spin-1/2 Consider the 2D rotation:

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

All transformations can be written in terms of a first order approximation, for instance position:

$$\psi(x+a) \approx \psi(x) + a\frac{\partial}{\partial x}\psi(x) = \psi(x) + \frac{ia}{\hbar}\hat{p}\psi(x)$$

Rotations in 3D A rotation in the z-axis in 3D can be written as:

$$\begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \approx \mathbb{I} + \theta \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

to first order in θ. Then we define:

$$\begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{i}{\hbar}\hat{L}_z$$

and similarly, we define momentum operators:

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} = \frac{i}{\hbar}\hat{L}_x$$

$$\begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} = \frac{i}{\hbar}\hat{L}_y$$

Then we have the commutation relations:

$$[L_x, L_y] = i\hbar L_z$$

and the cyclic permutations also give two other relations.

2.3 Thursday 9 Apr 2015

Most Probable Configuration - General Case Consider 2 isolated systems A_1 and A_2 with a thermally conducting barrier between them. Let A_1 have N_1 particles and A_2 have N_2 particles. Let the total energy $E = E_1 + E_2$ be a constant. Then the total number of states for the combined system is:

$$g^{tot}(N, V, E) = \sum_{E_1} g(N_1, V_1, E_1)g(N_2, V_2, E - E_1)$$

The most probable configuration corresponding to $E_1 = E_1^m$ will dominate the sum. This corresponds to the first order conditions:

$$\begin{aligned} \frac{\partial}{\partial E_1}[g_1(E_1)g_2(E-E_1)] = 0 &\implies -g_1(E_m)g_2'(E-E_m) + g_1'(E_m)g_2(E-E_m) = 0 \\ &\implies \frac{g_1'(E_m)}{g_1(E_m)} = \frac{g_2'(E-E_m)}{g_2(E-E_m)} \\ &\implies \frac{d}{dE_1}\ln g_1(E_1)\bigg|_{E_m} = \frac{d}{dE_2}\ln g_2(E_2)\bigg|_{E-E_m} \end{aligned}$$

Fundamental Entropy Define $\sigma = \ln g(E, V, N)$. This is related to the classical entropy $S = k_B\sigma$. Then the condition for equilibrium can be written as:

$$\left(\frac{\partial \sigma_1}{\partial E_1}\right)_{N_1,V_1} = \left(\frac{\partial \sigma_2}{\partial E_2}\right)_{N_2,V_2}$$

Fundamental Temperature Define:

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial E}\right)_{N,V}$$

which is related to the absolute temperature: $\frac{\tau}{k_B} = T$. Hence in terms of classical thermodynamics:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

Equilibrium, Entropy and Thermodynamics We want to consider what $g(E) \approx g_1(E_1)g_2(E_2)$ (or rather the logarithm) looks like near equilibrium. We want to Taylor expand $g(E)$ near E_1^m. Define $x_1 = E_1 - E_1^m, x_2 = E_2 - E_2^m$. Then:

$$\begin{aligned}\ln g_1(E_1) &= \ln g_1(E_1^m) + \frac{\partial \ln g_1}{\partial E_1}x_1 + \frac{1}{2}x_1^2\frac{\partial^2 \ln g_1}{\partial E_1^2} + \dots \\ &= \ln g_1(E_1^m) + \frac{1}{\tau_1}x_1 - \frac{1}{2}\lambda_1 x_1^2 + \dots\end{aligned}$$

where we define $\lambda_1 = -\frac{\partial^2 \ln g_1}{\partial E_1^2}$. We perform the same expansion for g_2 to obtain:

$$\ln g_2(E_2) = \ln g_2(E - E_1^m) + \frac{1}{\tau_2}x_2 - \frac{\lambda_2 x_2^2}{2} + \dots$$

where we define $\lambda_2 = -\frac{\partial^2 \ln g_2}{\partial E_2^2}$. Hence we combine the approximations and apply the equilibrium condition $\tau_1 = \tau_2$ to obtain:

$$\ln g^{tot} \approx \ln g_1(E_1)g_2(E_2) \approx \ln[g_1(E_1^m)g_2(E - E_1^m)] - \frac{1}{2}(\lambda_1 + \lambda_2)x^2$$

where we note that $x_2 = (E - E_1) - (E - E_1^m) = -x_1 = x$. Then we define $\lambda_0 = \lambda_1 + \lambda_2$ so:

$$\ln g^{tot} = \ln[g_1(E_1^m)g_2(E - E_1^m)] - \frac{\lambda_0}{2}x^2 \implies g^{tot} = g_1(E_1^m)g_2(E - E_1^m)e^{-\frac{\lambda_0}{2}(E - E_1^m)^2}$$

which peaks at $E_1 = E_1^m$ like a Gaussian with standard deviation $\frac{1}{\sqrt{\lambda_0}}$.

Figuring out the width of the Gaussian We want to find $g(E)$ so that we can find $\lambda = -\frac{\partial^2 \ln g}{\partial E^2}$. We proceed by considering the quantum square well (in 3D). Consider N_1 particles in a box and a second box with $N_2 = N_1$. Let the boxes be in thermal contact and let them reach thermal equilibrium. Then the energies are given by:

$$E = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

The number of states between n and $n + dn$ (where $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$) is given by the volume of the thin spherical shell quadrant:

$$g(n)dn = \frac{1}{8}(4\pi n^2)dn$$

Hence the density of states as a function of energy is given by:

$$dE = \frac{\hbar^2\pi^2}{2mL^2}2ndn = \frac{\hbar^2\pi^2}{mL^2}\sqrt{\frac{2mL^2E}{\hbar^2\pi^2}}dn = \sqrt{\frac{2E\hbar^2\pi^2}{mL^2}}dn$$

$$\rho(E) = \frac{\pi}{2}\frac{2mL^2E}{\hbar^2\pi^2}\frac{dn}{dE} = \frac{mL^2E}{\hbar^2\pi}\sqrt{\frac{mL^2}{2E\hbar^2\pi^2}} = \frac{\pi}{4}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)^{3/2}\sqrt{E}$$

The total number of states is given by the integral of the density of states up to the energy E.

$$g(E) = \frac{\pi}{6}\left(\frac{2mL^2}{\hbar^2\pi^2}\right)^{3/2} E^{3/2}$$

Note that the number of states for a system with N distinguishable particles is hence:

$$g(E) \propto \left[E^{3/2}\right]^N$$

and hence:

$$\ln g(E) = \frac{3N}{2}\ln E + \text{constant}$$

Hence we have:

$$\lambda = -\frac{\partial^2 \ln g}{\partial E^2} = \frac{3N}{2E^2}$$

Returning to the combined system with $N_1 = N_2$, we have:

$$\lambda_1 = \lambda_2 = \frac{3N_1}{2(E_1^m)^2}$$

where the most probable energy for each system is the same because the number of particles in each system is the same. Hence we have:

$$\lambda_0 = \lambda_1 + \lambda_2 = \frac{3N_1}{(E_1^m)^2}$$

and the width of the Gaussian approximation to the number of states is given by:

$$\Delta E_1 = \frac{1}{\sqrt{\lambda_0}} = \frac{E_1^m}{\sqrt{3N_1}}$$

and the fractional width is

$$\frac{\Delta E_1}{E_1} = \frac{1}{\sqrt{\frac{3N}{2}}}$$

where $N = N_1 + N_2 = 2N_1$ is the total number of particles in the system. Note that the fractional width vanishes as N increases to infinity.

Entropy at low energy QM predicts the existence of the ground state, which is a single or a few states. As the energy increases, the degeneracy increases. Hence at low energy, the entropy $\sigma = \ln g$ goes to zero. For N distinguishable particles in a box, we can write the entropy as:

$$\sigma \approx \frac{3N}{2}\ln\frac{E}{E_0}, \quad E_0 = \left(\frac{6}{\pi}\right)^{2/3}\frac{\hbar^2\pi^2}{2mL^2}$$

Zeroth Law of Thermodynamics If $\tau_1 = \tau_2$ and $\tau_2 = \tau_3$ then $\tau_1 = \tau_3$. If two systems are in thermal equilibrium with a third then they are in thermal equilibrium with each other.

First Law of Thermodynamics Heat is energy.

Second Law of Thermodynamics For an isolated system approaching equilibrium, the entropy is nondecreasing. The final entropy is greater or equal to the initial entropy.

Third Law of Thermodynamics As $\tau \to 0$, the entropy σ approaches a constant.

Classical vs Quantum Entropy Consider an isolated system of N particles in a volume V with energy E. This is called the macrostate of the system, which is made up of a large number of microstates. In QM, micro states correspond to volumes $\delta x \delta p_x \sim \hbar$ in phase space. Classically, the phase space is split into tiny volumes of dimension $\delta x \delta p_x \sim \delta y \delta p_y \sim \delta z \delta p_z \sim h_0$ for some constant h_0 so that the total number of accessible states is given by $\frac{\text{Volume in 6D phase space}}{h_0^3}$ where the available phase space volume is determined by N, V, E. Explicitly, we can write the multiplicity as:

$$g_{\text{classical}} = \frac{\iiint_{\text{available phase space}} dx_1 dy_1 dz_1 dp_{x_1} dp_{y_1} dp_{z_1} \cdots dp_{z_N}}{[h_0]^{3N}}$$

and so the entropy is given by:

$$\sigma_{\text{classical}} = \ln[\iiint \cdots] - 3N \ln h_0$$

hence there is a fixed constant that cannot be removed unless we look at changes in entropy alone.

Chapter 3

Week 3

3.1 Tuesday 14 Apr 2015

Contact with reservoir Consider a subsystem A_s in thermal contact with a heat reservoir A_R held at fixed τ. The subsystem is called the canonical ensemble with N_s, V, τ fixed. Let the number of particles be N_s and N_R respectively. Let the systems be isolated. We want to find the probability $P_s(E_i)$ that A_s is in one of its accessible states $E_s = E_i$ (exactly one of the associated states if the energy level is degenerate).

Because of the isolation, we have $E_{tot} = E_s + R_R =$ constant. By the Basic Postulate, all states are equally likely. Hence:

$$P_s(E_1) = P_R(E_{tot} - E_1) \propto g_R(E_{tot} - E_1)$$

But since $E_s = E_1 << E_{tot}$ hence we can expand the logarithm of the multiplicity function about E_{tot}:

$$\ln g_R(E_{tot} - E_1) = \ln g_R(E_{tot}) - E_1 \frac{\partial \ln g_R(E_{tot})}{dE} + \ldots = \ln g_R(E_{tot}) - E_1 \frac{1}{\tau} + \ldots$$
$$\implies g_R(E_{tot} - E_1) \approx g_R(E_{tot}) e^{-E_1/\tau}$$

Now since we know that the probabilities must sum to 1, we can solve for K and hence have the probability:

$$P_s(E_1) = \frac{e^{-E_1/\tau}}{\sum_{\text{states}} e^{-E_s/\tau}}$$

hence states where the energy is small compared to τ have a high probability, and if the energy is large compared to τ then the probability is low.

Partition function Define $Z \equiv \sum_{states} e^{-E_s/\tau}$ where the summation includes the degeneracy. We can perform the sum by including the degeneracy explicitly:

$$Z = \sum_i g(E_i) e^{-E_i/\tau}$$

Example: Partition function for hydrogen atom Recall that the energy levels in the hydrogen atom is given by $E_n = \frac{-R}{n^2}$. We may redefine the energy so that the exponent in the exponential is negative: $E_n = R - \frac{R}{n^2}$:

$$Z = \sum_{n=1}^{\infty} e^{(-R - \frac{R}{n^2})/\tau}$$

Now recall that the Bohr radius scales as $r_n = a_0 n^2$ so the volume scales as n^6. Since the volume is finite, there is a maximum value of n and hence the summation is not infinite. The partition function is defined for a finite volume, but the hydrogen wavefunctions extend to infinity.

Average energy from partition function Define $U = \langle E_s \rangle$, the average energy of the subsystem. Then:

$$\begin{aligned} U &= \sum_{\text{states}} E_i P_s(E_i) \\ &= \sum_{\text{states}} E_i \frac{e^{-E_i/\tau}}{\sum_{\text{states}} e^{-E_s/\tau}} \\ &= \frac{1}{Z} \sum_{\text{states}} \tau^2 \frac{\partial e^{-E_i/\tau}}{\partial \tau} \\ &= \frac{1}{Z} \tau^2 \frac{\partial}{\partial \tau} \sum_{\text{states}} e^{-E_i/\tau} \\ &= \frac{\tau^2}{Z} \frac{\partial Z}{\partial \tau} \\ &= \tau^2 \frac{\partial \ln Z}{\partial \tau} \end{aligned}$$

Example: Maxwell-Boltzmann Distribution Consider a non-interacting particle with $E = \frac{p_x^2+p_y^2+p_z^2}{2m}$ and a room with many atoms (i.e. the reservoir). Then we want to find the distribution of velocities for a given temperature T. Now we assume that the momentum values are continuous (classical) so we can integrate over all states instead of summing over all states. Then the probability density is given by:

$$P(\text{momentum between p and +dp}) d^3p \propto e^{-p^2/2m\tau} dp_x dp_y dp_z = e^{-p^2/2m\tau} p^2 \sin\theta d\theta d\phi dp$$

in spherical coordinates. Integrating and writing in terms of velocities:

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

and this is the Maxwell-Boltzmann distribution.

Free atom in uniform gravitational field Now the energy is $E = \frac{p^2}{2m} + mgz$. We note that there will be a z dependence. Hence we want the probability of finding an atom with momentum between p and p+dp and between z and z+dz. Then we have:

$$\begin{gathered} P(z,p) d^3r d^3p \propto d^3r d^3p e^{-(\frac{p^2}{2m}+mgz)\frac{1}{\tau}} \propto e^{-mgz/\tau} d^3r e^{-p^2/2m\tau} d^3p \\ \propto P(z)P(p) dp dz \\ P(v,z) = 4\pi \left(\frac{m}{2\pi\tau}\right)^{3/2} v^2 e^{-mv^2/2\tau} \left(\frac{mg}{\tau}\right) e^{-mgz/\tau} \end{gathered}$$

Note that this is a Maxwell-Boltzmann distribution multiplied by a position dependence $P(z) = \frac{mg}{\tau} e^{-mgz/\tau}$. The position dependence gives the Law of Atmospheres.

$$P(z) = c_0 e^{-z/H}$$

where $H = \frac{kT}{mg}$ is the scale height of the atmosphere for the density to drop by $\frac{1}{e}$ compared to the value on the ground.

Example: Earth's Atmosphere Let the atmosphere be filled with nitrogen gas, atomic weight 28. At room temperature, $kT \approx \frac{1}{40} eV$. Hence the scale height is estimated to be $H = 9km$.

Retention of Planetary Atmospheres The mean velocity can be calculated to be $\langle v \rangle = \sqrt{\frac{8\tau}{\pi m}}$ so lighter atoms are moving faster. The average value of the z-position can also be calculated to be $\langle z \rangle = H = \frac{\tau}{mg}$ so the lighter the gas the higher the scale height is. Hence the lighter the gas is, the more likely it is to escape. The system will have to re-equilibrate as the atoms leave.

More Thermodynamic Quantities Pressure = -Work/Change in Volume = $-\left(\frac{\partial U}{\partial V}\right)$. For a reversible change in volume, $\Delta\sigma = 0$, then we define:

$$P = -\left(\frac{\partial U}{\partial V}\right)_{N,\sigma}$$

3.2 Thursday 16 Apr 2015

Irreversible change If the imposition or removal of constraint can "never" restore the initial state, the change is irreversible $\Delta\sigma > 0$.

Reversible change During movement of constraint, the system is always infinitesimally "near" equilibrium. The entropy change is zero $\Delta\sigma = 0$.

Thermodynamic Identity Consider the total derivative of the entropy:

$$d\sigma(U,V) = \left(\frac{\partial \sigma}{\partial V}\right)_U dV + \left(\frac{\partial \sigma}{\partial U}\right)_V dU$$

then for a reversible change $d\sigma = 0$ hence we require that such a macroscopic change δ_V, δ_U has the relation:

$$\begin{aligned}\left(\frac{\partial \sigma}{\partial V}\right)_U (\delta V)_\sigma &= -\left(\frac{\partial \sigma}{\partial U}\right)_V (\delta U)_\sigma \\ \implies \left(\frac{\partial \sigma}{\partial V}\right)_U &= -\left(\frac{\partial \sigma}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_\sigma = -\frac{1}{\tau}(-p) \\ \implies p &= \tau \left(\frac{\partial \sigma}{\partial V}\right)_U\end{aligned}$$

Hence the thermodynamic relation can be written as (for constant N):

$$\begin{aligned}d\sigma &= \frac{p}{\tau} dV + \frac{1}{\tau} dU \\ \implies \tau d\sigma &= p dV + dU\end{aligned}$$

Helmholtz Free energy We know that at equilibrium, U is minimum. But at equilibrium, the second law says that the entropy is at a maximum. Hence when we define:

$$F = U - \tau\sigma$$

Then F is clearly a minimum at equilibrium. Returning to the thermodynamic identity, we can re-write the free energy as:

$$\begin{aligned}dF = dU - \sigma d\tau - \tau d\sigma &= -\sigma d\tau - p dV \\ \implies \sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V&, \quad p = -\left(\frac{\partial F}{\partial V}\right)_\tau\end{aligned}$$

Relation between F and Z Note that we can write the free energy:

$$\begin{aligned}F = U - \tau\sigma &= U + \tau\left(\frac{\partial F}{\partial \tau}\right)_V \\ \implies U = \tau^2\left[\frac{F}{\tau^2} - \frac{1}{\tau}\left(\frac{\partial F}{\partial \tau}\right)_V\right] &= -\tau^2\left(\frac{\partial (F/\tau)}{\partial \tau}\right)_V\end{aligned}$$

But we know that:

$$U = \tau^2 \left(\frac{\partial \ln Z}{\partial \tau}\right)_V$$

Hence equating the expressions,

$$\ln Z = -\frac{F}{\tau} + \alpha$$

Substituting this into:

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = \ln z + \tau \left(\frac{\partial (\ln z)}{\partial \tau}\right)_V + \alpha$$

At $\tau \to 0$, we require that:

$$z \to g_0 e^{-E_0/\tau}$$

the ground state and its multiplicity. Hence we have:

$$\ln z = \ln g_0 - \frac{E_0}{\tau}$$

and for the entropy to equal to the multiplicity of the ground state at $\tau = 0$, then we require that $\alpha = 0$ and hence:

$$F = -\tau \log Z$$

Key Relations

$$\begin{aligned} F = U - \tau\sigma &\quad \text{minimum at equilibrium when } \tau, V, N \text{ constant} \\ G = U - \tau\sigma + pV &\quad \text{minimum at equilibrium when } \tau, p, N \text{ constant} \\ H = U + pV &\quad \text{minimum at equilibrium when } \sigma, p, N \text{ constant} \end{aligned}$$

Independent variables in thermodynamics If the number of particles are allowed to vary, the thermodynamic relation becomes

$$dU = \tau d\sigma - pdV + \mu dN$$

where μ is the chemical potential.

Two-state system Consider a particle with two states, a ground state $E = 0$ and an excited state $E = E_0$ and let the excited state be three-fold degenerate. Now let the particle be in thermal equilibrium with a heat reservoir at a fixed temperature τ. We want to find σ. Assume the volume is constant. Hence we can use the Helmholtz free energy:

$$\begin{aligned} F = -\tau \log Z = -\tau \log \left[e^0 + 3e^{-E_0/\tau}\right] &= -\tau \log[1 + 3e^{-E_0/\tau}] \\ \sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N} &= \ln(1 + 3e^{-E_0/\tau}) + \frac{3(E_0/\tau)e^{-E_0/\tau}}{1 + 3e^{-E_0/\tau}} \end{aligned}$$

Ideal Gas Consider N non-interacting particles in volume V, in contact with a reservoir at τ. We want to find the thermodynamic variables p, σ, U in terms of N, τ. Now for the single particle, we have the partition function:

$$Z_1^{class} = \sum_{states} e^{-E_i/\tau}$$

Now the number of states given by the total phase volume divided by the size of a unit cell. Let the unit cell in phase space be given by h_0^3. Then we have:

$$Z_1^{class} = \frac{V}{h_0^3} \int_p d^3\vec{p} \exp\left[-\left(\frac{p_x^2 + p_y^2 + p_z^2}{2m\tau}\right)\right] = \frac{V}{h_0^3}\left(\sqrt{2\pi m\tau}\right)^3$$

and for N particles, we just take the single particle partition function to the power of N. Then we have the variables:

$$F = -\tau \log Z_N = -\tau N \left[\log \frac{V}{h_0^3}(2\pi m\tau)^{3/2}\right]$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_\tau = \frac{\tau N}{V}$$

$$\sigma = N \log\left[\frac{V}{h_0^3}(2\pi m\tau)^{3/2} + \frac{3}{2}\right]$$

Gibbs' Paradox Consider a box with a partition that splits the box into a section with N_1, V_1 and N_2, V_2. Then consider the entropy of the box without and with the partition:

$$\sigma_{initial} - \sigma_{final} = -N \ln 2 < 0$$

and hence we have a decrease in entropy. Doesn't make sense!

Chapter 4

Week 4

4.1 Tuesday 21 April 2015

Entropy of ideal gas Recall that the classical calculation of the ideal gas in 3D gives:

$$\sigma_{IG} = N \ln \left[V \left(\frac{2\pi m\tau}{h_0^2} \right)^{3/2} \right] + \frac{3N}{2}$$

Hence if we consider a single system and split it into two ($N \to N/2, V \to V/2$), the final entropy is:

$$\sigma_F = 2 \cdot \frac{N}{2} \ln \left[\frac{V}{2} \left(\frac{2\pi m\tau}{h_0^2} \right)^{3/2} \right] + 2 \cdot \frac{3(N/2)}{2}$$

hence the change in entropy is:

$$\sigma_F - \sigma_I = -\ln 2 < 0$$

which violates the second law. But the above process is reversible. Hence we needed $\Delta\sigma = 0$. Gibbs attempted to fix this by introducing an additional factor of $N!$:

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

Then the entropy of the ideal gas becomes:

$$\sigma_{IG} = N \ln \left[\frac{V}{N} \left(\frac{2\pi m\tau}{h_0^2} \right)^{3/2} \right] + \frac{5N}{2}$$

Note that when the same partitioning happens, the entropy does not change. Further note that when calculating the average energy from the partition function, the $N!$ term drops out, hence this additional factor has no effect. It does not affect the pressure either.

Effect of N! The additional factor does not have a classical explanation. However, in quantum mechanics, this is a reasonable factor because the particles are indistinguishable. Hence this is a quantum mechanical effect in the macroscopic world.

Low temperature issues However, this equation does not seem to hold as $\tau < 0$, because the entropy will become negative (and even reach negative infinity if $\tau = 0$), which does not make physical sense.

Recall that the internal energy of the ideal gas is:

$$U = \frac{3}{2}N\tau$$

Hence we may write the entropy as a function of energy as:

$$\sigma_{IG} = N \ln \left[\frac{V}{N} \left(\frac{2\pi m(2U/3N)}{h_0^2} \right)^{3/2} \right] + \frac{5N}{2}$$

Quantum mechanically, we know that there is a ground state which represents the minimum amount of energy the system can have. This energy will be positive. Hence the entropy cannot go to negative infinity.

We now examine the condition for negative entropy:

$$\frac{N}{V} > \left(\frac{2\pi m\tau}{h_0^2} \right)^{3/2} \implies \sigma < 0$$

But quantum mechanically, we know that there is a lower bound for h_0, which is on the order of Planck's constant. Hence we will obtain a "Quantum Gas" if the density $\frac{N}{V}$ exceeds the RHS, which we call the quantum concentration n_Q. Numerically, for $T = 300K$ and helium gas, the quantum concentration is about $8 \times 10^{30} m^{-3}$ which is about several orders of magnitude larger than RTP concentration. The corresponding pressure to the quantum concentration is 3×10^5 atmospheres.

Description of Quantum Gases Since the particles are indistinguishable, we need to use particle distributions in a given energy state. The spin of the particle is key to determining the occupation number in each state, based on the spin-statistics theorem from QFT.

Spin Statistics Theorem Half-integer spin particles are fermions, that is, they are governed by Fermi-Dirac statistics. Each state may have either 1 or 0 particles. Integer spin particles are bosons, that is, they are governed by Bose-Einstein statistics, and each state can have any number of particles.

Photon Gas: Blackbody Radiation The spin of the particles is 1. Hence each state can have any number of particles. Consider an "empty" box with no matter, heated to a temperature τ. Let the box have a small hole. We view the system as a perfect gas (i.e. non-interacting) of identical photons with energies $E_i = \hbar\omega_i$. Alternatively, we can view the walls as harmonic oscillators with energies $\left(i + \frac{1}{2}\right)\hbar\omega_i, i = 1, 2, 3 \ldots$

Begin by calculating the partition function.

$$Z = \sum_{states} e^{-\beta E_i}, \beta = \frac{1}{\tau}$$

Note the following:

- There are two polarization states per photon.
- The eigenfrequencies are given by the boundary conditions. Assume a simple cube of length L. Then the eigenfrequencies are:

  $$\omega_i = \frac{m_i \pi c}{L}, \quad m_i^2 = n_x^2 + n_y^2 + n_z^2$$

  and the eigenfunctions are:

  $$\psi = \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L}$$

- The energy of the state depends on the occupation numbers. However, the occupation numbers are not fixed since there are no conservation laws for the number of photons

Hence we need to evaluate the following partition function:

$$Z = \sum_{n_1,\ldots} \exp\left(-\beta \sum_r n_r E_r\right) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \exp\left(-\beta(n_1 E_1 + \ldots)\right)$$

But we note that we can just write it as a product:

$$Z = \prod_{r=1}^{\infty} \sum_{n_r=0}^{\infty} e^{-\beta n_r E_r} = \prod_{r=1}^{\infty} \frac{1}{1-e^{-\beta E_r}}$$
$$\implies \ln Z = -\sum_{r=1}^{\infty} \ln(1-e^{-\beta E_r})$$

Now we can evaluate the other parameters:

$$U = \tau^2 \frac{\partial \ln Z}{\partial \tau} = \sum_{r=1}^{\infty} \frac{E_r}{e^{E_r/\tau}-1} = \sum_{r=1}^{\infty} \frac{\hbar\omega_r}{e^{\hbar\omega_r/\tau}-1}$$

To evaluate this sum, note that if we have an arbitrary sum:

$$\sum_r f(m_r) \approx \frac{1}{8}\int_0^{\infty} 4\pi m^2 dm f(m)$$

Hence we may calculate the energy, taking into account that there are two polarization modes (letting $m = \frac{L\omega}{\pi c}, dm = \frac{Ld\omega}{\pi c}$):

$$U = \sum_{r=1}^{\infty} \frac{\hbar\omega_r}{e^{\hbar\omega_r/\tau}-1} = \sum_{r=1}^{\infty} f(\omega_r) = \frac{2\cdot 4}{8}\int_0^{\infty} \pi\left(\frac{L}{\pi c}\right)^3 \omega^2 d\omega f(\omega)$$
$$U = \int_0^{\infty} \frac{L^3}{\pi^2 c^3}\frac{\hbar\omega^3}{e^{\hbar\omega/\tau}-1} d\omega = \frac{L^3\hbar}{\pi^2 c^3}\frac{\pi^4}{15(\hbar/\tau)^4} = \frac{L^3\pi^2}{15c^3\hbar^3}\tau^4 = \frac{V\pi^2}{15(\hbar c)^3}\tau^4$$

Now we can write the total energy as the integral of the spectral energy density:

$$\frac{U}{V} = \int_0^{\infty} u(\omega,\tau) d\omega \implies u(\omega,\tau) = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\hbar\omega/\tau}-1}$$

4.2 Thursday 23 Apr 2015

Photon/Boson Gas Recall that the average occupancy of the energy level E_i is given by:

$$\begin{aligned}\langle n_i \rangle &= \frac{\sum_{n_1}\sum_{n_2}\cdots n_i e^{-\sum_r n_r E_r/\tau}}{Z} \\ &= -\tau \frac{\partial \ln Z}{\partial E_i}\end{aligned}$$

with the partition function being:

$$\ln Z = -\sum_{r=1}^{\infty} \ln(1-e^{-E_r/\tau})$$

Hence substituting this into the average occupancy:

$$\langle n_i \rangle = \tau \frac{e^{-E_i/\tau}(1/\tau)}{1 - e^{-E_i/\tau}} = \frac{1}{e^{\hbar\omega_r/\tau} - 1}$$

which is consistent with the average energy of the photons:

$$U = \sum_r \frac{\hbar\omega_r}{e^{\beta\hbar\omega_r} - 1} = \sum_r E_r \langle n_r \rangle$$

Photon Pressure Recall that $p = -\left(\frac{\partial F}{\partial V}\right)_\tau$ where $F = -\tau \ln Z$. Then we have:

$$p = \tau \left(\frac{\partial \ln Z}{\partial V}\right)_\tau$$

where the ω_r was dependent on V, the dimensions of the box.

$$\omega_r = \frac{n_r \pi c}{L} = \frac{n_r \pi c}{V^{1/3}}$$

Hence we use the chain rule to write:

$$\begin{aligned}
p &= \tau \sum_r \frac{\partial}{\partial \omega_r} \left(-\sum_r \ln(1 - e^{-\hbar\omega_r/\tau}) \right) \frac{\partial \omega_r}{\partial V} \\
&= \tau \frac{\hbar}{\tau} \sum_r \frac{-e^{-\hbar\omega_r/\tau}}{1 - e^{-\hbar\omega_r/\tau}} \frac{n_r \pi c(-1/3)}{V^{4/3}} \\
&= \hbar \sum_r \frac{1}{e^{\hbar\omega_r/\tau} - 1} \frac{-\omega_r}{3V} \\
&= \sum_r \frac{\hbar\omega_r}{e^{\hbar\omega_r/\tau} - 1} \frac{1}{3V} \\
&= \frac{U}{3V}
\end{aligned}$$

Hence the photon gas equation of state is:

$$P = \frac{U}{3V}$$

Compare this to the ideal gas, where we had $U = \frac{3}{2}N\tau$ and $pV = N\tau$ which gives us:

$$P = \frac{2U}{3V}$$

Black Body Radiation: Wien's Law Recall that we had the Spectral energy density:

$$u(\omega, \tau) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/\tau} - 1}$$

The peak of this function in frequency corresponds to:

$$\hbar\omega_{max} = 2.82\tau$$

which is called Wien's law. We can also derive this in terms of wavelength. Note however that $\lambda_{\max} \neq \frac{2\pi c}{\omega_{max}}$. This is because:

$$u(\lambda, \tau) = u(\omega, \tau) \left| \frac{d\omega}{d\lambda} \right|$$

and hence $u(\lambda, \tau)$ is not necessarily maximized at ω_{max}. In terms of wavelengths, we have:

$$\lambda_{max} T = 2.9 \times 10^{-3} m \cdot K$$

Radiation Intensity We will define the energy flux through a small hole of unit area and call this the radiation intensity.

$$I(\omega, \tau) = \frac{\text{Energy}}{\text{Unit area, Unit Time, Unit Frequency}}$$

We want to integrate the energy coming out from the hole across all possible angles in the right half space. Let θ represent the angle from the horizontal.

$$\begin{aligned}
I(\omega, \tau) &= \int u(\omega, \tau) v_z \frac{d\Omega}{4\pi}, \quad v_z = c\cos\theta \\
&= \int_0^{2\pi} d\phi \int_0^{\pi/2} c\cos\theta \frac{\sin\theta d\theta d\phi}{4\pi} u(\omega, \tau) \\
&= \frac{c}{4} u(\omega, \tau)
\end{aligned}$$

Total energy Flux We integrate over all frequencies to get the total energy flux:

$$\begin{aligned}
J(\tau) &= \int u(\omega, \tau) d\omega \\
&= \frac{c}{4} \int u(\omega, \tau) d\omega \\
&= \frac{cU}{4V} \\
&= \frac{\pi^2}{60\hbar^3 c^2} T^4 \\
&= \sigma_B T^4
\end{aligned}$$

where σ_B is the Stefan-Boltzmann constant.

Kirchoff's Law Characterises how good a blackbody is able to emit and absorb radiation. A perfect blackbody absorbs all EM radiation.

Note that for an object to be in thermal equilibrium, it has to absorb radiation at the same rate that it emits it. Then we can characterize the emissivity of a blackbody by comparing its rate of emission e or absorption to that of a perfect blackbody. We also define the reflectivity $r = 1 - e$. $e = 1$ if the object is a perfect blackbody.

Phonon Gas describes the elastic oscillations of a solid. We can use this model to estimate the heat capacity of the system:

$$C_v = \left(\frac{\partial U}{\partial \tau} \right)_V$$

For a periodic elastic solid, the normal modes give the eigenfrequencies. There is a cut-off frequency corresponding to the maximum mode - the zig-zag mode with a maximum wavelength equal to $2a$, the separation between "beads".

Debye Model We treat three types of oscillations: 2 transverse and one longitudinal. We treat it like an ideal photon gas with no interparticle interactions. Then the partition function is:

$$Z = \sum_{n_1} \sum_{n_2} \cdots e^{-\beta \sum_{r=1}^{r_{max}} n_r E_r}$$

Then the average occupancy is the same as in the photon gas:

$$\langle n_i \rangle = \frac{1}{e^{\hbar\omega_i/\tau} - 1}$$

Then the average energy is:

$$U = \sum_{r=1}^{r_{max}} \langle n_r \rangle \hbar\omega_r$$

which we can integrate using the density of states $\rho(\omega)$:

$$\sum_{r=1}^{r_{max}} = \int_0^{\omega_{max}} f(\omega)\rho(\omega)d\omega$$

Recall that for the harmonic oscillator,

$$\omega_r = \frac{n_r \pi v}{L}$$

where v is the velocity. We assume that the longitudinal velocity is the same as the transverse velocity. Then the density of states, which is the number of modes between n and $n + dn$ (n is large hence we index it as a continuous variable) is given by:

$$\rho(n)dn = \frac{1}{8} 4\pi n^2 dn(3)$$

where the 1/8 comes from considering only the positive octant and the 3 comes from the three possible polarizations. The index n can also be written as

$$n = \frac{\omega L}{\pi v} \implies dn = \frac{L d\omega}{\pi v}$$

and we substitute this into the expression for the energy:

$$\begin{aligned} U &= \int_0^{\omega_{max}} d\omega \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} \frac{3\pi}{2} \left(\frac{L}{\pi v}\right)^3 \omega^2 \\ &= \frac{3L^3\tau^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_{max}} \frac{x^3}{e^x - 1} dx \end{aligned}$$

Now we know that the total number of modes is given by $3N$, the total number of degrees of freedom. This means that:

$$\frac{3N}{V} = \int_0^{\omega_{max}} \rho(\omega)d\omega$$

and hence we obtain that $\omega_{max} = \left(\frac{6N\pi^2}{V}\right)^{1/3} v$

Chapter 5

Week 5

5.1 Tuesday 28 Apr 2015

Phonon Energy Recall that the phonon energy could be written as:

$$U = \frac{3V\tau^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_{max}} \frac{x^3 dx}{e^x - 1}, \quad x = \frac{\hbar\omega}{\tau}$$

where x_{max} is finite because there is a maximum frequency corresponding to a finite number of particles in the zig-zag mode. We write:

$$x_{max} = \frac{\hbar\omega_D}{\tau} = \frac{k\theta_D}{\tau}$$

where ω_D is the Debye frequency and θ_D is the Debye temperature. Now we implement the constraint on the density of states:

$$\int_0^{\omega_D} \rho(\omega) d\omega = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 v^3} d\omega = \frac{V\omega_D^3}{2\pi^2 v^3} = 3N$$

$$\implies \omega_D = \left(\frac{6N\pi^2}{V}\right)^{1/3} v$$

where N is the number of atoms.

Now we can calculate C_v by taking the derivative:

$$C_v = \left(\frac{\partial U}{\partial \tau}\right)_V$$

We consider low temperature and high temperature limits. When $\tau \to 0$, we have $x_{max} >> 1$ and hence we approximate it to infinity.

$$U = \frac{3V\tau^4}{2\pi^2 v^3 \hbar^3} \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{3V\tau^4}{2\pi^2 v^3 \hbar^3} \frac{\pi^4}{15} = \frac{V\pi^2\tau^4}{10 v^3 \hbar^3}$$

$$\implies C_V = \frac{2V\pi^2\tau^3}{5v^3\hbar^3}$$

as $\tau \to \infty$, we Taylor expand the denominator:

$$U = \frac{3V\tau^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_{max}} \frac{x^3 dx}{(1 + x + \ldots) - 1} \approx \frac{3V\tau^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_{max}} x^2 dx = \frac{V\tau^4 x_{max}^3}{2\pi^2 v^3 \hbar^3} = 3N\tau$$

$$\implies C_V = 3N$$

Chemical Potential Recall the different kinds of ensembles:

- Microcanonical Ensemble: (N,V,U) are held fixed and the properties of the system are obtained from the number of microstates $g(N,V,U)$. Properties can be obtained from $\sigma = \ln g$.
- Canonical Ensemble: (N,V,τ) are held fixed. Properties can be calculated from the partition function $Z = \sum_{\text{states}} e^{-E_i/\tau}$.
- **New:** Grand Canonical Ensemble (GCE): (V,τ,μ) are fixed. Properties come from the Grand Partition function $\mathcal{Z}$.

Derivation First consider the canonical ensemble and let the macrostate vary. Then:

$$\begin{aligned} d\sigma &= \left(\frac{\partial\sigma}{\partial U}\right)_{V,N} dU + \left(\frac{\partial\sigma}{\partial V}\right)_{U,N} dV + \left(\frac{\partial\sigma}{\partial N}\right)_{V,U} dN \\ &= \frac{1}{\tau}dU + \frac{P}{\tau}dV + \xi dN \end{aligned}$$

where we define:

$$\xi = \left(\frac{\partial\sigma}{\partial N}\right)_{V,U}$$

so that we have the thermodynamic identity:

$$dU = \tau d\sigma - pdV - \xi\tau dN$$

Now define:

$$\mu = -\xi\tau$$

so that the identity becomes:

$$\begin{aligned} dU &= \tau d\sigma - pdV + \mu dN \\ \mu &= -\tau\left(\frac{\partial\sigma}{\partial N}\right)_{V,U} \end{aligned}$$

What is the Chemical Potential? Consider the free energy:

$$\begin{aligned} F = U - \tau\sigma \implies dF \\ &= dU - \tau d\sigma - \sigma d\tau \\ &= \tau d\sigma - pdV + \mu dN - \tau d\sigma - \sigma d\tau \\ &= \mu dN - pdV - \sigma d\tau \\ \implies \mu &= \left(\frac{\partial F}{\partial N}\right)_{V,\tau} \end{aligned}$$

Hence μ is the free energy to add or remove 1 particle. For instance, in an ideal gas at fixed τ,

$$
\begin{aligned}
Z_N^{class} &= \frac{(n_Q V)^N}{N!}, \quad n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2} \\
\implies F &= -\tau \ln Z = -\tau N \ln(n_Q V) + \tau \ln N! \\
&= -\tau N \ln n_Q V + \tau N \ln N - \tau N \\
\implies \left(\frac{\partial F}{\partial N}\right)_{V,\tau} &= -\tau \ln n_Q V + \tau \ln N + \tau - \tau \\
&= -\tau \ln \frac{n_Q V}{N} \\
&= \tau \ln \frac{n}{n_Q}
\end{aligned}
$$

Chemical Potential in Equilibrium Consider a system with a fixed U, V, N and place a mesh to split the system into two parts (System 1 and System 2), with volumes V_1, V_2. The two systems can exchange U, V, N. At equilibrium, the most probable state dominates: $\sigma = \ln g$ is maximum and $d\sigma = 0$. Now the total infinitesimal entropy change is:

$$d\sigma = d\sigma_1 + d\sigma_2$$

Now the total energy, total volume and total particles is conserved:

$$
\begin{aligned}
d(U_1 + U_2) = 0 &\implies dU_1 = -dU_2 \\
d(V_1 + V_2) = 0 &\implies dV_1 = -dV_2 \\
d(N_1 + N_2) = 0 &\implies dN_1 = -dN_2
\end{aligned}
$$

and hence:

$$d\sigma = 0 = \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) dU_1 - \left(\frac{P_1}{\tau_1} - \frac{P_2}{\tau_2}\right) dV - \left(\frac{\mu_1}{\tau_1} - \frac{\mu_2}{\tau_2}\right) dN_1$$

and hence for the entropy change to vanish for arbitrary changes dU_1, dV_1, dN_1, we hence require at equilibrium:

$$
\begin{aligned}
\tau_1 &= \tau_2 \\
P_1 &= P_2 \\
\mu_1 &= \mu_2
\end{aligned}
$$

Example: Elevated half-system Now consider the situation where half the system is elevated with respect to the other half. Let System 2 be h above System 1 in uniform gravitational field g. Let $V_1 = V_2, N_1 = N_2, \tau_1 = \tau_2$. Note that μ has dimensions of energy. Hence it takes more energy to add a particle to 2 as compared to 1. Note that the internal energy of system 2 is:

$$
\begin{aligned}
U_2 &= \frac{3}{2} N\tau + Nmgh \\
\implies F_2 - F_1 &= (U_2 - U_1) - \tau_2\sigma_2 + \tau_1\sigma_1 = Nmgh
\end{aligned}
$$

This difference in free energy to add a particle is the external chemical potential.

The total chemical potential is the sum of the contributions from internal and external chemical potentials:

$$\mu_{tot} = \mu_{internal} + \mu_{external}$$

Grand Partition Function (Gibbs Sum) Consider a small system S that can exchange particles and energy with a large reservoir R. We want to calculate the probability that the system is in a particular combination of energy and number of particles: E_s, N_s. Note that the total energy and number of particles is a constant:

$$\begin{aligned} E_T &= E_s + E_R \\ N_T &= N_s + N_R \end{aligned}$$

The probability that the system has E_s, N_s is the same as the probability that the reservoir has $E_T - E_s, N_T - N_s$, which is proportional to the multiplicity of the reservoir with that parameters. We perform a Taylor expansion of the multiplicity function for the reservoir:

$$\begin{aligned} \ln g_R(E_R, N_R) &\approx \ln g_R(E_T, N_T) + (-E_s)\left(\frac{\partial \ln g_R}{\partial E_R}\right)_{E_T} + (-N_s)\left(\frac{\partial \ln g_R}{\partial N_R}\right)_{N_T} \\ &= \ln g_R(E_T, N_T) - E_s\frac{1}{\tau} - N_s\frac{-\mu}{\tau} \end{aligned}$$

and exponentiating both sides,

$$g_R(E_R, N_R) \approx g_R(E_T, N_T)\exp\left(-\frac{E_s}{\tau} + \frac{\mu N_s}{\tau}\right) = g_R(E_T, N_T)\exp\left(\beta(\mu N_s - E_s)\right)$$

Hence the probability is (using the normalization by summing over all states):

$$P_s(E_s, N_s) = \frac{e^{\beta(\mu N_s - E_s)}}{\sum_{\text{states}}\sum_{N_s=0}^{N} e^{\beta(\mu N_s - E_s)}}$$

where the states refer to energy states, hence we also need to sum over all N_s. We can also write:

$$\mathcal{Z} = \sum_{\text{states}}\sum_{N_s} \lambda^{N_s} e^{-E_s/\tau}, \quad \lambda = e^{\beta\mu}$$

where $\mathcal{Z}$ is the grand partition function. Something here is called the absolute activity. The thermodynamic average of a quantity is hence given by:

$$\langle A \rangle = \frac{\sum\sum A\lambda^{N_s} e^{-E_s/\tau}}{\mathcal{Z}}$$

and if $A = N_s$, then:

$$\langle N_s \rangle = \frac{\lambda}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \lambda}$$

Application of chemical potential Consider a system of ideal gas connected by a small hole in a heat bath with temperature τ. Partition the system into two halves, one above the other. Let the total height of the box be L. Hence $V_1 = V_2, \tau_1 = \tau_2$. Let there be a gravitational field g. We want to find the ratio of the particles in the top box as compared to that of the bottom box. Now for equilibrium we require $\mu_1 = \mu_2$. We know that:

$$\mu_{tot} = \mu_{ideal} + \mu_{external} = \mu_{ideal} + mgz$$

and the ideal chemical potential for the ideal gas is:

$$\mu_{ideal} = \tau \ln \frac{n}{n_Q}$$

Hence:

$$\mu_{tot}(z) = \tau \ln \frac{n(z)}{n_Q} + mgz$$

But at equilibrium, the chemical potential is constant everywhere. Hence $\mu_{tot}(z) = \text{constant}$. Hence solving for $n(z)$,

$$\frac{n(z)}{n_Q} = \frac{n(0)}{n_Q} e^{-mgz/\tau}$$

Real Chemical Equilibrium Consider hydrogen and oxygen becoming water. Abusing notation,

$$2H_2O - 2H_2 - O_2 = 0$$

In general, we have the stochiometric constraint:

$$\sum_i a_i X_i = 0$$

Now the condition for equilibrium at a constant temperature and volume is given by:

$$dF = 0 \implies \sum_i \left(\frac{\partial F}{\partial N_i}\right)_{V,\tau} dN_i = 0$$

Note that the partial derivative is the chemical potential. This means that if dN reactions occur, and component i changes by $dN_i = a_i dN$, then the equilibrium condition is:

$$\sum_i \mu_i a_i dN$$

and since dN is arbitrary, the condition for equilibrium is:

$$\sum_i \mu_i a_i = 0$$

5.2 Thursday 30 Apr 2015

Example of Chemical Equilibrium Consider room temperature $300K$. We want to find how many electron-positron pairs exist due to Blackbody radiation giving $\gamma + \gamma \to e^+ + e^-$. The stoichiometric equation is $2N_\gamma - N_{e^+} - N_{e^-} = 0$. From the chemical equilibrium condition,

$$\sum_i \mu_i a_i = 0 \implies 2\mu_\gamma - \mu_{e^+} - \mu_{e^-} = 0$$

But blackbody photons have zero chemical potential because the number of photons is not fixed. Hence:

$$\mu_{e^+} = -\mu_{e^-}$$

Since the temperature is high, we approximate the electrons as an ideal gas.

$$\mu_{e^\pm} = \tau \ln \frac{n_{e^\pm}}{n_Q} + m_{e^\pm} c^2$$

and imposing the chemical equilibrium condition (considering $\mu_{ext} = m_e c^2$ because it takes the rest mass energy to add a particle):

$$\mu_{e^+} = -\mu_{e^-} \implies \tau \ln \frac{n_{e^\pm}}{n_Q} + m_e c^2 = -\tau \ln \frac{n_{e^\pm}}{n_Q} - m_e c^2$$
$$\implies \frac{n_e^- n_e^+}{n_Q^2} = e^{2m_e c^2/\tau}$$

Now assuming that there is no initial charge in the room, we also require that:

$$n_e^+ = n_e^- = n$$

and hence:

$$n = n_Q e^{m_e c^2/\tau}, \quad n_Q = \left(\frac{m_e \tau}{2\pi\hbar^2}\right)^{3/2}$$

which gives a numerical value of practically zero because of the exponential dependence.

Quantum Gas Consider two identical particles in a 1D well. The Hamiltonian of the system is:

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) - (V(x_1) + V(x_2))$$

which has solutions:

$$\Phi_{12} = \frac{2}{L} \sin \frac{n_1 \pi x_1}{L} \sin \frac{n_2 \pi x_2}{L}$$

and energy eigenvalues:

$$E_{12} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2)$$

This wavefunction does not work for identical particles because it implies that we can tell the state that each particle is in. The actual wavefunction must be a superposition of the original wavefunction with the wavefunction in which the particles are switched:

$$\Phi_{21} = \frac{2}{L} \sin \frac{n_2 \pi x_1}{L} \sin \frac{n_1 \pi x_2}{L}, \quad E_{21} = E_{12} = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2)$$

and the 2-particle wavefunction should be an eigenstate of the exchange operator $\hat{\chi}$, which is defined as:

$$\hat{\chi}\Phi_{12} = \Phi_{21}$$

The eigenstates of the exchange operator are:

$$\Phi_S = \frac{1}{\sqrt{2}}(\Phi_{12} + \Phi_{21}) \quad \text{symmetric state}$$
$$\Phi_A = \frac{1}{\sqrt{2}}(\Phi_{12} - \Phi_{21}) \quad \text{antisymmetric state}$$

and the eigenvalues are:

$$\hat{\chi}\Phi_S = \Phi_S \implies \lambda = 1$$
$$\hat{\chi}\Phi_A = -\Phi_A \implies \lambda = -1$$

Note that if both particles are at the same energy level, $n_1 = n_2$, then $\Phi_{12} = \Phi_{21}$ so $\Phi_A = 0$. Hence the antisymmetric wavefunction cannot have two particles in the same state.

Also, due to relativistic quantum mechanics, all identical two-particle states must be in either Φ_A, Φ_S depending on the spin.

Spin-statistics Theorem, Qualitatively :

- All particles are either Fermions or Bosons given by the intrinsic spin of the particle (Fermions have half-integer spin when projected along a particular axis and Bosons have integer spin when projected along a particular axis - includes zero)
- Consider the rotation operator $\hat{R}$ which rotates the wavefunction about a certain axis for an angle:

  $$\hat{R}(\delta\phi)f(\phi) = f(\phi + \delta\phi)$$

  For a small rotation, we can perform a Taylor expansion:

  $$\hat{R}(\delta\phi)f(\phi) = f(\phi) + f'(\phi)\delta\phi + \frac{\delta\phi^2}{2!}f''(\phi)\ldots = \left(\hat{1} + \delta\phi\frac{\partial}{\partial\phi} + \frac{\delta\phi^2}{2!}\frac{\partial^2}{\partial\phi^2}\right)f(\phi)$$
  $$\implies \hat{R}(\delta\phi)f(\phi) = e^{\delta\phi\frac{\partial}{\partial\phi}}f(\phi)$$

  and since $\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$ we have $\hat{R} = e^{i\delta\phi L_z/\hbar}$
  and in general for a finite rotation $\Delta\phi = n\delta\phi$:

  $$\hat{R}(\Delta\phi) = \left[\hat{R}(\delta\phi)\right]^N = e^{-\Delta\phi L_z/\hbar}$$

  We now make the leap of faith that this formulation is also true for intrinsic spin angular momentum. That is, for the total angular momentum along the z-axis:

  $$\hat{R}(\Delta\phi) = e^{i\Delta\phi J_z/\hbar}$$

- We require that the exchange of particles is always accompanied by rotation of the space by 2π because space-time and spin are intertwined in Relativistic Quantum Mechanics.

Combining the above arguments,

$$\hat{R}(2\pi)\Phi_{\text{spin half}} = e^{i(2\pi)(\hbar/2)/\hbar} = e^{i\pi} = -1$$
$$\hat{R}(2\pi)\Phi_{\text{spin integer}} = e^{i(2\pi)(n\hbar)/\hbar} = e^{2n\pi i} = 1$$

Therefore, Fermions must be in the antisymmetric state Φ_A, and Bosons must be in the symmetric state Φ_S. Note that if the particle is composed of multiple particles (composite), then we need to take the sum of the individual intrinsic spins to determine if the particle is a Fermion or Boson, provided that the temperature is small compared to the rest mass of the particle so that the particle does not break up into the constituent quarks or elementary particles.

Examples of Fermions and Bosons Fermions: Electrons and protons (spin half), Delta particle (spin 3/2), Helium-3 (spin half), mercury-187 (spin 13/2). Bosons: Pion (spin 0), photon (spin 1), hydrogen molecule (spin 0 or 1, depending on ortho or para hydrogen)

Physical analogy: "Social" behaviour of particles Consider three energy levels, and consider the distribution of particles under each model (classical, Boson, Fermion).

Under the classical model, the particles are distinguishable and there are 6 possible combinations where there is one particle in each state, and 3 combinations where the particles are in the same state. Hence there are a total of 9 combinations.

For Bosons, there are three possibilities where the particles are in different states and three possibilities where the particles are in the same state. Hence there are a total of 6 combinations.

For Fermions, there are only three possibilities where the particles are in different states. The particles cannot be in the same state because the Fermions have an antisymmetric state and putting the particles in the same state results in a symmetric state.

Statistical Mechanics of Bosons and Fermions Consider a single state with energy E_i in contact with a reservoir, and let the system exchange energy and particles. We need the grand partition function:

$$\mathcal{Z} = \sum_N e^{(\mu N - N E_i)/\tau}$$

since the total energy is $E_{tot} = N E_i$. For Fermions, N is either 0 or 1:

$$\mathcal{Z}_{FD}(E_i) = \sum_{N=0}^{1} e^{(\mu N - N E_i)/\tau}$$

whereas for Bosons, N can take any integer value:

$$\mathcal{Z}_{BE}(E_i) = \sum_{N=0}^{\infty} e^{(\mu N - N E_i)/\tau}$$

5.3 Midterm Revision

Photon Partition Function

$$\begin{aligned}
Z &= \sum_r e^{-\beta E_r}, \quad E_r = \sum_i n_i \epsilon_i \\
Z &= \sum_{n_1, n_2, \ldots} \exp\left(-\beta \sum_i n_i \epsilon_i\right) \\
&= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \exp\left(-\beta \sum_i n_i \epsilon_i\right) \\
&= \prod_{j=1}^{\infty} \left(\sum_{n_j} e^{-\beta n_j \epsilon_j}\right) \\
&= \prod_{j=1}^{\infty} \frac{1}{1 - e^{-\beta \epsilon_j}} \\
\langle n_i \rangle &= -\frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \epsilon_i}\right)_{\beta, \epsilon_j} \\
&= \frac{1}{e^{\beta \epsilon_i} - 1}
\end{aligned}$$

Density of States in k-space Remember to multiply by 2 to account for polarization.

$$f(k)dk = \frac{Vk^2dk}{2\pi^2}$$

Energy in each mode

$$dE_\omega = \hbar\omega dN_\omega = \hbar\omega(\langle n_i\rangle f(\omega)d\omega) = \hbar\omega\frac{1}{e^{\beta\hbar\omega}-1}\frac{V\omega^2d\omega}{\pi^2c^3}d\omega = u(\omega,T)d\omega \times V$$
$$\implies u(\omega,T) = \frac{\hbar\omega^3}{\pi^2c^3(e^{\beta\hbar\omega}-1)}$$

Photon Entropy

$$S = \frac{4}{45}\pi^2k_B^4V\left(\frac{T}{c\hbar}\right)^3$$
$$\sigma = \frac{4}{45}\pi^2\tau^3V\frac{1}{c^3\hbar^3}$$

Radiation Pressure
For an ideal gas of N particles, each of mass m, write:

$$pV = \frac{1}{3}Nm\langle v^2\rangle$$
$$\implies p = \frac{1}{3}\frac{M}{V}\langle c^2\rangle \implies p = \frac{1}{3}\frac{E}{V} = \frac{1}{3}U(T)$$

Equipartition Theorem Each velocity component (linear or angular) has an average energy of $\frac{kT}{2} = \frac{\tau}{2}$ associated with it.

Single Harmonic Oscillator

$$\langle U\rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}$$

Chapter 6

Week 6

6.1 Tuesday 5 May 2015

Statistic mechanics of Fermions and Bosons Consider a perfect gas with no inter-atomic interactions. Then the single-state grand partition function (for a single state E_i, N number of particles) was:

$$\mathcal{Z}_{FD} = \sum_{N_s=0}^{1} \exp\left(\frac{\mu N_s - N_s E_i}{\tau}\right)$$
$$\mathcal{Z}_{BE} = \sum_{N_s=0}^{\infty} \exp\left(\frac{\mu N_S - N_s E_i}{\tau}\right)$$

Now the Bose-Einstein summation should have an upper limit of the number of particles, but we can approximate it to infinity.

Quantum gas of electrons in metals The concentration of electrons in a conducting metal exceeds that of the quantum concentration, hence we need to consider such quantum effects in calculating the heat capacity.

Fermi-Dirac Occupation Number By definition:

$$\begin{aligned} f_{FD}(E_i) &= \langle N_s \rangle \\ &= \frac{\sum_{N_s=0}^{1} N_s e^{(\mu N_s - N_s E_i)/\tau}}{\mathcal{Z}_{FD}} \\ &= \frac{e^{(\mu - E_i)/\tau}}{1 + e^{(\mu - E_i)/\tau}} \\ &= \frac{1}{e^{(E_i - \mu)/\tau} + 1} \end{aligned}$$

Consider the low-temperature behaviour $\tau \to 0$. Then:

$$\lim_{\tau \to 0} \left[\frac{1}{e^{(E_i - \mu)/\tau} + 1}\right] = \begin{cases} 1, & E_i - \mu < 0 \\ 0, & E_i - \mu > 0 \end{cases}$$

The transition from zero to one at low temperature occurs at the Fermi energy, which is defined by $E_F = \mu$. The Fermi energy represents the maximum energy level when all the lowest energy states are filled. We can solve for μ numerically (as a function of temperature) by noting that:

$$\sum_i \langle N_i \rangle = N$$
$$\implies \sum_{\text{states}} f(E_i) = \sum_{\text{states}} \frac{1}{e^{(E_i - \mu)/\tau} + 1} = N$$

which gives $\mu(T)$. The Fermi energy is then defined by:

$$E_F = \mu(\tau = 0)$$

Bose-Einstein Occupation Number Proceed by definition:

$$\begin{aligned}
f_{BE}(E_i) &= \langle N_s \rangle \\
&= \sum_{N_s=0}^{\infty} \frac{N_s e^{(\mu N_s - E_i N_s)/\tau}}{\mathcal{Z}_{BE}} \\
&= \frac{\sum_{N_s=0}^{\infty} N_s x^{N_s}}{\sum_{N_s=0}^{\infty} x^{N_s}}, \quad x = e^{(\mu - E_i)/\tau} \\
&= \frac{x \frac{d}{dx}\left(\frac{1}{1-x}\right)}{\frac{1}{1-x}} \\
&= \frac{x}{1-x} \\
&= \frac{1}{e^{(E_i-\mu)/\tau} - 1}
\end{aligned}$$

Note that for $\mu = 0$, we obtain the photon gas occupancy number for blackbody radiation:

$$f_{photon} = f_{BE}(\mu = 0) = \frac{1}{e^{E_i/\tau} - 1} = \frac{1}{e^{\hbar\omega_i/\tau} - 1}$$

We now examine the low-temperature limit as $\tau \to 0$. Then:

$$\lim_{\tau \to 0} \frac{1}{e^{(E_i-\mu)/\tau} - 1} = 0, \quad E_i > \mu$$

But if $\mu \lessapprox E_0$ for $\tau \gtrapprox 0$ for the ground state energy E_0, we expect that all the particles will be in the ground state, so that $f_{BE}(E_0) = N$:

$$f_{BE}(E_0) = \frac{1}{e^{(E_0-\mu)/\tau} - 1} \approx \frac{1}{1 + \frac{E_0-\mu}{\tau} + \ldots - 1} = N \implies \mu = E_0 - \frac{\tau}{N}$$

Clearly, as $\tau \to 0$, the ground state occupancy must go to the total number of particles, hence the chemical potential has to be given by:

$$\mu(\tau) = E_0 - \frac{\tau}{N}$$

Approach of Fermi/Bose gases to classical gas behaviour To get a classical gas, we want the probability of any state being occupied to be small. That is,

$$f_{FD}(E_i), f_{BE}(E_i) << 1, \quad \forall E_i$$

For the FD distribution, this occurs when:

$$\frac{E_i - \mu}{\tau} >> 1 \implies \tau << E_i - \mu$$

which seems to indicate a low temperature. Does it? We examine the classical approximation (since we expect that both Fermi and Bose gases will converge to behave like a classical gas under low occupancies):

$$f_{class}(E_i) = f_{FD}(E_i; \tau << E_i - \mu) = f_{BE}(E_i; \tau << E_i - \mu) = e^{-(E_i - \mu)/\tau}$$

Solving for the chemical potential, we impose the condition that the sum of the expectation occupancies across all states E_i must equal N, the number of particles. Then:

$$\sum_i \langle N_i \rangle = N \implies \sum e^{\mu/\tau} e^{-E_i/\tau} = e^{\mu/\tau} \sum e^{-E_i/\tau} = e^{\mu/\tau} Z_1 = N$$

Hence the classical chemical potential is:

$$\mu(\tau) = \tau \ln \frac{N}{Z_1} = \tau \ln \frac{N}{n_Q V} = \tau \ln \frac{n}{n_Q}$$

Hence when $n << n_Q$, $\ln \frac{n}{n_Q}$ is a large negative number. The chemical potential of an ideal gas is highly negative. The free energy goes down when we add a particle (adding a particle causes the entropy to increase, and since $F = U - \tau\sigma$, F decreases). Hence the classical limit condition:

$$\tau << E_i - \mu_{class}, \quad \forall E_i$$

has the RHS actually subtracting a large negative number. Hence the RHS can actually be very large (and we can ignore E_i), and the inequality holds as long as :

$$n << n_Q \implies \frac{N}{V} << \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2} \implies \tau >> \frac{2\pi\hbar^2 n^{2/3}}{m}$$

We call the RHS the quantum temperature:

$$\tau_Q = \frac{2\pi\hbar^2 n^{2/3}}{m}$$

which has value of $0.01K$ for nitrogen at 1 atmosphere. Clearly, nitrogen behaves like a classical ideal gas at room pressure.

Concluding topics for Ideal Gas :

- A classical gas with "internal" degrees of freedom (like real atoms with other forms of kinetic energy other than translational). A molecule can have rotational and vibrational degrees of freedom. Consider the canonical ensemble:

  $$Z_N = \frac{(Z_1^{class})^N}{N!}$$
  $$Z_1^{class} = \sum e^{-E_i/\tau}$$

  Recall that we derived

  $$Z_1^{class} = n_Q V$$

  by making the assumption that $E_i = \frac{P_i^2}{2m}$ (i.e. we only considered translational kinetic energy). More complicated systems have other contributions to E_i. For instance:

$$\begin{aligned} E_i &= E_{\text{translational}} + E_{\text{electronic}} + E_{\text{rotational}} + E_{\text{vibrational}} \\ &= \frac{P^2}{2m} + (\text{a few eV, not very important}) + \frac{\hbar^2 J(J+1)}{2I} + \hbar\omega \end{aligned}$$

Now the electronic energy levels are separated by a few eVs, which is not very important at room temperature, which is associated with a thermal average energy of around $\frac{1}{40}eV$. Vibrational energy levels are spaced by around $0.1eV$, and hence are more significant than the electronic energy transitions. Rotational energy levels have a energy difference of around $10^{-3} - 10^{-4}eV$, and hence are even more important that the vibrational energy transitions at lower energies.

With all these energy contributions, we note that the partition function factors into the product of several individual functions since their quantum numbers are independent:

$$\begin{aligned} Z_1^{class} &= \sum_{T,V,E,R} e^{-(E_T+E_V+E_E+E_R)/\tau} \\ &= \left(\sum_T e^{-E_T/\tau}\right)\left(\sum_V e^{-E_V/\tau}\right)\left(\sum_E e^{-E_E/\tau}\right)\left(\sum_R e^{-E_R/\tau}\right) \\ &= Z_1^T Z_1^V Z_1^E Z_1^R \\ &= Z_1^T (Z_1^{int}), \quad Z_1^{int} = Z_1^V Z_1^E Z_1^R \end{aligned}$$

Hence when calculating the thermodynamic parameters, there are additional additive contributions from the other degrees of freedom (logarithm turns products into sums).

$$\begin{aligned} F &= F_T + F_{int} \\ \sigma &= \sigma_T + \sigma_{int} \\ \mu &= \tau \ln \frac{n}{n_Q} - \tau \ln Z^{int} \end{aligned}$$

- Heat Capacity of electrons in a metal. Recall that the heat capacity at constant volume for an ideal gas is just:

$$\begin{aligned} C_V &= \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_V \\ \sigma_{ideal} &= N\left[\ln \frac{n_Q}{n} + \frac{5}{2}\right] \\ \implies C_V &= \frac{3}{2}N \end{aligned}$$

The heat capacity at constant pressure can also be calculated:

$$\begin{aligned} C_P &= \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_P \\ PV = N\tau &\implies V = \frac{N\tau}{P} \\ \implies \sigma(P) &= N\left[\ln \frac{n_Q}{N/(N\tau/P)} + \frac{5}{2}\right] = N\left[\ln \frac{\tau n_Q}{P} + \frac{5}{2}\right] \\ \implies C_P &= \frac{5}{2}N \end{aligned}$$

6.2 Thursday 7 May 2015

Fermi Energy Recall that the Fermi energy was defined at $\tau = 0$, when all energy levels from the ground state were filled up to E_F. Consider a 3D quantum cube. Then the energy levels are:

$$E_{n_T} = \frac{n_T^2 \pi^2 \hbar^2}{2mL^2}, n_T^2 = n_x^2 + n_y^2 + n_z^2$$

then number of states is given by the volume of the sphere octant such that all the states are filled up to the "Fermi Surface". Analytically,

$$N = \frac{1}{8}\frac{4\pi}{3} n_{max}^3 \times 2$$

where the 2 should actually be more generally $2s+1$, where s is the spin of the fermi system. Solving,

$$n_{max} = \left(\frac{3N}{\pi}\right)^{1/3}$$

$$\text{If the spin is arbitrary, } n_{max} = \left(\frac{6N}{(2s+1)\pi}\right)^{1/3}$$

$$E_F = E(n_T = n_{max}) = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}, \quad n = \frac{N}{V}$$

Now we can calculate the total energy of the Fermi system at $\tau = 0$:

$$U(\tau = 0) = 2\sum_{n_T=0}^{n_{max}} E_{n_T} \approx 2\int_0^{n_{max}} E_{n_T} \frac{4\pi n_T^2}{8} dn_T = \frac{3}{5} N E_F$$

This is a significant nonzero amount of energy at zero temperature.

Fermi Gas at nonzero temperatures Consider the thermal average energy:

$$U = \langle E \rangle = 2\sum_{n_x}\sum_{n_y}\sum_{n_z} E_{n_T} f_{FD}(E_{n_T})$$

and for large N we can replace the sum with an integral. Consider the arbitrary function:

$$\begin{aligned}\langle A(E) \rangle &= A(E) f_{FD}(E) \\ &= \frac{2}{8}\int_0^\infty 4\pi n_T^2 dn_T A(E) f_{FD}(E) \\ &= \int_0^\pi A(E) f_{FD}(E)\rho(E) dE\end{aligned}$$

where $\rho(E)$ is the density of states after making the change of variables. Analytically,

$$\rho(E) = \frac{V}{2\pi^2\hbar^3}(2m)^{3/2} E^{1/2}$$

Note that for a general fermi gas, the total number of particles has to satisfy:

$$N = \int_0^\infty \rho(E) f_{FD}(E) dE$$

which will indirectly give $\mu(\tau)$ because f_{FD} is dependent on τ. Note that $\rho(E)$ is not dependent on τ, but only on the energy structure of the system. Recall that:

$$f_{FD}(E) = \frac{1}{e^{(E-\mu)/\tau} + 1}$$

hence this constraint yields $\mu(\tau)$.

Application of Fermi Gas Note that the equations describing a Fermi gas are only different from a Bose gas at low temperatures.

- **Explanation of Low Temperature heat capacity of Metals** Recall that the Debye model used the elastic oscillations of atoms in a solid to give the heat capacity at constant volume for phonons:

  $$C_V^{phonons} = \left(\frac{2V\pi^2}{5\hbar^3 v^3}\right)\tau^3 = \frac{12\pi^2 N}{5}\left(\frac{\tau}{k\theta_D}\right)^3$$

  which works very well for materials in which the primary contribution to the heat capacity are phonons. For metals, this formula fails because a large contribution is from the electrons at high concentration.

  Consider a metal that has 1 free conduction electron per atom. The density of electrons is much larger than the quantum concentration, hence we cannot use classical means to explain the electron gas in the metal $n \sim 10^{23} cm^{-3}, n_Q \sim 10^{18} cm^{-3}$. Furthermore, the fermi energy for the electrons is around $8eV$, indicating that room temperature (corresponding to around $\frac{1}{40}eV$) is cold as compared to that of the Fermi energy. We call this a degenerate system, or a degenerate Fermi gas.

  To obtain the heat capacity, we need an expression for the internal energy:

  $$U = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3}\int_0^\infty \frac{E^{3/2}dE}{e^{(E-\mu(\tau))/\tau}+1}$$

  where we are using the formula from above with $A(E) = E$. We will like this expression to be evaluated for $E \approx E_F = \mu(\tau = 0)$. Change variables $x = \frac{E}{\tau}$. Then:

  $$U = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3}\tau^{5/2}\int_0^\infty \frac{x^{3/2}}{e^{-\alpha}e^x+1}dx, \quad \alpha = \frac{E_F}{\tau}$$

  Note that $\alpha >> 1$, so there is an approximation (Sommerfeld?)

  $$\int_0^\infty \frac{\phi(x)}{e^{x-\alpha}+1} \approx \int_0^\alpha \phi(x)dx + \frac{\pi^2}{6}\frac{d\phi(x)}{dx}\bigg|_{x=\alpha} + \frac{7\pi^4}{360}\frac{d^3\phi(x)}{dx^3}\bigg|_{x=\alpha} + \dots$$

  and hence:

  $$U = \frac{(2m)^{3/2}V}{2\pi^2\hbar^3}\tau^{5/2}\left[\frac{2}{5}\left(\frac{E_F}{\tau}\right)^{5/2} + \frac{\pi^2}{6}\frac{3}{2}\left(\frac{E_F}{\tau}\right)^{1/2} + \dots\right]$$

  note that the first term gives no temperature dependence, while the second term has a τ^2 dependence:

  $$\begin{aligned} U &= \frac{(2m)^{3/2}V}{5\pi^2\hbar^3}E_F^{5/2}\left[1 + \frac{5\pi^2}{8}\left(\frac{\tau}{E_F}\right)^2 + \dots\right] \\ &= \frac{3}{5}NE_F\left[1 + \frac{5\pi^2}{8}\left(\frac{\tau}{E_F}\right)^2 + \dots\right] \end{aligned}$$

  Hence taking the partial with respect to temperature:

  $$\begin{aligned} C_V^{electron} &= \left(\frac{\partial U}{\partial \tau}\right)_V \\ &= \frac{3\pi^2 N}{4}\frac{\tau}{E_F} \end{aligned}$$

Compare this to the Debye heat capacity.

$$C_V^{phonons} = \left(\frac{2V\pi^2}{5\hbar^3 v^3}\right)\tau^3 = \frac{12\pi^2 N}{5}\left(\frac{\tau}{k\theta_D}\right)^3$$

Note that in both cases, the heat capacity scales as N, which makes sense since the heat capacity should be an extrinsic variable. However, the electronic heat capacity only scales as τ, hence at small τ, it will dominate the Debye phonon heat capacity. Hence we can write the total heat capacity as the sum of the two contributions:

$$C_V = a\tau^3 + b\tau$$

Chapter 7

Week 7

7.1 Recitation 11 May 2015

Fermion Orbital Consider a single orbital that may be occupied by a fermion. The grand partition function is:

$$\mathcal{Z} = 1 + \lambda e^{-\epsilon/\tau}$$

where λ is the activity. The thermal average occupancy of this orbital is given by the Fermi-Dirac distribution:

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau} + 1}$$

Fermi Energy Consider the chemical potential at zero temperature to be the Fermi energy.

Bose-Einstein distribution Proceed similarly and calculate the grand partition function:

$$\mathcal{Z} = \sum_{n=0}^{\infty} \lambda^n e^{-n\epsilon/\tau} = \frac{1}{1 - \lambda e^{\epsilon/\tau}}$$

and the occupation number is:

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau} - 1}$$

Classical limit In the limit of large $\frac{\epsilon-\mu}{\tau}$ (occupancy of each orbital is small),

$$f(\epsilon) \approx \lambda e^{-\epsilon/\tau}$$

Distribution from Partition function

$$\langle N \rangle = f = \lambda \frac{\partial}{\partial \lambda} \log \mathcal{Z}$$

Ideal gas in a centrifuge Consider a tube of length R spinning at angular frequency ω containing an ideal gas. We want to find the concentration of the gas as a function of the radial coordinate r. We write the chemical potential taking into account the potential energy due to the spinning (more like the rotational kinetic energy):

$$\mu(r) = \tau \ln \frac{n(r)}{n_Q} - \frac{mr^2\omega^2}{2} = \mu(0)$$

where we have imposed the condition that the chemical potential is constant along the tube Then we have:

$$n(r) = n(0) e^{mr^2\omega^2/2\tau}$$

7.2 12 May 2015 Lecture

Fermi Gas in White Dwarfs Recall the Hertzsprung-Russell diagram, which plots the absolute magnitude (logarithm) against he maximum wavelength (which represents the temperature from Wien's law). The absolute luminosity is:

$$L_{abs} = 4\pi R_*^2 J$$

where J is the flux, σT^4. The mass of a white dwarf is about a solar mass, $2 \times 10^{33} g$ and has a very small radius of $2 \times 10^9 cm$ as compared to the solar radius of $7 \times 10^{10} cm$. This translates into an average mass density of $6 \times 10^4 gcm^{-3}$. The core temperature is around $10^7 K$ which corresponds to energy units of $\tau \approx 800 eV$. The star is stabilised through gravitational contraction acting against electron degeneracy pressure.

$$pdV = dE_{grav} \implies P(4\pi R^2)dR = d\left[-\frac{3}{5}\frac{GM^2}{R}\right] = \frac{3}{5}\frac{GM^2}{R^2}dR \implies P = \frac{3}{5}\frac{GM^2}{4\pi R^4}$$

Consider an ideal gas with $\tau = 800eV$. Then $P_{ideal} = \frac{N\tau}{V}$. Let the core of the white dwarf be filled with iron atoms. This gives us an estimate of:

$$P_{ideal} = \frac{(M/m_{FE})}{\frac{4}{3}\pi R^3}\tau \approx 2.6 \times 10^{17} dy/cm^2$$

But the gravitational considerations gives a pressure of around $1.3 \times 10^{21} dy/cm^2$., which certainly does not match the ideal gas law.

Now consider the pressure associated with a quantum gas. Let there be a single electron for each bound proton. Then the number of electrons (assuming a core of iron, and one neutron for each proton) is:

$$N_{e-} = \frac{M_*}{2m_p} \approx 6 \times 10^{56}$$

which gives a number density of $\frac{N_{e-}}{V} = 2 \times 10^{28} cm^{-3}$ and a Fermi energy of $E_F = 30keV$. Since the temperature is much smaller than the Fermi energy, this should be treated as a degenerate Fermi gas. We now want to calculate the effect of this electron degeneracy pressure. We do this by calculating the total energy U, then calculating the pressure from:

$$P = -\left(\frac{\partial U}{\partial V}\right)_{\tau,N}$$

Note that when we compress a degenerate Fermi gas, the entropy is not going to change much because there are no new states. Hence the process will be automatically isentropic. Since the energies are very high, we will need to use the relativistic form of the energy. Recall that:

$$U = 2 \times \frac{1}{8}\int_0^{n_{max}} E_{n_T} 4\pi n_T^2 dn_T$$

The relativistic energy is:

$$E_e^2 = p_e^2 c^2 + m_e^2 c^4$$

where the de Broglie formula gives the momentum:

$$p_e = \hbar k_e, \quad k_e = \frac{n_T \pi}{L} \implies n_T = \frac{Lp_e}{\pi\hbar}$$

Hence we perform the integrating using the momentum variable instead:

$$U = \pi \left(\frac{L}{\pi\hbar}\right)^3 \int_0^{p_{max}} (p_e^2c^2 + m_e^2c^4)^{1/2} p_e^2 dp_e, \quad p_{max} = p_F = \frac{\pi\hbar n_{max}}{L}$$
$$\implies p_F = (3\pi^2 n)^{1/3}\hbar$$

Non-dimensionalizing the integral using $x = \frac{p_e}{m_e c}$,

$$U = \frac{V}{\pi^2\hbar^3}(m_e c^2)(m_e c)^3 \int_0^{x_{max}} (1+x^2)^{1/2} x^2 dx$$

For highly relativistic particles, let $x^2 >> 1$, hence we perform a binomial expansion and keep the first order term:

$$\begin{aligned} U &= \frac{V m_e^4 c^5}{\pi^2\hbar^3} \int_0^{x_{max}} x^3 \left(1 + \frac{1}{2x^2}\right) dx \\ &= \frac{V m_e^4 c^5}{\pi^2\hbar^3} \left[\frac{x_{max}^4}{4} + \frac{x_{max}^2}{4}\right] \\ &= V\alpha \left[\frac{\beta^4}{V^{4/3}} + \frac{\beta^2}{V^{2/3}}\right], \alpha = \frac{m_e^4 c^5}{4\pi^2\hbar^3}, \beta = \frac{(3\pi^2 N)^{1/3}\hbar}{m_e c} \end{aligned}$$

We may now take the volume derivative:

$$P = -\left(\frac{\partial U}{\partial V}\right)_{\sigma,N} = \frac{\alpha\beta^4}{3V^{4/3}} - \frac{\alpha\beta^2}{3V^{2/3}} = \frac{\alpha_1}{R^4} - \frac{\alpha_2}{R^2}$$

where $\alpha_1 = \frac{\alpha\beta^4}{3(4\pi/3)^{4/3}}, \alpha_2 = \frac{\alpha\beta^2}{3(4\pi/3)^{2/3}}$.

At equilibrium,

$$\frac{\alpha_1}{R^4} - \frac{\alpha_2}{R^2} = \frac{3M^2G}{20\pi R^4} \implies R^2 = \frac{\alpha_1}{\alpha_2}\left(1 - \frac{3M^2G}{20\pi\alpha_1}\right)$$

Interestingly, the radius appears to vanish if the term $\frac{3M^2G}{20\pi\alpha_1}$ is unity. Note that the radius of the white dwarf decreases with increasing mass. We estimate the maximum mass of the white dwarf to be:

$$M_{max} = \sqrt{\frac{20\pi\alpha_1}{3G}} = \sqrt{\frac{m_e^4 c^5}{4\pi^2\hbar^3}\left[\frac{(3\pi^2 N)^{1/3}\hbar}{m_e c}\right]^4 \frac{20\pi}{3G}\frac{1}{3(4\pi/3)^{4/3}}}$$
$$\implies M_{max} = \left(\frac{5\hbar c}{9\pi G}\right)^{3/2}\left(\frac{9\pi}{8m_p}\right)^2 \approx 3.4 \times 10^{33} g = 1.7 m_{Sun}$$

where we note that N depends on the mass of the white dwarf. For the equation to be consistent, we shift the dependence on M_{max} to the LHS.

A more correct derivation takes into account the inhomogeneity of the density:

$$\frac{dP(r)}{dr} = \frac{-G\rho(r)M_i(r)}{r^2}$$

where M_i is the internal radius:

$$M_i(r) = \int_0^r 4\pi r^2 \rho(r) dr$$

Which gives the Chandrasekhar mass of 1.4 solar masses.

7.3 Wednesday 13 May 2015 Section

Fermi Gas at low temperatures The ground state energy per particle is:

$$\frac{U_{tot}}{N} = \frac{3}{5}\epsilon_F$$

which is large because the Fermions cannot go to a lower energy since all lower levels are filled.

Converting Sum to Integral

$$\langle x \rangle = \sum_n X_n f(\epsilon_n, \tau, \mu) \approx \int d\epsilon \mathcal{D}(\epsilon) f(\epsilon, \tau, \mu) X(\epsilon)$$

Heat Capacity of a Metal

$$\begin{aligned}\Delta U &= U(\tau) - U(0) \\ &= \int_0^\infty d\epsilon \mathcal{D}(\epsilon)\epsilon f(\epsilon, \tau, \mu) - \int_0^{\epsilon_F} d\epsilon \mathcal{D}(\epsilon) \cdot \epsilon\end{aligned}$$

Now the total number of particles is a constant:

$$N = \int_0^\infty d\epsilon f(\epsilon, \tau, \mu(\tau))\mathcal{D}(\epsilon) = \int_0^{\epsilon_F} d\epsilon \mathcal{D}(\epsilon)$$

Multiplying this identity by ϵ_F and including this in the energy difference,

$$\Delta u = \int_{\epsilon_F}^\infty d\epsilon(\epsilon - \epsilon_F) f(\epsilon)\mathcal{D}(\epsilon) + \int_0^{\epsilon_F} (\epsilon_F - \epsilon)(1 - f(\epsilon))\mathcal{D}(\epsilon)$$

we approximate the density of states to be the same as the density of states at the Fermi energy, and take the chemical potential as a constant.

$$C_{el} = \frac{\partial U}{\partial \tau} = \mathcal{D}(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{\partial f}{\partial \tau} d\epsilon = \frac{1}{2}\pi^2 N \frac{\tau}{\tau_F}$$

Fermi Velocity and Momentum Let $\epsilon_F = \frac{1}{2}mv_F^2 = \frac{p_F^2}{2m}$.

Maximum Mass of Neutron Star Consider a Fermi gas with Fermi energy:

$$\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

and total energy:

$$U_{tot} = \frac{3}{5}N\epsilon_F = \frac{3}{10}\frac{\hbar^2}{m}(3\pi^2)^{2/3}\frac{N^{5/3}}{V^{2/3}}$$

Consider an isentropic compression of the neutron star:

$$p = -\left(\frac{\partial U}{\partial V}\right)_{\sigma, N} = \frac{\hbar^2}{5m}(3\pi^2)^{2/3}\left(\frac{N}{V}\right)^{5/3}$$

This is the neutron degeneracy pressure. Now we need to find the gravitational pressure:

$$U_G = -\frac{3}{5}\frac{GM^2}{R} = -\frac{3}{5}\frac{GM^2}{(3V/4\pi)^{1/3}}, \quad M = m \cdot N$$

Hence the gravitational pressure is:

$$p_G = -\left(\frac{\partial U}{\partial V}\right)_{\sigma,N} = -\frac{G(m\cdot N)^2}{5(3/4\pi)^{1/3}}\frac{1}{V^{4/3}}$$

Equating the pressures, we obtain that the critical density is:

$$\left(\frac{9\pi^4\hbar^2}{m^8}\frac{3}{4\pi}\frac{1}{V^2}\right)^{1/3} = G\rho^{1/3}$$

Relating Partial Derivatives: Euler's Triple Product Rule

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

7.4 14 May 2015

Bose Gas Recall that for low temperature, the chemical potential of the Bose gas was:

$$\mu \approx E_0 - \frac{\mu}{N_0}, \quad N_0 >> 1$$

and all the particles crowd into the ground state. We want to calculate the temperature at which this is important, which will be when the particles in the excited states is small.

$$N_{ex} = \int_{E_{\text{1st excited}}}^{\infty} f_{BE}(E)\mathcal{D}(E)dE$$
$$\mathcal{D}(E) = \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}E^{1/2} \quad \text{for zero spin}$$

Note that the density of states excludes the ground state because it vanishes at zero energy. Hence we let the ground state be at zero energy and integrate from zero to infinity:

$$\begin{aligned}
N_{ex} &= \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^\infty \frac{1}{e^{(E-\mu)/\tau}-1}E^{1/2}dE \\
&= \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^\infty \frac{1}{e^{(E-(E_0-\tau/N_0))/\tau}-1}E^{1/2}dE, \quad N_0 >> 1 \\
&= \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^\infty \tau^{3/2}\frac{x^{1/2}}{e^x-1}dx \quad x = \frac{E}{\tau} \\
&= \frac{V}{4\pi^2\hbar^3}(2m\tau)^{3/2}2.61\left(\frac{\pi}{4}\right)^{1/2} \\
&= 2.61\left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}V \\
&= 2.61 n_Q V
\end{aligned}$$

and hence the number of particles in the ground state is large if $N_{ex} < N_0$ which is equivalently when $2.61 n_Q V < N_0$. Define the Einstein temperature to be the temperature when equality occurs. Then:

$$\tau_E = \frac{2\pi\hbar^2}{m}\left(\frac{n}{2.61}\right)^{2/3}$$

For the density and mass of air, the Einstein temperature is $0.005K$.

For liquid helium, $n \approx 1.8 \times 10^{22} cm^{-3}$ (does not change much with temperature). Then the Einstein temperature is 2.9K. Liquid helium is at 4.2K upon formation. To cool below 3K, we use evaporative cooling.

The pressure goes exponentially with the temperature:

$$p = p_0 e^{-L_0/\tau}$$

where L_o is the latent heat per particle.

Properties of Liquid Helium :

- **Heat Capacity** Recall that $C_v = \left(\frac{\partial U}{\partial \tau}\right)_V$. As Liquid Helium is cooled, its heat capacity suddenly increases at around 2.17K (the λ temperature) to infinity, then decreases as the temperature goes lower.
- **Thermal Conductivity** The thermal conductivity goes to infinity as the temperature drops below the λ point. Infinity thermal conductivity means that the system cannot have any temperature gradient; the entire system is at the same temperature. No bubbles will form. This system is called a superfluid. This fluid also has zero viscosity.
- **Creep** The liquid sticks better to glass than to each other (stronger interaction with glass than with each other). Hence it will start climbing up the glass wall against gravity out of the container.
- **Fountain Effect**

Chapter 8

Week 8

8.1 Monday 18 May 2015

Degenerate Quantum Gases Roughly when $n \geq n_Q$, which can be written as:

$$\tau_0 = \frac{2\pi\hbar^2}{m} n^{2/3}$$
$$\tau << \tau_0 \implies \text{Degenerate quantum state}$$

8.2 Tuesday 19 May 2015

Einstein Temperature Recall that the Einstein temperature for Bose condensation was:

$$T_E = \frac{1}{k_B} \frac{2\pi\hbar^2}{m} \left(\frac{n}{2.61}\right)^{2/3}$$

Note that this temperature goes inversely proportional to m. For nitrogen at room pressure, $n \approx 2.5 \times 10^{19} cm^{-3}$, giving a $T_E = 5mK$, which is hard to achieve since almost all atomic species are either liquid or solid at that temperature. To ensure that the sample does not become a liquid/solid, we have to decrease the density, which also decreases the Einstein temperature. Hence a balance needs to be found.

Units BTU: energy to raise 1 pound of water by $1°F$ at $63°F$. About 1055 joules.

Heat and Work To first order,

$$\Delta Q = C_V \Delta\tau = \tau \left(\frac{\partial\sigma}{\partial\tau}\right)_{V,N} \Delta\tau \implies \Delta Q = \tau d\sigma$$

Where we use ΔQ instead of dQ because the heat is not a function of the independent variables of the system (state function) and hence is not an actual derivative.

Thermodynamic identity Recall:

$$dU = \tau d\sigma - pdV = \Delta Q - pdV + \mu dN$$

where pdV is the mechanical work done by the system and μdN is the chemical work done by the system.

Heat Engine Consider a reservoir at temperature τ_1 that transfers q_1 to an engine, which converts some of it to work w. This process must be cyclic so the device must be returned to its initial state after each cycle. This means that the engine entropy does not change over one cycle (state function). But since the reservoir has supplied heat q_1 at temperature τ_1, its entropy must decrease. To ensure that the entropy of the whole universe is non-decreasing, we require that the device releases heat to increase entropy elsewhere. Let the device transfer q_2 to another reservoir at temperature τ_2. Then:

$$q_1 = w + q_2$$

and the total change in entropy for the universe is:

$$-\frac{q_1}{\tau_1} + \frac{q_2}{\tau_2} \geq 0$$
$$\implies -\frac{q_1}{\tau_1} + \frac{q_1 - w}{\tau_2} \geq 0$$

Rearranging,

$$\frac{w}{q_1} \leq \left(1 - \frac{\tau_2}{\tau_1}\right) = \frac{\tau_1 - \tau_2}{\tau_1}$$

We define the efficiency

$$\eta = \frac{w}{q_1}$$

so that:

$$\eta \leq 1 - \frac{\tau_2}{\tau_1}$$

a heat engine at maximum efficiency hence has:

$$\frac{w}{q_1} = 1 - \frac{\tau_2}{\tau_1}$$

which represents the maximum efficiency of a heat engine operating between two reservoirs at fixed temperature. This is a **Carnot engine**.

Maximum efficiency engine: Carnot Engine Consider a 4-step process. Begin with a volume of gas at τ_1.

- Expand at constant τ_1. Absorb q_1 of heat.
- Expand adiabatically (constant entropy) to new temperature $\tau_2 < \tau_1$.
- Compress at constant temperature τ_2. Release q_2 of heat.
- Compress adiabatically (constant entropy) back to τ_1.

To calculate the work done by the system, we return to the entropy of an ideal gas:

$$\sigma = N \ln\left[\frac{V}{N}\left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}\right] + \frac{5N}{2}$$

and hence for a constant entropy, constant particle number process, $V\tau^{3/2}$ must be constant. Call this α_0:

$$V_i\tau_i^{3/2} = V_f\tau_f^{3/2} = \alpha_0$$

Using the equation of state:

$$P = \frac{N}{V}\left(\frac{\alpha_0}{V}\right)^{2/3} = \frac{N\alpha_0^{2/3}}{V^{5/3}}$$

Hence $PV^{5/3}$ is a constant for an adiabatic process. The efficiency of the Carnot cycle is $1 - \frac{\tau_2}{\tau_1}$, the maximum Carnot efficiency.

Refrigeration Consider two reservoirs with $\tau_2 < \tau_1$. Let the τ_2 reservoir transfer q_2 to the device. Let w work be done on the device, and let it release q_1 to the τ_1 reservoir. By the first law of thermodynamics:

$$q_2 + w = q_1$$

and considering the entropy:

$$\begin{aligned} -\frac{q_2}{\tau_2} + \frac{q_1}{\tau_1} &\geq 0 \\ \implies -\frac{q_2}{\tau_2} + \frac{q_2 + w}{\tau_1} &\geq 0 \\ \implies \frac{w}{q_2} \geq \tau_1 \left(\frac{1}{\tau_2} - \frac{1}{\tau_1} \right) &= \frac{\tau_1 - \tau_2}{\tau_2} = \frac{\tau_1}{\tau_2} - 1 \\ \implies \frac{q_2}{w} &\leq \frac{\tau_2}{\tau_1 - \tau_2} \end{aligned}$$

Call $\gamma = \frac{q_2}{w}$ the quality or the coefficient of refrigeration.

8.3 21 May 2015

Expansion of Ideal Gas Recall for an ideal gas:

$$U = \frac{3}{2} N\tau, \quad PV = N\tau \quad dU = \tau d\sigma - PdV$$

For a reversible isothermal expansion, let a spring-loaded piston expand slowly - i.e. slower than the speed of sound. Since N and τ stay constant,

$$dU = 0$$

Hence the heat that the gas absorbs is equal to the work done by the gas.

$$\Delta Q = \int_{V_i}^{V_f} PdV = \int_{V_i}^{V_f} \frac{N\tau}{V} dV = N\tau \ln \frac{V_f}{V_i}$$

Recall also that the entropy of an ideal gas was:

$$\sigma = N \ln \left[\frac{V}{N} \left(\frac{m\tau}{2\pi\hbar^2} \right)^{3/2} \right] + \frac{5N}{2}$$

and the entropy change of the system is:

$$\Delta\sigma = \sigma_f - \sigma_i = \frac{\Delta Q}{\tau} = N \ln \frac{V_f}{V_i}$$

Since $V_f > V_i$, the entropy of the system increases during the expansion. Since the process is reversible, the entropy change of the universe is constant and the reservoir must experience a reduction in entropy of the same amount.

Free Expansion Consider a free expansion from V_i to V_f. The entropy change in this case is:

$$\Delta\sigma = N \ln \frac{V_f}{V_i}$$

by considering the entropy of an ideal gas equation above. This entropy change is the same as in the reversible isothermal expansion. However, the work done by the gas is zero. No heat flows into the gas, hence the reservoir does not change in entropy. The net effect is that the total universe entropy increases as a result of the free expansion. This process is irreversible. During the expansion, the temperature and pressure are not well-defined quantities because the system is not in equilibrium. However, we may still use:

$$\Delta U = \Delta Q + \Delta w$$

which are not differentials but path-dependent changes.

Isentropic Reversible Expansion Recall that for an isentropic expansion we require that:

$$\begin{aligned} V\tau^{3/2} &= \text{constant} \\ V^{2/3}\tau &= \text{constant} \end{aligned}$$

which is only true for monoatomic ideal gases. For multiatom gases we have:

$$\tau V^{\gamma - 1} = \text{constant}, \quad \gamma = \frac{C_p}{C_V}$$

Summary of Thermodynamics :

1. Thermodynamic Identity: $dU = \tau d\sigma - pdV + \mu dN$.
2. Consider N, V, τ as independent variables. Rewrite the thermodynamic identity as:

$$\begin{gathered} dU = d(\tau\sigma) - \sigma d\tau - pdV + \mu dN = d(\tau\sigma) + dF \\ dF \equiv -\sigma d\tau - pdV + \mu dN \\ \implies dF = dU - d(\tau\sigma) \implies F = U - \tau\sigma \\ \implies \sigma = -\left(\frac{\partial F}{\partial \tau}\right)_{V,N}, \quad p = -\left(\frac{\partial F}{\partial V}\right)_{N,\tau}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,\tau} \end{gathered}$$

3. Consider N, τ, p as independent variables (e.g. chemical processes). Then the thermodynamic identity can be written as:

$$\begin{gathered} dU = d(\tau\sigma) - d(pV) - \sigma d\tau + Vdp + \mu dN = d(\tau\sigma) - d(pV) + dG \\ dG \equiv -\sigma d\tau + Vdp + \mu dN \\ \implies G = U - \tau\sigma + pV \\ \implies \sigma = -\left(\frac{\partial G}{\partial \tau}\right)_{p,N}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{\tau,p}, V = \left(\frac{\partial G}{\partial p}\right)_{\tau,N} \end{gathered}$$

4. Consider N, p, σ as independent variables (e.g. isentropic processes). Then we write:

$$\begin{gathered} dU = -d(pV) + \tau d\sigma + Vdp + \mu dN = -d(pV) + dH \\ dH \equiv \tau d\sigma + Vdp + \mu dN \\ \implies H = U + pV \\ \implies \tau = \left(\frac{\partial H}{\partial \sigma}\right)_{p,N}, \quad V = \left(\frac{\partial H}{\partial p}\right)_{\sigma,N}, \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{\sigma,p} \end{gathered}$$

Gibbs' Free Energy and Chemical Potential Recall that G is minimum at equilibrium for systems in contact with a thermal and pressure reservoir (temperature and pressure are externally controlled by the reservoir). Consider two identical systems with N_0, τ, V_0 and combine them. Note that some variables stay the same, such as the pressure, temperature and chemical potential. These are intensive variables. On the other hand, the volume, number of particles, energy and entropy changes. These are extensive variables (variables that change when you add more identical systems together). Since $G = U - \tau\sigma + pV$, G is extensive as it depends on the extensive variables U, σ, V. G has to scale as N, since in $G(N, p, \tau)$, two of these independent parameters are intensive and only N is extensive. Hence we write:

$$G = N \times f(p, \tau)$$

But we also knew that the chemical potential could be obtained from G:

$$\left(\frac{\partial G}{\partial N}\right)_{\tau,p} = \mu = \left(\frac{\partial N f(p,\tau)}{\partial N}\right)_{\tau,p} = f(p,\tau)$$
$$\implies f(p,\tau) = \mu$$
$$\implies G(N,p,\tau) = N\mu(p,\tau)$$

which is only true if a single species of particle is present. Where there are multiple species, we just write:

$$G_{tot}(N,p,\tau) = \sum_i N_i \mu_i(p,\tau)$$

Compare this to the chemical equilibrium condition:

$$dG = 0 \implies d\sum_i N_i \mu_i(p,\tau) = 0$$

But this is precisely the formula for chemical equilibrium that we used previously.

Helmholtz Free Energy and Chemical Potential Recall that:

$$F(N,V,\tau) = U - \tau\sigma$$

and F is extensive since U and σ are extensive. However, in this case, we cannot write $F(N,V,\tau) = N \times g(V,\tau)$ because V is an extensive variable as well.

Chapter 9

Week 9

9.1 Tuesday 26 May 2015

Phase Transitions Note that we cannot use ideal gas assumptions since we require inter-particle interactions to understand PT. Each phase is characterized by its own uniform thermodynamic state (density n, entropy σ, temperature τ).

Phase Equilibrium Consider two phases in chemical-like equilibrium. We use the Gibbs free energy $G(N, p, \tau) = U - \tau\sigma + pV$ to characterize the system. Equilibrium occurs when $dG = 0$ or G is minimized. Recall that we can factor the Gibbs free energy into the number of particles in each phase multiplied by another function. Define the Gibbs free energy PER PARTICLE $g_1(p, \tau), g_2(p, \tau)$ for each system, so that the total Gibbs free energy is

$$G = N_1 g_1 + N_2 g_2$$

Note that if the phases each have a single component, the Gibbs free energy per particle is simply the chemical potential. Hence:

$$g_1 = \mu_1, \quad g_2 = \mu_2$$

The differential at constant pressure and temperature is hence:

$$dG = \mu_1 dN_1 + \mu_2 dN_2 = 0$$

But we impose that $N = N_1 + N_2$ is a constant, hence $dN_1 = -dN_2$. This gives:

$$\mu_1 = \mu_2$$

Phase Diagram Plot pressure against temperature. The phase equilibrium curve exists as a locus of points that satisfy $g_1 = g_2 \iff \mu_1 - \mu_2$. We only expect the curve to exist only up to a maximum temperature, up to the point where the thermal energy exceeds the binding energy between the molecules. Call this the critical point τ_c, where both phases coexist but we are unable to tell the difference between them.

Phase Equilibrium Curve Consider two points on the curve separated by $d\tau$ and dp. Then:

$$\begin{gathered} g_1(p + dp, \tau + d\tau) = g_2(p + dp, \tau + d\tau) \quad g_1(p, \tau) = g_2(p, \tau) \\ \implies g_1(p + dp, \tau + d\tau) - g_1(p, \tau) = g_2(p + dp, \tau + d\tau) - g_2(p, \tau) \end{gathered}$$

Note that:

$$dg_i = d(U_N^i - \tau\sigma_N^i + pV_N^i)$$

where the subscripts indicate values per particle. By the thermodynamic identity for a fixed number of particles, which is valid here for $N = 1$,

$$dU_N = \tau d\sigma_N - pdV_N$$

Hence combining and using the product rule,

$$dg_i = -\sigma_N^i d\tau + V_N^i dp$$

Because $dg_1 = dg_2$ at equilibrium, we hence have:

$$\begin{aligned} -\sigma_{N2}d\tau + V_{N2}dp &= -\sigma_{N1}d\tau + V_{N1}dp \\ \implies (V_{N2} - V_{N1})dp &= (\sigma_{N2} - \sigma_{N1})d\tau \\ \implies \frac{dp}{d\tau} &= \frac{\Delta\sigma}{\Delta V} \end{aligned}$$

and the slope of the equilibrium curve is given by the ratio between the entropy and volume difference between the phases. If the entropy and volume are discontinuous across the phase equilibrium curve, then we call the phase transition first order. If the entropy and volume are continuous across the phase transition, we call this a second order phase transition (examples are like magnetic phase transitions).

Hence for a first order phase transition, $\Delta\sigma \neq 0, \tau\Delta\sigma \neq 0$ which indicate heat flow into (or out of) the system. This corresponds to the latent heat flowing into the system. Write:

$$L = \tau\Delta\sigma$$

so that we have:

$$\frac{dp}{d\tau} = \frac{L}{\tau\Delta V}$$

which is called the **Clausius-Clapeyron Relation**. If ΔV is the volume per mole of particles, then L is given as the latent heat per mole of particles.

Example: Gas into Liquid The volume per mole for the gas will usually be much larger than the volume per mole for the liquid. Hence

$$\Delta V_N \approx \frac{V_{gas}}{N_{gas}}$$

Approximating the gas as ideal, $pV = N\tau \implies \frac{N}{V} = \frac{\tau}{p}$. Substituting this into the C-C relation, we obtain a differential equation:

$$\frac{dp}{d\tau} = \frac{L_N}{\tau}\frac{p}{\tau}$$

where we introduced L_N which is the latent heat per mole of particles. We assume that the Latent heat is independent of temperature. Separating variables,

$$\begin{aligned} \ln p &= -\frac{1}{\tau}L_N + c \\ \implies p &= Ae^{-L_N/\tau} \end{aligned}$$

This gives the phase equilibrium curve.

Three Phase Equilibrium Consider a three phase system. We can have equilibrium between any two phases by picking $g_1 = g_2, g_2 = g_3, g_2 = g_3$. We can have all three phases in equilibrium at a single point where $g_1 = g_2 = g_3$, which is called the triple point. Note that the curves are generally positive because entropy increases as volume increases across the phase transition $\frac{dp}{d\tau} = \frac{\Delta\sigma}{\Delta V}$. However, there is a major exception in the form of water ice and water. From solid ice to liquid water, the entropy increases but the volume decreases. Hence the derivative is negative for the solid-liquid phase equilibrium curve.

Intermolecular forces Recall that an electric field can induce a dipole moment in a polarizable atom. The dipole field falls off as $\frac{1}{r^3}$. Now another dipole does not feel the dipole field directly but feels the gradient in the field:

$$\vec{F}_x = (\vec{p} \cdot \nabla)\vec{E}_x$$

The dipole moment of the second dipole goes as the field strength, which went as $\frac{1}{r^3}$. Taking these together, the force between the two dipoles goes as $-\frac{1}{r^4}\frac{1}{r^3} = -\frac{1}{r^7}$. Since the force is the negative gradient of the potential, the potential goes as $-\frac{1}{r^6}$. Note the negative signs, which indicates an attractive force.

There is also a short range repulsive force due to the Pauli exclusion principle - the exchange force. This prevents the electron clouds from completely coalescing. This force can be modelled (rather arbitrarily) as a $\frac{1}{12}$ potential. This results in the Lennard-Jones potential:

$$U(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}, \quad A, B > 0$$

Equation of State for Real Classical Gas Recall that for the ideal gas, we used the following process:

$$\begin{aligned} Z_1 &= n_Q V \\ Z_N &= \frac{(Z_1)^N}{N!} \\ F &= -\tau \ln Z_N \\ p = -\left(\frac{\partial F}{\partial V}\right)_{N,\tau} &= \frac{N\tau}{V} \end{aligned}$$

We want to replicate this line of thought. The partition function for a non-ideal gas needs to include the interactions between particles in the form of the additional potential:

$$\begin{aligned} Z_1^{class} &= \frac{1}{h_0^3}\int_{\text{6D phase space}} d^3r d^3p e^{-\beta E} \\ E = KE + PE &= \frac{p^2}{2m} + U(r) \\ \implies Z_1^{class} &= \frac{1}{h_0^3}\int_{\vec{r}} d^3r e^{-\beta U(r)} \int_{\vec{p}} d^3p e^{-\beta p^2/2m} = n_Q \int_{\vec{r}} d^3r e^{-\beta U(r)} \end{aligned}$$

Recall that when $U(r) = 0$ as in the ideal gas case, the position integral just became V. For a single particle in a field of many others, $U(r) = \sum_i U_{1,i}$. We approximate the potential as a square well that is infinite at small R_o and steps up to zero at R_w. The value of the potential between $R_o < r < R_w$ is negative. Then we may approximate the position integral as:

$$\int_{R_o}^{\infty} d^3r e^{-\beta U(r)}$$

because molecules cannot get within R_o of each other (infinite potential). Then we use the mean-field approximation:

$$U = \sum_i U_{1,i} \approx \bar{U} = \int_{R_o}^{\infty} U_{approx}(r) n(r) 4\pi r^2 dr$$

We may also assume that the particle density $n(r)$ is uniform and equal to $\frac{N}{V}$. U_{approx} is also equal to some negative constant between R_o and R_w and is zero outside. Hence the integral is trivial:

$$U \approx -a\frac{N}{V}$$

for some positive constant a

9.2 Thursday 28 May 2015

Equation of state for non-ideal gas Recall that the single particle partition function was (from above):

$$Z_1^{class} = n_Q \int_{\vec{r}} d^3r e^{-\beta U(r)}$$

where the potential between two particles, $U_{12}(r)$ was:

$$U_{12}(r) = \begin{cases} \infty, & r < R_0 \\ -U_0, & R_0 < r < R_w \\ 0, & r > R_w \end{cases}$$

The actual potential is the sum over all possible two body interactions. We write:

$$U(r) = \sum_i U_{1i}(r)$$

which we can simplify using mean-field theory:

$$\bar{U} = \int_{R_0}^{\infty} U(r)n(r)d^3r \approx -a\frac{N}{V}$$

where a is a positive constant with units energy times volume. If n was such that the atoms were just touching, we would have:

$$-n_{max}a = U_0$$

Then the space integral can be written as:

$$\int_{\vec{r}} d^3re^{-\beta U(r)} \approx e^{-\beta\bar{U}} \int_{R_0}^{\infty} d^3r \approx e^{-\beta\bar{U}}(V - \frac{4\pi}{3}R_o^3N) = e^{-\beta\bar{U}}V_{net}$$
$$V_{net} = V - \frac{4\pi}{3}R_o^3N = V - bN$$

where we note that the excluded volume corresponds to the volume of the other atoms. We take R_o to be twice the electron orbital radius, since the atoms can be considered to be overlapping when they are within two electron orbital radii of each other. Hence the partition functions are:

$$Z_1 = n_Q e^{-an/\tau}(V - bN)$$
$$Z_N = \frac{Z_1^N}{N!}$$

We can calculate the other thermodynamic parameters:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N}, \quad F = -\tau \ln Z_N$$
$$\implies F = \tau \ln N! - \tau N \ln n_Q - \tau N \ln(V - bn) - \tau N \frac{an}{\tau}$$
$$\implies p = \frac{\tau N}{V - bN} - \frac{aN^2}{V^2}$$
$$\implies \left(p + \frac{aN^2}{V}\right)(V - bN) = N\tau$$

This is the **Van-de-waals equation of state**. We may also write it using a **Virial expansion** in n:

$$p = \frac{N\tau}{V}\left[\frac{1}{1-bn} - \frac{an}{\tau}\right] \approx \frac{N\tau}{V}\left[1 + n\left(b - \frac{a}{\tau}\right) + \ldots\right], bn << 1$$
$$\implies \frac{p}{\tau} = n + B_2(\tau)n^2 + B_3(\tau)n^3 + \ldots, \quad B_2 = b - \frac{a}{\tau}$$

Note that at high temperatures, the pressure is larger than that of an ideal gas due to the volume-reducing effect of other atoms $\frac{1}{1-bn} > 1$. At low temperatures, p is decreased due to the interatomic interactions governed by a.

Van de Waals Equation of State and Phase Transitions Consider p as a function of $\frac{V}{N}$ and at fixed τ. Then:

$$p = \frac{\tau}{\frac{V}{N} - b} - \frac{a}{(V/N)^2} = \frac{\tau}{x - b} - \frac{a}{x^2}, \quad x = \frac{V}{N}$$

We examine the derivative:

$$\frac{dp}{dx} = -\frac{\tau}{(x-b)^2} + \frac{2a}{x^3}$$

and the slope is negative when x is close to b and positive when it is far away. b is also small, hence we expect that the slope is negative for small x. Near zero, the gradient is large and negative, which acts against increases in the density (reduced $\frac{V}{N}$). It is effectively incompressible, and hence acts like a liquid. However, as $\frac{V}{N}$ increases, $\frac{2a}{x^3}$ begins to dominate and the gradient becomes positive. This is unstable and unphysical. This is probably due to the approximations in describing the interactions.

Maxwell Construction Fixing the unphysical aspect of positive $\frac{dp}{dx}$. This process minimizes the Gibbs free energy to find the correct equilibrium curve at fixed τ and N. Recall that the Gibbs free energy is:

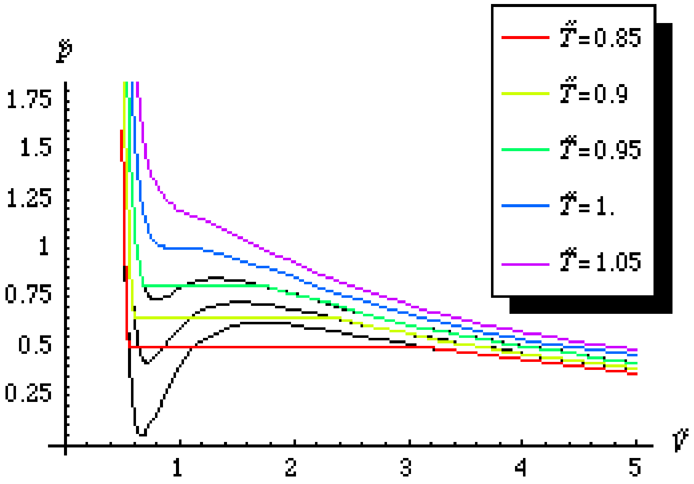
$$g = U_N - \tau\sigma_N + pV_N$$
$$dg = dU_N - \tau d\sigma_N + pdV_n + V_N dp = V_N dp = 0$$

where we used the thermodynamic identity for fixed particle number.

$$dU_N - \tau d\sigma_N + pdV_N = 0$$

Hence equilibrium corresponds to $V_N dp = 0$. We pick a horizontal line so that the local max and local min of the p versus x graph contributes equal areas. Then there is a horizontal region of $\frac{V}{N}$ values at which liquid and gas can coexist and the pressure there is called P_{co}. For $\frac{V}{N}$ values smaller than this range, the gas behaves more like a liquid. For $\frac{V}{N}$ values larger than this range, the gas is more gas-like.

Effect of temperature on Maxwell Construction :



Note that as temperature increases, there is a narrower region of coexistence, until it vanishes into a single point at which $\frac{V}{N}$ gives phase coexistence (gradient equals zero).

Opalescence at Critical point At the critical point, $\frac{dp}{dx}$ vanishes, or $\frac{dx}{dp} \to \infty$. A small change in pressure causes a massive change in volume. There will hence be large density fluctuations throughout the gas. The index of refraction of a gas is proportional to the density, hence the index of refraction at the critical point varies widely from point to point. This results in critical opalescence.

Chapter 10

Final Review

Topics Probability/Binary Model Systems. Notion of entropy, temperature, equilibrium. Boltzmann distribution, partition functions. Photons/phonons/blackbody radiation. Chemical potential/GCE. Ideal Fermi+Bose gases. Heat, Work, Engines, Refrigerators. Phase transitions.

Example 1: Photon Gas Consider a photon gas in a volume V at temperature T, with energy $\epsilon = pc$. We want to calculate the chemical potential and the number of photons as a function of temperature.

Now for a photon gas, the number of photons is not fixed. Hence N varies independently of the temperature and the volume of the system. We can determine the equilibrium by minimizing the free energy of the photon gas with respect to this independent variable:

$$\left(\frac{\partial F}{\partial N}\right)_{\tau,V} = 0$$

But note that this is precisely the expression for μ. Hence $\mu = 0$.

To calculate the number of photons, we use the density of states. Hence:

$$\epsilon = pc = \frac{c\pi\hbar}{L}\sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{c\pi\hbar n}{L}$$

The number of orbitals contained within an $n-$sphere is:

$$2 \times \frac{1}{8} \times \frac{4}{3}\pi n^3 = \frac{\pi n^3}{3}$$

The energy can be written in terms of frequency:

$$\begin{aligned} \epsilon = \hbar\omega \implies n = \frac{L\omega}{c\pi} \implies N(\omega) = \frac{V\omega^3}{3c^3\pi^2} \\ \implies \mathcal{D}(\omega) = \frac{dN}{d\omega} = \frac{V\omega^2}{c^3\pi^2} \end{aligned}$$

Hence we have the density of states in terms of frequency. Evaluating the number of photons using the Bose distribution function:

$$N = \int_0^\infty d\omega \frac{V}{\pi^2 c^3} \frac{\omega^2}{e^{\hbar\omega/\tau} - 1} = \frac{V}{\pi^2 c^3}\frac{\tau^3}{\hbar^3} 2\zeta(3)$$

Blackbody Shells Consider concentric shells of radius R_1 and $R_2 < R_1$ and temperatures T_1, T_2 respectively. Let there be a solid sphere of radius $R_3 < R_2$ inside the shells. Let there be a point source of power with output power W at the center. We want to find the steady-state temperatures of all the shells as a function of the radii and the power.

Start with the outer shell. Note that for a shell, the effective surface area is twice the surface area because it is radiating in both directions inside the shell and outside the shell. Hence the energy per time leaving the outer shell is:

$$2 \cdot 4\pi R_1^2 \sigma_B T_1^4 = 4\pi R_2^2 \sigma_B T_2^4$$

For the next shell,

$$2 \cdot 4\pi R_2^2 \sigma_B T_2^4 = 4\pi R_1^2 \sigma_B T_1^4 + 4\pi R_3^2 \sigma_B T_3^4$$

For the inner sphere,

$$4\pi R_3^2 \sigma_B T_3^4 = W + 4\pi R_2^2 \sigma_B T_2^4$$

This is a set of simultaneous equations with solution:

$$\begin{aligned} 4\pi R_1^2 \sigma_B T_1^4 &= W \\ 4\pi R_2^2 \sigma_B T_2^4 &= 2W \\ 4\pi R_3^2 \sigma_B T_3^4 &= 3W \end{aligned}$$

Discrete System Statistics Consider two particles which can occupy a system with orbitals at $0, \epsilon, 2\epsilon$ and with degeneracy $2, 1, 1$ respectively.

We first write down the grand canonical partition function assuming they are Fermions (and fixing the number of particles):

$$\mathcal{Z} = 1 + 2e^{-\epsilon/\tau} + 2e^{-2\epsilon/\tau} + e^{-3\epsilon/\tau}$$

The energy can be calculated to be:

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{\epsilon}{Z} e^{-\beta\epsilon} \left[2 + 4e^{-\beta\epsilon} + 3e^{-2\beta\epsilon}\right]$$

If the particles are Bosons, then we have:

$$\mathcal{Z} = 3 + 2e^{-\beta\epsilon} + 3e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$$

Boltzmann Statistics Write the partition function for distinguishable particles (same orbital system as above):

$$Z = 4 + 4e^{-\beta\epsilon} + 5e^{-2\beta\epsilon} + 2e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$$

Bose Gas in 1D First compute the occupancy of the excited orbitals. Recall the quantum box energies:

$$E_n = \frac{\hbar^2 n^2 \pi^2}{2mL^2} \implies N(E) = \frac{L}{\hbar\pi}\sqrt{2mE} \implies D(E) = \frac{dN(E)}{dE} = \frac{L}{2\hbar\pi}\frac{1}{\sqrt{2mE}}$$

Now we calculate the occupation of the excited state orbitals:

$$N_e(\tau) = \int_0^\infty dED(E)\frac{1}{e^{\epsilon/\tau}-1}$$

where we approximated $\mu = 0$ for low temperatures assuming that $\mu = 0$. This integral does not converge. Hence the approximation that BEC occurs is wrong.

10.1 Tuesday 02 June 2015

Velocity and Speed Distributions Consider a classical non-relativistic ideal gas at constant τ, V, N (canonical ensemble). We want to find the probability of a particle with mass m having a velocity component between $v_x, v_x + dv_x$. Then:

$$\int P(\epsilon)d\epsilon = \int f(\epsilon)\mathcal{D}(\epsilon)d\epsilon$$

We can also perform this calculation using phase space considerations (in momentum and position space). The probability of the particle occupying a certain volume in phase space is given by the volume of the phase space element multiplied by the probability that it is occupied. The latter goes as $e^{-E/\tau}$.

$$\begin{aligned}
P(p_x)dp_x &= \frac{\int_V \int_{P_y} \int_{P_z} e^{-E/\tau} dxdydzdp_xdp_ydp_z}{\int_V \int_p e^{-E/\tau} d^3r d^3p} \\
E &= \frac{m}{2}(v_x^2 + v_y^2 + v_z^2) \\
\implies P(v_x)dv_x &= \frac{\left[\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dv_ydv_z e^{-(m/2\tau)(v_y^2+v_z^2)}\right] e^{-mv_x^2/2\tau}dv_x}{\iiint dv_xdv_ydv_z e^{-(m/2\tau)(v_x^2+v_y^2+v_z^2)}} \\
&= \frac{e^{-mv_x^2/2\tau}dv_x}{\left(\frac{2\tau}{m}\right)^{1/2}\int_{-\infty}^{\infty} e^{-u^2}du} = \left(\frac{m}{2\pi\tau}\right)^{1/2} e^{-mv_x^2/2\tau}dv_x
\end{aligned}$$

Note that the distribution is symmetric, so $\langle v_x \rangle = 0$. We also have:

$$\langle v_x^2 \rangle = \frac{\tau}{m} \implies \langle E \rangle = \frac{m}{2}\langle v_x^2 + v_y^2 + v_z^2 \rangle = \frac{3\tau}{2}$$

Each translational degree of freedom contributed $\frac{\tau}{2}$ of average thermal energy.

Specific heats $C_P = C_V + N$. For air, $\gamma = \frac{C_P}{C_V} = 1.4$ which corresponds to $C_P = \frac{7}{2}N, C_V = \frac{5}{2}N$. Note that this is not equal to the expected $\gamma = \frac{9/2}{7/2}$ if rotational and vibrational contributions were counted as well. This arises because τ must be much larger than the energy spacing of that degree of freedom so that the equipartition theorem applies. Rotational states have separations of around $10^{-4}eV$ and $\tau = \frac{1}{40}eV$ so rotational states contribute. However, the vibrational energy separations are on the order of $0.1eV$, which is comparable to the thermal energy. Hence the vibrational terms do not feature significantly in the calculation of heat capacity.

Distribution of speeds: Maxwell Boltzmann Distribution The speed is scalar. We hence may use spherical coordinates to describe the speed itself. The unit element in speed space is hence:

$$\begin{aligned}
dv_xdv_ydv_z &= v^2 \sin\theta d\theta d\phi dv \\
P(v)dv &= \frac{\int_0^\pi \int_0^{2\pi} e^{-mv^2/2\tau} v^2 dv \sin\theta d\theta d\phi}{\int_0^\pi \int_0^{2\pi} \int_0^\infty e^{-mv^2/2\tau} v^2 dv \sin\theta d\theta d\phi} \\
&= \frac{v^2 e^{-mv^2/2\tau}dv}{\left(\frac{2\tau}{m}\right)^{3/2}\int_0^\infty u^2 e^{-u^2}du}, \quad u^2 = \frac{mv^2}{2\tau} \\
\implies P(v)dv &= 4\pi v^2 \left(\frac{m}{2\pi\tau}\right)^{3/2} e^{-mv^2/2\tau}
\end{aligned}$$

Useful Integrals

$$\int_0^\infty ue^{-u^2}du = \frac{1}{2}$$
$$\int_0^\infty u^2e^{-u^2}du = \frac{\sqrt{\pi}}{4}$$
$$\int_0^\infty u^3e^{-u^2}du = \frac{1}{2}$$
$$\int_0^\infty u^4e^{-u^2}du = \frac{3\sqrt{\pi}}{8}$$
$$\int_0^\infty u^5e^{-u^2}du = 1$$

Means in the Maxwell-Boltzmann Distribution

$$\langle v\rangle = \int_0^\infty vP(v)dv = \sqrt{\frac{8\tau}{\pi m}}$$
$$\sqrt{\langle v^2\rangle} = \sqrt{\frac{3\tau}{m}}$$
$$v_{mp} = \max v = \sqrt{\frac{2\tau}{m}}$$
$$\implies v_{mp} < \bar{v} < \sqrt{\bar{v^2}}$$

Application of Velocity Distribution: Effusion Consider a box of dilute atoms at temperature τ with a small hole compared to the mean distance between collisions. Let the outside be a vacuum. We want to find the flux of atoms leaving the box Φ_{tot}.

Crude estimate: Consider a cylinder of length $l = \bar{v}dt$ at the hole. The number of particles that leave can be approximated to be one sixth (6 possible directions) the number of atoms in that cylinder. Then:

$$\Phi_{tot}dAdt = \frac{1}{6}n(dA \times l) \implies \Phi_{tot} = \frac{n\bar{v}}{6}$$

Exact Calculation: We have to include the velocity distribution. Then:

$$\Phi_{tot} = \int_0^\infty \Phi(v_z)dv_z$$

where $\Phi(v_z)$ is the flux through the hole for particles with velocities in $v_z, v_z + dv_z$. The number of exiting atoms with velocities in the neighbourhood of v_z is hence:

$$\Phi(v_z)dAdt = ndldAP(v_z), \quad dl = v_zdt \implies \Phi(v_z) = nv_zP(v_z)$$

Integrating over all possible velocities:

$$\Phi_{tot} = \int_0^\infty nv_zP(v_z)dv_z = \int_0^\infty nv_z\left(\frac{m}{2\pi\tau}\right)^{1/2}e^{-mv_z^2/2\tau}dv_z = n\sqrt{\frac{\tau}{2m\pi}} = \frac{n\bar{v}}{4}$$

which is on the same order of magnitude as the crude estimate. If we use the ideal gas approximation,

$$P = n\tau \implies \Phi_{tot} = \frac{P\bar{v}}{4\tau} = \frac{P}{\sqrt{2\pi m\tau}}$$

Note that the flux exiting the hole is smaller for large mass.

10.2 Final Review II

Condition for equilibrium Consider a system in thermal equilibrium with a reservoir. The entropy of the reservoir and system combined is maximized at the equilibrium:

$$S_R(E - E_s) \approx S_R(E) - \frac{\partial S_R}{\partial E} E_s = S_R(E) - \beta E_s$$

By the Boltzmann factor,

$$P(E_s) = P(0)e^{-\beta E_s}$$
$$\implies P(E_s) = \frac{e^{-\beta E_s}}{Z}$$

Example: DNA Consider base pairs with two states: bound or dissociated. Let the bound energy be 0 and the dissociated energy be ϵ. Assuming that the base pair states are independent. Then the energy of the system is:

$$U = \epsilon N_d$$

Consider the partition function for a single base pair:

$$Z_1 = 1 + e^{-\beta\epsilon}$$

and hence the combined partition function assuming the states are distinguishable is:

$$Z_N = (1 + e^{-\beta\epsilon})^N$$

The thermal average energy is:

$$U\langle E\rangle = -\tau^2 \left(\frac{\partial Z}{\partial \tau}\right)_{N,V} = -\left(\frac{\partial \log Z}{\partial \beta}\right)_{N,V} = N\epsilon\frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}$$
$$\implies \langle n\rangle = N\frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}$$

Example 2: Dependent DNA Consider DNA that can only unzip from one end. That is, the nth base pair can only dissociate if the first $n - 1$ base pairs have already dissociated. Proceed by calculating the partition function, letting k be the number of dissociated base pairs:

$$Z = \sum_{k=0}^{N} (e^{-\beta\epsilon})^k = \frac{1 - (e^{-\beta\epsilon})^{N+1}}{1 - e^{-\beta\epsilon}}$$

Note that the thermal average energy becomes independent of N when N is large. Interestingly, it becomes:

$$U \approx \frac{1}{e^{\beta\epsilon} - 1}$$

which is in fact a useful approximation to the boson statistics. The previous example modelled a fermion two-state system.

Density of States: Massive Particles The dispersion relation is:

$$E = \frac{\hbar^2 k^2}{2m}$$

where the allowed values for k in an infinite square well is

$$|k|^2 = \frac{(n_x^2 + n_y^2 + n_z^2)\pi^2}{L^2}$$

In D dimensions,

$$N(\epsilon) = \frac{C_D}{2^D}\left(\frac{2mL^2\epsilon}{\hbar^2\pi^2}\right)^{D/2}$$

which goes as $L^D\epsilon^{D/2}$. Hence the density of states goes as $\frac{dN}{d\epsilon} \sim L^D\epsilon^{D/2-1}$.

Solving ideal gases at fixed chemical potential Consider the Bose Einstein distribution:

$$f_{BE} = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

Then the thermal average number of particles in a particular state with β, μ is:

$$\langle N(\beta,\mu)\rangle = \int_0^\infty d\epsilon \frac{dN}{d\epsilon} f_{BE}(\epsilon,\mu) \propto \int_0^\infty d\epsilon V \epsilon^{D/2-1}\frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

We require that this integral equals N, the actual number of particles. Note that this method fails to work when Bose Einstein condensation occurs. That is, there is no value of μ such that the thermal average of particles is equal to the total number of particles.

For example, bosons have a negative μ, hence it is bounded above by zero. If:

$$\langle N\rangle_\mu < \infty \text{ when } \mu \to 0$$

then μ cannot be tuned to match any arbitrary N. We want to find the values of D such that this occurs. Consider a first order approximation in terms of $\beta\epsilon$ near $\epsilon = 0$:

$$\langle N\rangle_\mu \sim \int d\epsilon \epsilon^{D/2-1}\frac{1}{1+\beta\epsilon-1} = \int d\epsilon \epsilon^{D/2-2}$$

Note that the RHS integral is only convergent when:

$$D/2 - 2 > -1 \implies D > 2$$

Density of states for photons in D-dimensions The dispersion relation is

$$E = \hbar c|\vec{k}| = \frac{\hbar c\pi}{L}|\vec{n}|$$

Hence the number of states contained within a D-sphere is:

$$N(\epsilon) = \left(\frac{\epsilon L}{\hbar c \pi}\right)^D \frac{C_D}{2^D} \sim L^D \epsilon^D \implies \frac{dN}{d\epsilon} \sim \epsilon^{D-1}$$

The thermal average energy is:

$$E = \int_0^\infty d\epsilon \frac{dN}{d\epsilon} \epsilon \epsilon^{D-1} V \frac{1}{e^{\beta\epsilon} - 1} \sim \frac{1}{\beta^{D+1}} \int_0^\infty dx \frac{x^D}{e^x - 1}$$

White Dwarf Stars Consider the energy of a spherical box or radius R made of fermions so that the system is as the ground state:

$$E = \int_0^{p_F} dp \frac{dN}{dp} \sqrt{p^2 c^2 + m^2 c^4}$$

where we integrate up to the fermi momentum. Note that the momentum of the fermions goes as $p \sim \frac{n\pi\hbar}{R}$, and the total number of particles goes as R^3, so the momentum scales as $p_F \sim \frac{N^{1/3}}{R}$.

10.3 Thursday 4 June 2015

Kinetic theory of transport We want to characterize the transport of heat, velocity and particles in non-equilibrium situations. We make the following assumptions:

- The collision time is negligible as compared to the time between collisions.
- The only collisions that occur are 2 particle collisions.
- Particles are classical: $\lambda_{\text{deBroglie}} <<$distance between particles.

First consider hard-sphere collisions between particles of radius R. Hence if two particles approach within 2R, there is a collision which redirects the velocity of the particles. The cross-sectional area for a collision is given by:

$$\sigma_0 = \pi(2R)^2$$

The probability of a collision in a thin box of width dl and area L^2 is hence:

$$dP = \frac{N\pi(2R)^2}{L^2} = \frac{nL^2 dl \pi(2R)^2}{L^2} = 4ndlR^2$$

Then the probability of colliding at a distance l is

$$P_c(l) = 1 - P_{\text{no collision}}(l)$$

Note that:

$$P_{NC}(l + dl) = P_{NC}(l) \times (1 - n\sigma_0 dl)$$
$$\implies \frac{dP_{NC}}{dl} = -P_{NC} n\sigma_0$$
$$\implies P_{NC} = Ce^{-n\sigma_0 l}$$

Implementing the normalization condition, we realize that if $l = 0$, then the probability of no-collision is just 1. Hence $C = 1$, so:

$$P_{NC}(l) = e^{-n\sigma_0 l} \implies P_C(l) = 1 - e^{-n\sigma_0 l}$$

Define the mean free path:

$$l_{mfp} = \frac{1}{n\sigma_0}$$

so that we can write the probability of a collision to be:

$$P_C(l) = 1 - e^{-l/l_{mfp}}$$

Transport Theory Consider a simple empirical linear law governing fluxes:

$$\text{Flux} \propto \text{Driving Force} \propto \text{Gradient}$$

For instance, Ohm's law states:

$$\vec{J}_{\text{electric current}} = -\frac{1}{R}\nabla Q, \quad Q = \text{electric potential}$$

and there is the self-diffusion equation:

$$\vec{J}_{\text{particles}} = -D\nabla n, \quad D = \text{Diffusion coefficient or diffusivity}$$

Example: Diffusion Let there be a gradient in density along the z-axis. We want to calculate the flux of particles crossing a fixed plane z_0 normal to the z-axis. Consider two planes just above and below this plane: z_u and z_l. Let the separation between planes be smaller than the mean free path length so that we may ignore particle collisions. Then the flux of particles through z_0 is given by the net number of particles going up between z_0 and z_l multiplied by the RMS velocity and divided by the volume (to attain a flux).

Continuity equation

$$\frac{\partial n}{\partial t} = \frac{\partial J_z}{\partial z} = \frac{\partial}{\partial z}\left(-D\frac{\partial n}{\partial z}\right) \implies \frac{\partial n}{\partial t} = -D\frac{\partial^2 n}{\partial n^2}$$

Applying Random Walk Results Consider how long it takes for a photon at the middle of the sun to get to the surface. Let the radius of the sun be $7 \times 10^{10} cm$, and let the time to surface to collisions be t_s. The mean square distance travelled in the simple random walk theory is given by:

$$\langle d^2 \rangle = N l_{mfp}^2$$

where N is the number of time steps.

Then the time taken to travel to the surface of the sun is:

$$t_s = N \times \frac{l_{mfp}}{c} = \frac{\langle d^2 \rangle}{l_{mfp}^2}\frac{l_{mfp}}{c} = \frac{R_{sun}^2}{l_{mfp}c}$$

The collisions can be estimated based on the cross section with electrons:

$$\sigma_0 = 0.67 \text{ barns} = 0.67 \times 10^{-24} cm^2$$

and the average number density of electrons:

$$\langle n_e \rangle = 8 \times 10^{23} cm^{-3}$$

so that the mean free path is:

$$l_{mfp} = \frac{1}{n\sigma_0} \approx 1cm$$

Hence $t_s \approx 5000 years$

Advanced Treatment We need to consider the actual velocity distribution.

Liouville's theorem from Classical Mechanics The volume of phase space is conserved.

10.4 Friday Recitation / Final Review

Types of ensembles

- Microcanonical: U fixed. Use:

$$dU = \tau d\sigma - pdV + \mu dN$$

- Canoncial: τ, N fixed. Use Helmholz:

$$dF = -\sigma d\tau - pdV + \mu dN$$

- Grand-Canonical: fix τ, μ.

Expected number of particles from Grand Canonical partition function

$$\langle N \rangle = \tau \frac{\partial}{\partial \mu} \ln \mathcal{Z}$$

Density of states Changing variables from summing across states to energies:

$$\langle X \rangle = \sum_n f(\epsilon_n, \tau, \mu) X_n = \int d\epsilon \mathcal{D}(\epsilon) f(\epsilon, \tau, \mu) X(\epsilon)$$

PH12C FINAL FORMULAE SHEET

Stirling Approximation (1.26 Pg 19)

$$N! \approx (2\pi N)^{1/2} N^N \exp(-N + 1/12N)$$
$$\ln N! \approx N \ln N - N$$

Binomial Distribution

$$P_N(n_r) = \frac{N!}{n_r!(N-n_r)!} p^{n_r} q^{N-n_r}$$

Approximation for Poisson (Week 1 Notes, A1)

$$(1-p)^{N-n_r} \approx e^{-Np}, \quad n_r << N, p << 1$$

e Definition

$$\lim_{x\to\infty} (1+1/x)^x = e$$

Poisson Distribution

$$P_N(n_r) \approx \frac{\mu^{n_r} e^{-\mu}}{n_r!}, \quad \mu = Np$$

Gaussian Normal Distribution

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}$$

Multiplicity sharpness (1.35-36 Pg 20)

$$g(N,s) = \frac{N!}{(N/2+s)!(N/2-s)!}$$
$$\approx g(N,0) e^{-2s^2/N}$$
$$g(N,0) \approx 2^N \sqrt{\frac{2}{\pi N}}$$

Multiplicity for harmonic oscillators (1.55, Pg 25)

$$g(N,n) = \frac{(N+n-1)!}{n!(N-1)!}$$

1D Harmonic Oscillator Partition Function (10.26, Pg 285)

$$\epsilon_n = n\hbar\omega - \epsilon_0$$
$$Z_s = \frac{e^{\epsilon_0/\tau}}{1 - e^{-\hbar\omega/\tau}}$$

Combining system multiplicities (2.6, Pg 35)

$$g(N,s) = \sum_{s_1} g_1(N_1, s_1) g_2(N_2, s - s_1)$$

Entropy (2.21, Pg 40)

$$\sigma(N,U) = \ln g(N,U)$$

Temperature (2.26, Pg 41)

$$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_{N,V}$$
$$\tau = k_B T$$
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}$$

Boltzmann Factor (3.9, Pg 61)

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{e^{-\epsilon_1/\tau}}{e^{-\epsilon_2/\tau}}$$

Partition Function (3.10, Pg 61)

$$Z(\tau) = \sum_s e^{-\epsilon_s/\tau} = \sum_\epsilon g(\epsilon) e^{-\epsilon/\tau}$$

Average Energy (3.12, Pg 61)

$$U = \tau^2 \left(\frac{\partial \ln Z}{\partial\tau}\right) = -\left(\frac{\partial \ln Z}{\partial\beta}\right)$$

Heat Capacity (3.17ab, Pg 63)

$$C_V = \left(\frac{\partial U}{\partial\tau}\right)_V = \tau \left(\frac{\partial\sigma}{\partial\tau}\right)_V$$
$$6.37: \quad C_p = \tau \left(\frac{\partial\sigma}{\partial\tau}\right)_p$$
$$= \left(\frac{\partial U}{\partial\tau}\right)_p + p\left(\frac{\partial V}{\partial\tau}\right)_p$$
$$6.38a: \quad C_p = C_V + N$$
$$6.38b: \quad C_p = C_V + Nk_B$$

Estimating Heat Capacity (6.39, Pg 167)

$$\sigma(\tau) - \sigma(0) = \int_0^\tau \frac{C_p}{\tau} d\tau$$

Pressure (3.26,3.32, Pg 66-67)

$$p = -\left(\frac{\partial U}{\partial V}\right)_{\sigma,N} = \tau\left(\frac{\partial\sigma}{\partial V}\right)_U$$

Thermodynamic Identity (3.34ab, Pg 67-68, 5.39 Pg 134)

$$\tau d\sigma = dU + pdV - \mu dN$$
$$dU = TdS - pdV + \mu dN$$

where pdV is the work done by the system.

Helmholtz Free Energy (3.35, Pg 68)

$$F = U - \tau\sigma$$
$$dF = 0 \quad \text{for reversible process}$$
$$6.24: F_{\text{ideal gas}} = N\tau[\ln(n/n_Q) - 1]$$

The free energy is extrinsic.

Volume and Pressure from F (3.49, Pg 70)

$$\sigma = -\left(\frac{\partial F}{\partial\tau}\right)_{V,N}$$
$$p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N}$$

Maxwell Relations (3.51, Pg 71)

$$\left(\frac{\partial\sigma}{\partial V}\right)_\tau = \left(\frac{\partial p}{\partial\tau}\right)_V$$

F from Z (3.55, Pg 72)

$$F = -\tau \ln Z \iff Z = e^{-F/\tau}$$

Quantum Concentration and Ideal Gas (3.63, Pg 73)

$$n_Q = \left(\frac{M\tau}{2\pi\hbar^2}\right)^{3/2}$$
$$Z_1 = n_Q V, \quad Z_N = \frac{(n_Q V)^N}{N!}$$

Sackur-Tetrode Equation (3.76, Pg 77)

$$\sigma = N\left[\ln(n_Q/n) + \frac{5}{2}\right]$$

Energy Fluctuations (3.89, HW3Q2)

$$\langle(\epsilon - \langle\epsilon\rangle)^2\rangle = \tau^2\left(\frac{\partial U}{\partial\tau}\right)_V$$

Finite Geometric Series

$$\sum_{s=0}^N x^s = \frac{1-x^{N+1}}{1-x}$$

Gaussian Integrals

$$\int_0^\infty e^{-\alpha n^2} dn = \sqrt{\frac{\pi}{4\alpha}}$$

Planck Distribution Function (4.6, Pg 91)

$$\langle s\rangle = \frac{1}{e^{\hbar\omega/\tau} - 1}$$

Photon Gas Parameters

Dispersion Relation 4.15 $\omega_n = \frac{n\pi c}{L}$

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

Energy density 4.20 $\frac{U}{V} = \frac{\pi^2\tau^4}{15\hbar^3c^3}$

Spectral density 4.22 $u_\omega = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{e^{\hbar\omega/\tau}-1}$

Entropy 4.23 $\sigma = \frac{4\pi^2V}{45}\frac{\tau^3}{\hbar^3c^3}$

Energy Flux 4.25 $J_U = \frac{cU(\tau)}{4V} = \frac{\pi^2\tau^4}{60\hbar^3c^2}$

$$J_\omega = \frac{cu_\omega}{4}$$

S-B constant 4.26a $\sigma_B = \frac{\pi^2k_B^4}{60\hbar^3c^2}$

Part. Fn. 4.53 $Z = \prod_n [1-\exp(-\hbar\omega_n/\tau)]^{-1}$

EOS (Week 4 notes) $pV = \frac{U}{3}$

Frequency Peak (4.27, Pg 98, Week 4 notes)

$$\frac{\hbar\omega_{max}}{k_BT} \approx 2.82$$

$$\lambda_{max}T = 0.290cmK = 2.898\times10^{-3}mK$$

Nyquist Theorem for Thermal Voltage Fluctuations (4.28, Pg 100)

$$\langle V^2\rangle = 4R\tau\Delta f$$

Debye Phonon Model (104-106)

$$N_{tot} = 3N$$

$$U = \frac{3L^3\tau^4}{2\pi^2\hbar^3v^3}\int_0^{x_D} dx\frac{x^3}{e^x-1}$$

$$x_D = \frac{\hbar v}{\tau}\left(\frac{6\pi^2N}{V}\right)^{1/3} \equiv \frac{k_B\theta}{\tau}$$

$$\tau\to 0, U \approx \frac{3\pi^4Nk_BT^4}{5\theta^3}$$

$$\implies \frac{U}{V} \approx \frac{\pi^2\tau^4}{10\hbar^3v^3}$$

Virial Theorem

$$KE = -\frac{1}{2}PE$$

Radiation Pressure (4.52, Pg 112)

$$p = \frac{1}{3}\frac{U}{V} = \frac{\pi^2\tau^4}{45\hbar^3c^3}$$

Density of States (Midterm Q2, Week 6 notes)

$$\sum_n f(\epsilon_n,\tau,\mu)X_n \approx \int d\epsilon\mathcal{D}(\epsilon)f(\epsilon,\tau,\mu)X(\epsilon)$$

$1D$ spinless : $\frac{L}{\pi\hbar}\sqrt{\frac{m}{2}}\frac{1}{\sqrt{E}}$

$1D$ spin s : $\frac{2s+1}{2}\frac{V}{2\pi\hbar}(2m)^{1/2}E^{-1/2}$

$2D$ spinless : $\frac{mL^2}{2\pi\hbar^2}$

$2D$ spin s : $\frac{2s+1}{2}\frac{V}{2\pi\hbar^2}(2m)$

$3D$ spinless : $\frac{L^3}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$

$3D$ spin half : $\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$

$3D, \frac{1}{2}(7.14) : N(E) = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{3/2}$

$3D$ spin s : $\frac{2s+1}{2}\frac{V}{2\pi^2\hbar^3}(2m)^{3/2}\sqrt{E}$

Energy Minimization (Week 3 Notes)

τ, V, N const. F minimized

$$F = U - \tau\sigma$$

τ, p, N const. G minimized

$$G = U - \tau\sigma + pV$$

σ, p, N const. H minimized

$$H = U + pV$$

Types of Ensembles (Week 5 notes)

Microcanonical: N, V, U fixed

Canonical: N, V, τ fixed

Grand Canonical: V, τ, μ fixed

Chemical Potential (Week 5 notes) The work required to transfer one particle into the system from a reservoir at zero chemical potential (Pg 250).

5.5 : $\mu(U,V,N) \equiv \left(\frac{\partial F}{\partial N}\right)_{\tau,V}$

5.7 : $\mu_j = \left(\frac{\partial F}{\partial N_j}\right)_{\tau,V,N_1,N_2,\ldots}$

$5.12a$: $\mu_{\text{ideal gas}} = \tau\ln\frac{n}{n_Q}$

5.30 : $\mu = -\tau\left(\frac{\partial\sigma}{\partial N}\right)_{U,V}$

Table 5.1: $\mu = \left(\frac{\partial U}{\partial N}\right)_{\sigma,V}$

$$dF = \mu dN - pdV - \sigma d\tau$$

Shifted zero energy: 6.20: $\mu = \Delta + \tau\ln\frac{n}{n_Q}$

Chemical Potential with Internal Degrees of Freedom (Pg 169-170)

Given: $\epsilon = \epsilon_n + \epsilon_{int}$

6.44 : $Z_{int} = \sum_{int} e^{-\epsilon_{int}/\tau}$

6.45 : $\mathcal{Z} = 1 + \lambda Z_{int}e^{-\epsilon_n/\tau}$

6.47 : $\lambda = \frac{n}{n_QZ_{int}}$

6.48 : $\mu = \tau[\ln(n/n_Q) - \ln Z_{int}]$

6.49 : $F_{int} = -N\tau\ln Z_{int},$

$$F = F_0 + F_{int}$$

6.50 : $\sigma_{int} = -\left(\frac{\partial F}{\partial\tau}\right)_V,$

$$\sigma = \sigma_0 + \sigma_{int}$$

For spin alone, 6.51: $Z_{int} = 2s+1$

Barometric Equation (5.18-19)

$$n(h) = n(0)e^{-Mgh/\tau}$$

$$p(h) = p(0)e^{-Mgh/\tau}$$

Gibbs' Factor (5.52, Pg 137)

$$\frac{P(N_1,\epsilon_1)}{P(N_2,\epsilon_2)} = \frac{\exp[(N_1\mu-\epsilon_1)/\tau]}{\exp[(N_2\mu-\epsilon_2)/\tau]}$$

Grand Partition Function

$$\mathcal{Z}(\mu,\tau) = \sum_{N=0}^{\infty}\sum_{s(N)}\exp[(N\mu-\epsilon_{s(N)})/\tau]$$

$$P(N_1,\epsilon_1) = \frac{\exp[(N_1\mu-\epsilon_1)/\tau}{\mathcal{Z}}$$

$$= \sum_s\sum_{N_s}\lambda^{N_s}e^{-E_s/\tau}$$

$$\lambda \equiv e^{\mu/\tau}$$

5.68 : $\lambda_{\text{ideal gas}} = \frac{n}{n_Q} = \frac{p}{\tau n_Q}$

Averages using Grand Partition Function

$$\langle A\rangle = \frac{\sum_s\sum_{N_s}A\lambda^{N_s}e^{-E_s/\tau}}{\mathcal{Z}}$$

5.59 : $\langle N\rangle = \tau\frac{\partial\ln\mathcal{Z}}{\partial\mu}$

5.62 : $\langle N\rangle = \lambda\left(\frac{\partial\ln\mathcal{Z}}{\partial\lambda}\right)$

5.65 : $U = \left(\frac{\mu}{\beta}\frac{\partial}{\partial\mu} - \frac{\partial}{\partial\beta}\right)\ln\mathcal{Z}$

5.81 Prob 10 : $\langle N^2\rangle = \frac{\tau^2}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\mu^2}$

Chemical Equilibrium

For the reaction: $\sum_i a_iX_i = 0$

Equilibrium $\implies \sum_i \mu_ia_i = 0$

Partition function for Fermions and Bosons (Week 6 Notes)

$$\mathcal{Z}_{FD}(E_i) = \sum_{N_s=0}^{1} \exp[(\mu N_s - N_s E_i)/\tau]$$

$$6.1: \quad \mathcal{Z}_{FD} = 1 + \lambda e^{-\epsilon/\tau}$$

$$\mathcal{Z}_{BE}(E_i) = \sum_{N_s=0}^{\infty} \exp[(\mu N_s - N_s E_i)/\tau]$$

$$6.7: \quad \mathcal{Z} = \frac{1}{1-\lambda e^{-\epsilon/\tau}}$$

FD and BE Distribution Functions (6.4 Pg 154, 6.10 Pg 158)

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau}+1}$$

$$f_{BE}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/\tau}-1}$$

$$f_{classical}(\epsilon) = \lambda e^{-\epsilon/\tau}$$

Fermi Energy (6.5 Pg 155)

$$\mu(\tau = 0) = \epsilon_F$$

$$7.7: \quad \epsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

Classical Regime A gas is in the classical regime when $f << 1$ for all orbitals (Pg 159).

Low temperature Boson chemical potential (Week 6 Notes)

$$\mu \approx E_0 - \frac{\tau}{N}$$

$$7.55: \quad \mu = -\tau/N$$

Quantum Temperature (Week 6 Notes)

$$\text{For classical limit: } n << \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2}$$

$$\implies \tau >> \frac{2\pi\hbar^2 n^{2/3}}{m} = \tau_Q$$

Fermion Parameters (Week 6 Notes)

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} \text{ spin half}$$

$$E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{2s+1}\right)^{2/3} \text{ spin s}$$

$$U(\tau = 0) = \frac{3NE_F}{5} \text{ spin half}$$

$$C_V = \frac{3\pi^2 N}{4}\frac{\tau}{E_F}, \tau << E_F$$

$$HW5E15: \mu_{FD} = E_F\left[1 - \frac{\pi^2}{12}\frac{\tau^2}{E_F^2}\right],$$

$$\tau << E_F$$

$$7.28: \quad C_{el} = \int_0^\infty d\epsilon(\epsilon - \epsilon_F)\frac{df}{d\tau}\mathcal{D}(\epsilon)$$

$$7.37: \quad C_{el} \approx \frac{1}{2}\pi^2 N\tau/\epsilon_F$$

$$7.36: \mathcal{D}(\epsilon_F) = \frac{3N}{2\epsilon_F}$$

$$7.90: p = \frac{(3\pi^2)^{2/3}}{5}\frac{\hbar^2 n^{5/3}}{m}, \quad \tau << \tau_F$$

$$\text{HW6Q7.3: } \sigma = \frac{\pi^2}{2}N\frac{\tau}{\tau_F}, \quad \tau << \tau_F$$

Sommerfeld's Lemma (Week 6 Notes)

$$\int_0^\infty \frac{\phi(x)dx}{e^{x-\alpha}+1} \approx \int_0^\alpha \phi(x)dx + \frac{\pi^2}{6}\left(\frac{d\phi}{dx}\right)_{x=\alpha}$$

$$\alpha >> 1$$

Gravitational Pressure on White Dwarf (Week 6 Notes)

$$P = \frac{3}{5}\frac{GM^2}{4\pi R^4}$$

Relativistic Stuff

$$E^2 = p^2c^2 + m^2c^4$$

$$p = \hbar k, \quad k = \frac{n\pi}{L}$$

$$\text{Ultrarelativistic 7.88: } \epsilon_F = \hbar\pi c\left(\frac{3n}{\pi}\right)^{1/3}$$

$$\text{Ultrarelativistic 7.89: } U_0 = \frac{3}{4}N\epsilon_F$$

Einstein Temperature (Week 6 Notes, Pg 204-206)

$$7.70: \quad N_e = 2.612 n_Q V, \quad \tau \text{ small}$$

$$7.72: \quad \tau < \frac{2\pi\hbar^2}{m}\left(\frac{n}{2.61}\right)^{2/3} = \tau_E$$

$$7.73: \quad \implies \frac{N_e}{N} \approx \left(\frac{\tau}{\tau_E}\right)^{3/2}$$

$$7.74: N_0 = N - N_e = N\left[1 - \left(\frac{\tau}{\tau_E}\right)^{3/2}\right]$$

Carnot Efficiency/Coefficient

$$8.7: \quad \eta_c = \frac{W}{Q_H} = \frac{\tau_H - \tau_C}{\tau_H}$$

$$8.13: \quad \gamma_C = \frac{Q_C}{W} = \frac{\tau_C}{\tau_H - \tau_C} > 1$$

Entropy change of isothermal expansion

$$\Delta\sigma = N\ln\frac{V_f}{V_i}$$

Work done by isothermal expansion (6.57, Pg 172)

$$W = N\tau\ln\frac{V_2}{V_1}$$

Work done by Carnot Cycle (8.27, Pg 240)

$$W = N(\tau_h - \tau_l)\ln\frac{V_2}{V_1}$$

Reversible and Irreversible Inequalities (8.28-29, Pg 243)

For work done ON gas

$$\delta W_{irr} > \delta W_{rev}$$

$$\delta Q_{irr} < \delta Q_{rev}$$

Ideal Gas Isentropic Process (Pg 174-176)

$$6.66: \quad \tau V^{\gamma-1} = \text{constant}$$

$$6.67: \quad \tau^{\gamma/(\gamma-1)}p = \text{constant}$$

$$6.68: \quad pV^\gamma = \text{constant}$$

$$\text{Table 6.3:} \quad W = U_2 - U_1$$

$$U_2 - U_1 = -\frac{3}{2}N\tau_1\left[1 - \left(\frac{V_1}{V_2}\right)^{2/3}\right]$$

Gibbs Free Energy (Week 8 Notes) is used when N, p, τ are independent variables. Minimized at constant pressure and temperature (Pg

262).

$$G = U - \tau\sigma + pV$$

$$9.5: \quad dG = -\sigma d\tau + Vdp + \mu dN$$

$$9.7: \quad \left(\frac{\partial G}{\partial N}\right)_{\tau,p} = \mu$$

$$9.8: \quad \left(\frac{\partial G}{\partial \tau}\right)_{N,p} = -\sigma$$

$$9.9: \quad \left(\frac{\partial G}{\partial p}\right)_{N,\tau} = V$$

$9.13: \quad G(N,\tau,p) = N\mu(p,\tau)$ one species

$9.14: \quad G = \sum_i N_i\mu_i$ multiple species

$$9.16: dG = \sum_i \mu_i dN_i - \sigma d\tau + Vdp$$

$$9.21: \quad G_{ideal} = N\tau \ln \frac{p}{\tau n_Q}$$

$9.30: \sum_i v_i\mu_i = 0$ for reactions at const. p, τ

Law of Mass Action (9.35, Pg 268)

$$\prod_i n_i^{v_i} = K(\tau) = \prod_i n_{Q,i}^{v_i} \exp[-v_i F_i(int)/\tau]$$

Saha Equation (HW7, 9.48 Pg 273)

$$[e] = [H]^{1/2} n_Q^{1/2} e^{-I/2\tau}$$

Enthalpy (Week 8 Notes)

$$H = U + pV$$
$$dH = -\tau d\sigma + Vdp + \mu dN$$

used when N, p, σ are independent variables.

Types of Reversible Work performed ON the system (Pg 245-246)

$$\text{Constant } \tau \implies \delta W = dF$$
$$\text{Constant } p \implies \delta W = dH - \delta Q$$
$$\text{Constant } \tau, p \implies \delta W = dG$$

Chemical Work (8.51, Pg 250)

$$\delta W_c \equiv \mu dN$$

Free Energy in Superconductors (8.56a, Pg 256)

$$\frac{F_N(\tau) - F_S(\tau)}{V} = \frac{B_c^2(\tau)}{2\mu_0}$$

Condition for phase coexistence (10.2, Pg 278) The phase with lower chemical potential will alone be stable.

$$\mu_l(p,\tau) = \mu_g(p,\tau)$$

Clausius-Clapeyron Equation Let s, v be the specific entropy and volume $\sigma/N, V/N$.

$$10.11: \quad \frac{dp}{d\tau} = \frac{s_g - s_l}{v_g - v_l}$$

$$10.15: \quad \frac{dp}{d\tau} = \frac{L}{\tau\Delta v}$$

Latent Heat (10.13, Pg 280). Use the specific entropy $s = \sigma/N$.

$$L \equiv \tau(s_g - s_l)$$

Idealized Phase Coexistence Curve (10.20-21, Pg 282)

$$p(\tau) = p_0 e^{-L_0/\tau}$$
$$p(T) = p_0 e^{-L_0/RT}$$

Thermodynamic identity across the phase coexistence curve (10.22, Pg 284)

$$\tau d\sigma = dU + pdV - (\mu_g - \mu_l)dN$$

Constant p (10.23):

$$L = \tau\Delta\sigma = \Delta U + p\Delta V = H_g - H_l$$

Lennard Jones 6-12 Potential

$$U(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

Van de Waals gas (Week 9 Notes)

Mean field potential energy: $\bar{U} \approx -a\dfrac{N}{V}$

$$V_{net} = V - bN$$

$$Z = \frac{1}{N!}\left[n_Q(V - bN)e^{aN/V\tau}\right]^N$$

$$10.38: F = -N\tau\left[\ln\frac{n_Q(V - Nb)}{N} + 1\right]\ldots$$
$$-\frac{N^2 a}{V}$$

$$10.33: \quad \left(p + a\frac{N^2}{V^2}\right)(V - bN) = N\tau$$

$$\iff p = \frac{\tau}{V/N - b} - \frac{a}{(V/N)^2}$$

$$10.46: G = \frac{N\tau V}{V - Nb} - \frac{2N^2 a}{V}\ldots$$
$$-N\tau\left[\ln\frac{n_Q(V - Nb)}{N} + 1\right]$$

$$10.73: \sigma = N\left[\ln\frac{n_Q(V - Nb)}{N} + \frac{5}{2}\right]$$

$$10.74: U = \frac{3}{2}N\tau - \frac{N^2 a}{V}$$

$$10.75: H(\tau, V) = \frac{5}{2}N\tau + \frac{N^2 b\tau}{V} - \frac{2N^2 a}{V}$$

$$10.76: H(\tau, p) = \frac{5}{2}N\tau + Nbp - \frac{2Nap}{\tau}$$

Van de Waals critical points (10.41, Pg 289)

$$p_c = \frac{a}{27b^2}$$
$$V_c = 3Nb$$
$$\tau_c = \frac{8a}{27b}$$

$$10.42: \left(\frac{p}{p_c} + \frac{3}{(V/V_c)^2}\right)\left(\frac{V}{V_c} - \frac{1}{3}\right) = \frac{8\tau}{3\tau_c}$$

$$10.44: \left(\hat{p} + \frac{3}{\hat{V}^2}\right)\left(\hat{V} - \frac{1}{3}\right) = \frac{8}{3}\hat{\tau}$$

Critical Point (10.45, Pg 291)

$$\left(\frac{\partial \hat{p}}{\partial \hat{V}}\right)_{\hat{\tau}} = 0$$
$$\left(\frac{\partial^2 \hat{p}}{\partial \hat{V}^2}\right)_{\hat{\tau}} = 0$$

are satisfied by $\hat{p} = \hat{V} = \hat{\tau} = 1$, the critical pressure, volume and temperature. Above τ_c, no phase separation exists.

Virial Expansion (Week 9 Notes)

$$\frac{p}{\tau} = n + B_2(T)n^2 + B_3(T)n^3\ldots$$
$$B_2(\tau) = b - \frac{a}{\tau}$$

Maxwell's Construction

$$\text{Equilibrium condition: } dg = V_N dp = 0$$
$$\int_{V_A}^{V_B} Vdp = 0$$

Landau Theory of Phase Transitions (298-304)

$$F(\tau) = \min_\xi F_L(\xi,\tau) = U(\xi,\tau) - \tau\sigma(\xi,\tau)$$

$$\text{Let } F_L(\xi,\tau) = g_0(\tau) + \frac{1}{2}g_2(\tau)\xi^2 + \ldots$$

10.5 Additional useful stuff from other books

Calculating entropy change

$$\Delta S = \int \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{C_v}{T} dT$$

Thermal De Broglie Wavelength

$$\lambda = \frac{h}{\sqrt{2\pi mkT}}$$

$$n_Q = \frac{1}{\lambda^3}$$

Density of states in frequency (photons)

$$\frac{D(\omega)}{V} = \frac{u_\omega}{\hbar\omega} = \frac{\omega^2}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/\tau} - 1}$$