

Statistical Physics (PHY831), Part 2 - Exact results and solvable models

Phillip M. Duxbury, Fall 2012

Systems that will be covered include:(10 lectures)

Classical ideal gases, Non-interacting spin systems, Harmonic oscillators, Energy levels of a non-relativistic and relativistic particle in a box, ideal Bose and Fermi gases. One dimensional and infinite range ising models. Applications to atom traps, white dwarf and neutron stars, electrons in metals, photons and solar energy, phonons, Bose condensation and superfluidity, the early universe.

I. CLASSICAL PARTICLE SYSTEMS

A. Exact results for systems described by $H = \sum_i p_i^2/2m + V(\{\vec{r}_i\})$

We have already seen some general results for classical particle systems described by a Hamiltonian H , including the equipartition theorem,

$$\langle p_i \frac{\partial H}{\partial p_j} \rangle = k_B T \delta_{ij}; \quad \langle q_i \frac{\partial H}{\partial q_j} \rangle = k_B T \delta_{ij} \quad (1)$$

which is proven by integrating by parts. Using Hamilton's equations,

$$\frac{\partial q_i}{\partial t} = \frac{\partial H}{\partial p_i}; \quad \frac{\partial p_i}{\partial t} = -\frac{\partial H}{\partial q_i} \quad (2)$$

gives,

$$\langle p_i \frac{\partial q_i}{\partial t} \rangle = k_B T \delta_{ij}; \quad \langle q_i \frac{\partial p_i}{\partial t} \rangle = -k_B T \delta_{ij} \quad (3)$$

Another general result is the virial theorem,

$$PV = Nk_B T + \frac{1}{3} \sum_i \vec{F}_i \cdot \vec{r}_i \quad (4)$$

which can be proven using kinetic theory and by considering the time derivative of the virial $G = \sum_i \vec{p}_i \cdot \vec{r}_i$. (see Part 1, Eq. (108)).

The Maxwell Boltzmann (MB) distribution of velocities is a general result for the non-relativistic gas and comes from considering the probability distribution of any one of the velocities in the system. We consider $p(v_i^\alpha) = p(v)$, as the MB distribution is the same for any velocity component of any particle in the system. We have,

$$p(v_i^\alpha) = \frac{\int \prod_{j \neq i}^{dN} dp_j \prod_j^{dN} dq_j e^{-\beta \sum_j p_j^2/2m + V}}{\int \prod_j^{dN} dp_j \prod_j^{dN} dq_j e^{-\beta \sum_j p_j^2/2m + V}} = \frac{e^{-\frac{1}{2}\beta m (v_i^\alpha)^2}}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m (v_i^\alpha)^2}} \quad (5)$$

so that,

$$p(v^\alpha) = \left(\frac{m\beta}{2\pi}\right)^{1/2} e^{-\frac{1}{2}\beta m (v^\alpha)^2}; \quad \text{or in three dimensions} \quad p(\vec{v}) = \left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m \vec{v}^2} \quad (6)$$

From this expression we can find the average kinetic energy,

$$\langle KE \rangle = \frac{1}{2} \sum_i m \langle v_i^2 \rangle = \frac{d}{2} N k_B T \quad (7)$$

or $\frac{1}{2}k_B T$ per component of the velocity. This is a property of quadratic terms in the Hamiltonian and as we saw in problem 15 of Part1 if we consider a harmonic or quadratic term in the co-ordinates, there is an additional $k_B T/2$ for every harmonic term in the co-ordinates.

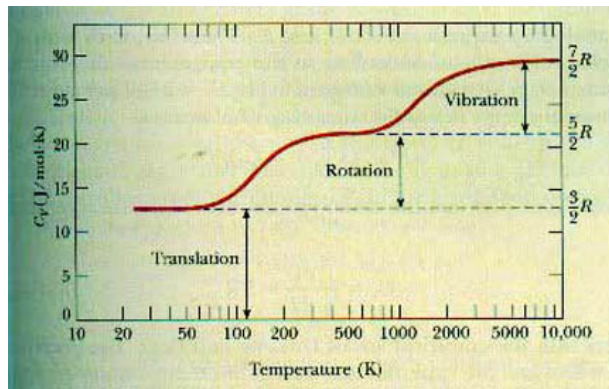


FIG. 1. The molar heat capacity of a diatomic gas indicating contributions from translations, rotational and vibrational degrees of freedom. Here R is the gas constant.

B. Equipartition and heat capacity, the importance of quantum level spacing

Counting of degrees of freedom is often used to understand even complex systems such as glasses and biological structures. It is also relevant to problems such as polyatomic gases where there are rotational and internal harmonic degrees of freedom. Measurements of specific heat are often assessed in terms of constraint counting, however understanding of the onset of each contribution to the specific heat requires analysis of the rotational and vibrational energy level spacings. For example the behavior expected from a full quantum mechanical treatment of the specific heat of a diatomic molecular gas is illustrated in Figure 1. Classically we should expect three translational contributions ($3R/2$), two rotational contributions (R), and the vibrational contribution that is a sum of a kinetic and potential component in one co-ordinate (R). Classically we would then expect to have a molar heat capacity of $7R/2$ at all temperatures. Actually we already ignored a third rotational component around the axis of the diatomic molecule. This is ignored due to a quantum argument noting that the energy level spacing of rotational energy levels is proportional to $1/I$, where I is the moment of inertia about the axis in question. Since the moment of inertia about the axis of the diatomic molecule (i.e. the axis along the vector joining the two atoms in the molecule) is very small, the rotational levels along this axis are never active so we ignore this contribution. The other rotational contributions also have a level spacing of their quantum rotational levels and they become active when the temperature is greater than the level spacing. Even for the translational degrees of freedom there is a level spacing and we discuss this spacing followed by the level spacing for rotational and vibrational degrees of freedom, using the nitrogen molecule as an example.

For the translational degrees of freedom the relevant quantum mechanical energy levels are those of a particle in a box,

$$E_k = \frac{\hbar^2 k^2}{2m}; \quad \text{with} \quad \vec{k} = \frac{\pi}{L}(n_x, n_y, n_z) \quad (8)$$

where n_x, n_y, n_z are integers so the level spacing is proportional to $1/L^2$. For most gases, this is really small so the classical argument is correct for all accessible temperatures. Note that if we make the box smaller (nanoscale L) or the mass small then the quantum effects become more important.

For the rotational degrees of freedom, assuming a rigid rotor, we have,

$$E_{rot} = \frac{L^2}{2I}; \quad \text{with} \quad L^2 = l(l+1)\hbar^2 \quad (9)$$

so the level spacing is proportional to $2\hbar^2/(mr^2)$ where m is the mass of a nitrogen atom and r is the bond length of the nitrogen molecule. Using $m = 14 \times 1.66 \times 10^{-27} \text{kg}$, $r = 145 \times 10^{-12} \text{m}$, $\hbar = 1.05 \times 10^{-34} \text{Js}$, gives level spacing $\delta E \approx 2.8 \times 10^{-4} \text{eV}$. The two rotational degrees of freedom that are not around the molecule axis are then correctly treated by classical equipartition even at room temperature. However for the rotational degree of freedom about the molecule axis, the moment of inertia is smaller by a factor of roughly 10^{-4} so its level spacing is a factor of 10^8 larger and hence not seen in the temperature range of the figure.

The vibrational degrees of freedom of the N_2 molecule have a frequency set by the stiffness of the bond stretching interaction k , so we have,

$$E_n = \hbar\omega(n + \frac{1}{2}); \quad \text{with} \quad \omega = \left(\frac{k}{m}\right)^{1/2}. \quad (10)$$

The vibrational energy level spacing for N_2 is roughly $0.34eV$, so the vibrational contributions to the heat capacity are seen only at very high temperatures.

C. Classical ideal gas in a box with volume $V = L^3$, phase space method

Since there are no interactions in the ideal gas, the equipartition theorem gives the internal energy of an ideal monatomic gas in three dimensions $U = 3Nk_B T/2$. This is not sufficient for us to find all of the thermodynamics as for that we need $U(S, V, N)$. To find all of the thermodynamics, we can work in the microcanonical, canonical or grand canonical ensembles. First lets look at the canonical ensemble.

To find the canonical partition function, we consider the phase space integral for N monatomic particles in a volume V at temperature T , so that,

$$Z = \frac{1}{N!h^{3N}} \int dq_1^3 \dots dq_N^3 \int dp_1^3 \dots dp_N^3 e^{-\beta H}. \quad (11)$$

where H is the Hamiltonian, that for a non-interacting gas is simply $H = \sum_i \vec{p}_i^2/2m$. The prefactor $1/(N!h^{3N})$ are due to the Gibb's paradox and Heisenberg uncertainty principle respectively. The Gibb's paradox notes that if we integrate over all positions for each particle, we overcount the configurations of identical particles. That is we count the $N!$ ways of arranging the particles. This factor should only be counted if the particles are distinguishable. The factor $1/h^{3N}$ is due to the uncertainty relation $\delta x \delta p > \hbar/2$, which states that the smallest region of phase space that makes sense quantum mechanically is $\hbar^3/8$. The fact that the normalization is $1/h^3$ per particle is to ensure that the classical or Maxwell-Boltzmann gas defined above agrees with the high temperature behavior of the ideal Bose and Fermi gases, as we shall show later.

For an ideal gas, the integrals over position in (11) give V^N , while the integrals over momenta separate into $3N$ Gaussian integrals, so that,

$$Z = \frac{V^N}{N!h^{3N}} I^{3N} \quad \text{where} \quad I = \int_{-\infty}^{\infty} e^{-\beta p^2/2m} = \left(\frac{2m\pi}{\beta}\right)^{1/2}. \quad (12)$$

This may be written as,

$$Z = \frac{V^N}{\lambda^{3N} N!} \quad \text{where} \quad \lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \quad (13)$$

is the thermal de Broglie wavelength. Note that the partition function is dimensionless. The thermal de Broglie wavelength is an important length scale in gases. If the average interparticle spacing, $L_c = (V/N)^{1/3}$ is less than λ quantum effects are important, while if $L_c > \lambda$, the gas can be treated as a classical gas. We shall use this parameter later to decide if particles in atom traps are expected to behave as classical or quantum systems. The thermal de Broglie wavelength of Eq. (13) is for massive particles with a free particle dispersion relation, that is $\epsilon(p) \propto \vec{p}^2$. For massless particles or particles with different dispersion relations, a modified de Broglie wavelength needs to be defined. From the canonical partition function we find the Helmholtz free energy,

$$F = -k_B T \ln(Z) = -k_B T \ln\left(\frac{V^N}{\lambda^{3N} N!}\right) \quad (14)$$

This expression is in terms of its natural variables $F(T, V, N)$, so we can find all of the thermodynamics from it as follows:

$$dF = -SdT - PdV + \mu dN = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN \quad (15)$$

and hence

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k_B \ln\left(\frac{V^N}{\lambda^{3N} N!}\right) + \frac{3}{2} N k_B \quad (16)$$

The internal energy is found by combining (14) and (16), so that,

$$U = F + TS = \frac{3}{2} N k_B T \quad (17)$$

The pressure is given by,

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = k_B T \frac{N}{V} = \frac{k_B N T}{V}, \quad (18)$$

which is the ideal gas law, while the chemical potential is,

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = k_B T \ln(\lambda^3 N/V) \quad (19)$$

The response functions are then,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} = \frac{3Nk_B}{2}, \quad C_P = \left(\frac{\partial H}{\partial T} \right)_{P,N} = \frac{5Nk_B}{2} \quad (20)$$

where we used $H = U + PV = 5Nk_B T/2$.

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N} = \frac{1}{P}, \quad \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{S,N} = \frac{C_V}{C_P} \kappa_T = \frac{3}{5P} \quad (21)$$

and

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N} = \frac{1}{T} \quad (22)$$

It is easy to verify that the response function results above satisfy the relation,

$$C_P = C_V + \frac{TV\alpha_P^2}{\kappa_T} \quad (23)$$

To use the micro-canonical ensemble we calculate the density of states $\Omega(E)$ directly. Since the KE is a sum of the squares of the momenta, this sum is a constant on the surface of a sphere in a $3N$ dimensional space. In three dimensions, the density of states on a the surface of the sphere is $4\pi p^2$. In n dimensions the density of states is $s_n = nc_n p^{n-1}$. (see e.g. Pathria and Beale - Appendix C), To find c_n , we can use a Gaussian integral trick as follows (for n even),

$$\int_{-\infty}^{\infty} \prod dx_i e^{-\sum_i x_i^2} = (\pi)^{n/2} = \int_0^{\infty} nc_n R^{n-1} e^{-R^2} DR = \frac{n}{2} c_n \Gamma\left(\frac{n}{2}\right) \quad (24)$$

so that $c_n = \pi^{n/2}/(n/2)!$ for n even (as $\Gamma(n/2) = (n/2 - 1)!$ for n even). For odd n , $c_n = \frac{2^{(n+1)/2} \pi^{(n-1)/2}}{n!!}$, where $n!! = n(n-2)(n-4)\dots$. Using $s_n = nc_n R^{n-1}$ (for n even) with $R \rightarrow p$ and $n = 3N$ gives,

$$s_{3N} = \frac{2 \pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} p^{3N-1} \quad (25)$$

Applying the Gibb's correction ($1/N!$), the phase space correction ($1/h^{3N}$), including the spatial contribution V^N , with $p^2 = 2mE$ gives the micro-canonical density of states,

$$\Omega(E) = \frac{2\pi^{1/2} V^N (2\pi m E)^{3N/2-1/2}}{N! h^{3N} \left(\frac{3N}{2} - 1\right)!} \quad (26)$$

Using Stirling's approximation and keeping the leading order terms gives the Sackur-Tetrode equation for the entropy of an ideal gas,

$$S = k_B \ln(\Omega(E)) = Nk_B \left[\ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3N h^2} \right)^{3/2} \right] + \frac{5}{2} \right] \quad (27)$$

The internal energy is then,

$$U = \frac{3h^2 N^{5/3}}{4\pi m V^{2/3}} \text{Exp} \left[\frac{2S}{3Nk_B} - \frac{5}{3} \right] \quad (28)$$

From (27) or (28) the other thermodynamic properties of interest can be calculated. Using the equipartition result it is easy to show that Eq. (27) and (16) are equivalent.

Finally we would like to find the grand canonical partition function. This can be calculated from the canonical partition function by summing over all numbers of particles as follows,

$$\Xi(T, V, \mu) = \sum_{N=1}^{\infty} z^N Z_N = \sum_{N=1}^{\infty} z^N \frac{\alpha^N}{N!} = e^{\alpha z} \quad (29)$$

where $z = e^{\beta\mu}$ is the fugacity, and $\alpha = V/\lambda^3$. We have,

$$\Phi_G = -PV = -k_B T \ln(\Xi) = -k_B T \alpha e^{\beta\mu} \quad (30)$$

$$d\Phi_G = -SdT - PdV - Nd\mu = \left(\frac{\partial \Phi_G}{\partial T} \right)_{V, \mu} dT + \left(\frac{\partial \Phi_G}{\partial V} \right)_{T, \mu} dV + \left(\frac{\partial \Phi_G}{\partial \mu} \right)_{T, V} d\mu \quad (31)$$

Which again can be used to calculate all thermodynamic quantities, for example

$$-N = \left(\frac{\partial \Phi_G}{\partial \mu} \right)_{T, V} = -k_B T \beta \alpha e^{\beta\mu} = -\beta PV \quad (32)$$

which is the ideal gas law again (to find the last expression we used Eq. (30)).

D. More realistic ideal gas models

The simple ideal gas model above is an approximation in that it ignores interactions, but it also ignores all degrees of freedom except the translational motion of the center of mass. Even atoms are not correctly described by this model at high temperatures where electronic excitations can occur. Of course for atomic Hydrogen or Helium the temperature to excite the first electronic level is large so we don't have to worry about it in most calculations. However for heavier atoms the first excited state may be accessible at realistic energies so we have to take it into account. If we want to treat molecular systems then we also have to include the vibrational and rotational degrees of freedom. Often, these different degrees of freedom are treated as independent so we get a contribution from each and ideal gas canonical partition function including these degrees of freedom can be written as,

$$Z_N = \frac{V^N}{N! h^{3N}} (Q_n Q_e Q_v Q_r)^N = \frac{V^N}{N! \lambda^{3N}} (Q_e Q_v Q_r)^N \quad (33)$$

where the nuclear Q_n , electronic Q_e , vibrational Q_v and rotational Q_r contributions are included as an independent product. Each of these terms is a canonical single particle sum over the available energy levels. If there is coupling between the electronic, vibrational and rotational levels a more sophisticated quantum chemistry calculation yields the energy level spectrum and these energy levels are used in the partition sum. At the highest level of sophistication, the energy levels cannot be treated as independent, so the partition sum cannot be reduced to the form Q^N . In that case we are forced to treat the many body problem where configuration sums have to be carried out. In quantum chemistry this is called a configuration interaction calculation.

E. Non-interacting gas models for earth's atmosphere

Here we discuss two simple models for the atmosphere of a planet; an equilibrium model; and a non-equilibrium model. In both models the forces have to be balanced so we equate the gas pressure gradient and the gravitational force to give,

$$A(P(z) - P(z + dz)) = mg\rho(z)Adz \quad \text{so that} \quad \frac{dP}{dz} = -\rho mg \quad (34)$$

If we assume that the atmosphere obeys the ideal gas law, we have, $P = \rho k_B T$ where R is the gas constant and $\rho = N/V$ is the number density. If we assume that the atmosphere is at equilibrium so that T is constant, we find,

$$\frac{dP}{dz} = -P \frac{mg}{k_B T} \quad \text{so that} \quad P = P_0 e^{-z/z_0} \quad (35)$$

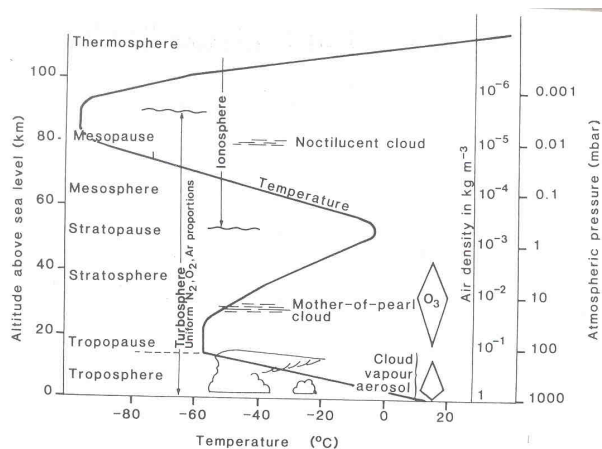


FIG. 2. Dependence of air temperature with altitude in the earth's atmosphere

where $z_0 = k_B T / mg$, where m is the average mass of a gas molecule. Since T is constant, the density is proportional to P , so the density also decreases exponentially with height. The characteristic length of the atmosphere z_0 turns out to be about 8.4 km . Humans start to die at altitudes where $P < 0.5 \text{ atm}$, which occurs at roughly $19,000 \text{ ft}$, which explains why climbers need oxygen climbing Everest, and why we need pressurized cabins in aeroplanes that typically fly at $32,000 \text{ ft}$. Actually planes are pressurized to roughly 0.85 atm while the outside pressure is roughly 0.35 atm , so the pressure difference is roughly 0.5 atm . The planes must be built to withstand this pressure. The higher the cabin pressure or the higher a plane flies, the stronger the aircraft construction must be in order to maintain the cabin pressure.

It is clear that the assumption of constant temperature is wrong as we know that the temperature on top of Mount Everest is much lower than the temperature at the foot of Mount Everest. An estimate of the temperature drop with altitude is roughly $9.8 \text{ Kelvin per kilometer}$ but only in the lower atmosphere (troposphere). The temperature profile in the earth's atmosphere is quite complicated (see Fig. 2). Modeling of this complete temperature profile is too difficult for us, however we can develop an understanding of the temperature profile in the troposphere based on a non-equilibrium ideal gas. Before doing that it is interesting to note that the increase in temperature in the thermosphere is due to absorption of UV radiation by ozone and the temperature can reach over $1000 \text{ degrees centigrade}$ in this layer. This layer is also ionized so radio waves are reflected from it, enabling radio transmissions over large distance on earth. In the turbosphere and troposphere the atmospheric gases are quite well mixed however in the thermosphere they are layered according to molecular weight. Though UV radiation is mainly absorbed in the outer atmosphere, the main infrared and visible light absorption occurs at the earth's surface. The thermal energy input to the earth/atmosphere system is then predominately at the earth surface and in the outer atmosphere, leading to an interesting driven gas system.

To estimate the temperature profile of the atmosphere in the troposphere we argue that although the gas must remain in hydrostatic equilibrium, the heat in the gas is not at equilibrium and in the simplest case, we assume no heat transfer. This is justified by arguing that air is a poor thermal conductor and in the troposphere the atmosphere is well mixed. We are then in an adiabatic regime. In that case, the relation between pressure and temperature for the ideal gas is,

$$P^{1-\gamma} T^\gamma = \text{constant}, \quad \text{where} \quad \gamma = \frac{C_P}{C_V} \approx 1.4 \quad \text{for a diatomic gas} \quad (36)$$

Here we take $C_P = C_V + Nk_B$, with $C_V = 5Nk_B/2$ as the earth's atmosphere consists mainly of diatomic molecules and in the temperature range of interest here the rotational degrees of freedom are activated but the vibrational degrees of freedom are not. We may then write,

$$\frac{dP}{P} = \frac{\gamma}{\gamma - 1} \frac{dT}{T}. \quad (37)$$

Using the equation for hydrostatic equilibrium (Eq. (34)), we find,

$$\frac{\gamma}{\gamma - 1} \frac{dT}{T} = -\frac{mg}{k_B T} dz, \quad \text{so} \quad T(z) = T_0 \left(1 - \frac{\gamma - 1}{\gamma} \frac{z}{z_0}\right) \quad (38)$$

Using Eq. (37) and the ideal gas law; $\rho \propto P/T$, we also find,

$$P(z) = P_0 \left(1 - \frac{\gamma - 1}{\gamma} \frac{z}{z_0}\right)^{\gamma/(\gamma-1)}; \quad \rho(z) = \rho_0 \left(1 - \frac{\gamma - 1}{\gamma} \frac{z}{z_0}\right)^{1/(\gamma-1)} \quad (39)$$

These equations lead to the prediction that the density of the atmosphere goes to zero at a critical thickness as opposed to a diffuse atmosphere as predicted by Eq. (35). Actually the exponential decay of the pressure leads to a behavior not too different than the power law of Eq. (39) as $a = \gamma/(\gamma - 1) \approx 3.5$ is quite large. In fact in the limit $a \rightarrow \infty$ we have,

$$\left(1 - \frac{x}{a}\right)^a \rightarrow e^{-x} \quad (40)$$

so in that limit the adiabatic and isothermal pressure profiles are the same. Suprisingly the predictions of the adiabatic model are quite good for earth's atmosphere for heights less than about $z = 15km$.

II. SPIN MODELS

The study of models for magnetic behavior have applications in all areas of physics and in many areas outside of physics. They have played a key role in statistical physics, particularly in developing an understanding of phase transitions. Ising in his PhD thesis showed that the one dimensional Ising magnet does not have a phase transition at finite temperature while Onsager in a beautiful piece of work proved that the Ising model in two dimensions does have a phase transition. Ferromagnets are materials that exhibit spontaneous symmetry breaking and breaking of ergodicity where at low temperatures magnetization spontaneously appears without the application of an external field. In contrast paramagnets require an applied field in order to exhibit magnetization and at low field, h , the magnetization, m is proportional to the applied field. We first consider paramagnets.

1. Spin half and continuous spin paramagnets

We consider a case where the applied field lies along the easy axis of a magnet, so that the Hamiltonian is,

$$H = -\mu_s h \sum_i S_i \quad (41)$$

where μ_s is the magnetic moment of the system, h is the applied field and $S = \pm 1$ is the spin. The statistical mechanics is easy to carry through as follows,

$$Z = \prod_i \left(\sum_{S_i \pm 1} e^{\beta \mu_s h S_i} \right) = 2^N \text{Cosh}^N(\beta \mu_s h) \quad (42)$$

The magnetization is given by,

$$m = \frac{M}{N} = \frac{\mu_s}{N} \sum_i \langle S_i \rangle = \frac{1}{N} \frac{\partial(\ln(Z))}{\partial(\beta h)} = \mu_s \tanh(\beta \mu_s h) \quad (43)$$

Other thermodynamic quantities of interest are the internal energy,

$$U = -\frac{\partial \ln(Z)}{\partial \beta} = -N \mu_s h \tanh(\beta \mu_s h) \quad (44)$$

the Helmholtz energy and the entropy,

$$F = -k_B T \ln(Z) = -k_B T \ln(2 \cosh(\beta \mu_s h)); \quad S = \frac{1}{T}(U - F) = N k_B [\ln(2 \cosh(\beta \mu_s h)) - \beta \mu_s h \tanh(\beta \mu_s h)] \quad (45)$$

Surprisingly several important and general physical phenomena are contained in this model. The first two are related to the response functions, the magnetic susceptibility and the specific heat. The magnetic susceptibility,

$$\chi = \frac{\partial m}{\partial h} = \beta \mu_s^2 \text{sech}^2(\beta \mu_s h) \rightarrow \frac{\mu_s^2}{k_B T}, \text{ as } h \rightarrow 0. \quad (46)$$

The behavior $\chi \propto 1/T$ is called the Curie law and is used in experiments to see if the spins in the system are paramagnetic and to extract an effective value for the spin moment, μ_s , for the system. The specific heat of the model is given by,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_h = Nk_B \left(\frac{\beta\mu_s h}{\cosh(\beta\mu_s h)} \right)^2 \quad (47)$$

The specific heat approaches zero exponential at low temperatures and at high temperatures approaches zero as a power law $\approx 1/T^2$. There is a peak in the specific heat at roughly $k_B T_p \approx \text{level spacing}/2 = \mu_s h$. Simple ideas about the peak in the specific heat and entropy are used to interpret data such as that in Fig. 1 (left). The right figure shows the analogy between magnetic cooling and refrigeration using a gas cycle. Magnetic cooling is used to reduce the temperature below about 0.1K by using an intriguing property called negative temperature. This non-equilibrium property can be produced in our simple spin half paramagnetic system. The origin of the effect is seen by considering the entropy of the paramagnet as a function of its energy in the microcanonical ensemble with N, V, E as the control variables. If the number of up spins is n and the number of down is $N - n$, then the entropy and energy as a function of the number of up spins is,

$$E = -\mu_s h(n - (N - n)) = -\mu_s hN(2\frac{n}{N} - 1); \quad S(E) = k_B \ln \frac{N!}{n!(N-n)!} = -k_B N [\ln(\frac{n}{N}) + \ln(1 - \frac{n}{N})] \quad (48)$$

The entropy may be written in terms of the energy using,

$$\frac{n}{N} = \frac{1}{2} - \frac{E}{2\mu_s hN} \quad (49)$$

Of course the entropy is a maximum at $n = N/2$ where half of the spins are up and half are down. At this point the energy is 0. The lowest energy state is where all spins are aligned with the field and at that point $E = -\mu_s hN$. As we increase the energy from this value the entropy increases until we reach the highest entropy state at $E = 0$. However, and this is the key feature of this system, if the energy is raised further, the entropy decreases. Now consider the fact that the temperature is given by,

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad (50)$$

so if the entropy increases with energy the temperature is positive and this is what happens at equilibrium. However when we are away from equilibrium there is no need for the temperature to be positive. If we can prepare a state in a regime where the entropy decreases with energy, as in the paramagnetic model above, then the temperature is negative. Clearly this is not a stable state so the system absorbs energy (heat) to return to a positive temperature state. This leads to the possibility of magnetic cooling where magnetic work is carried out to prepare the system in a state where the spins are aligned with a field. If the field is then switched off the system wants to return to the high entropy state at $E = 0$ and this leads to absorption of energy from the sample. This process is cycled to achieve cooling (see figure 3). Mechanical work is done in polarizing the field and this work is used to produce refrigeration.

In many systems the spin is not restricted to the value 1/2 and instead we have combinations of spins (like in Fe due to Hund's rule), which leads to many more possibilities. It is actually a good approximation in many cases to consider the spin to be able to rotate to any angle on either the perimeter of a circle or on the surface of a sphere, so that the field energy is given by,

$$H = - \sum_i \vec{\mu}_i \cdot \vec{h} \quad (51)$$

where $\vec{\mu}_i = \mu_s \vec{S}$ and \vec{S} is a vector with unit length that can lie on the surface of a sphere (Heisenberg model) or circle (XY model). We set the length of S to be one for convenience by absorbing the factor $(S(S+1))^{1/2}$ into μ_s . The model is still a non-interacting model so the canonical partition function is Z_1^N , and for the (classical) continuous Heisenberg spin case,

$$Z_1 = \int \sin(\theta) d\theta d\phi e^{\beta\mu_s h \cos(\theta)} = \frac{4\pi \sinh(\beta\mu_s h)}{\beta\mu_s h} \quad (52)$$

The magnetization per spin is given by,

$$m = \frac{M}{N} = \frac{\partial}{\partial(\beta h)} (\ln(Z_1)) = \mu_s [\coth(\beta\mu_s h) - \frac{1}{\beta\mu_s h}] \quad (53)$$

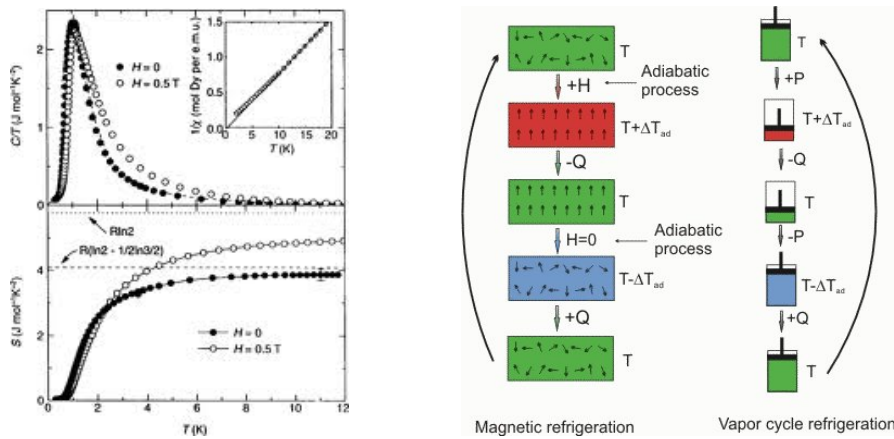


FIG. 3. left: Example of specific heat and entropy measurements of a magnetic system. Right: Comparison of magnetic cooling and cooling use a gas cycle (from Wikipedia)

For low fields (and sufficiently high temperatures) we find,

$$m \approx \frac{\mu_s^2}{3k_B T} h; \quad \text{so} \quad \chi = \frac{\partial m}{\partial h} = \frac{\mu_s^2}{3k_B T} \quad (54)$$

For both the spin half and continuous spin cases we find the Curie law which is characteristic of “classical” paramagnets. As we shall see when we study the Fermi gas, a very different behavior occurs when the gas has quantum degeneracy.

2. Spin half nearest neighbor Ising model in one dimension and two dimensions

A key question in statistical physics is whether a system is capable of having a phase transition. The Ising model is a comparatively simple system where we can address this question with some precision. The first question is whether a one dimensional Ising model has a phase transition at finite temperature and this can be answered by solving the problem exactly. First however we go through a simple argument due to Peierls that shows a finite temperature phase transition is not possible for the one-dimensional spin-half Ising model with nearest-neighbor interactions.

The one-dimensional nearest neighbor Ising model has Hamiltonian,

$$H = -J \sum_{i=1}^N S_i S_{i+1} \quad (55)$$

where $S_i = \pm 1$. The Peierls argument considers the stability of the ground state (all up spins) to topological excitations where in this problem the excitations are domains of the opposite orientation. In a problem with free boundaries we can consider a simpler problem consisting of a single “domain wall” between a region of all up spins and a region of all down spins. If the free energy of this excitation is lower than the ground state, then the ground state is unstable. The difference in Helmholtz free energy between a system with a domain wall and that without a domain wall is given by,

$$\delta F = \delta U - T\delta S = 4J - k_B T \ln(N) \quad (56)$$

where we consider a fixed temperature. Since $\delta F < 0$ for finite T provided N is sufficiently large, the one dimensional Ising ground state is unstable to long wavelength fluctuations. It therefore cannot have a phase transition at finite temperature.

Now we solve the problem exactly and check if the Peierls argument is right. We use periodic boundary conditions so the model is defined on a ring. It is useful to solve this problem using transfer matrices as they can be generalized to many problems and provide a method for transforming a classical problem at finite temperature into the ground state of a quantum problem in one lower dimensions. The transfer matrix for the one dimensional Ising model is a two by two matrix, with matrix elements,

$$T_{S,S'} = e^{\beta J S S'} \quad (57)$$

where S, S' take values ± 1 as usual. The partition function may then be written as,

$$Z = \sum_{S_1} \sum_{S_2} \dots \sum_{S_N} e^{\beta J \sum_i S_i S_{i+1}} = \sum_{S_1} \sum_{S_2} \dots \sum_{S_N} \langle S_1 | \hat{T} | S_2 \rangle \langle S_2 | \hat{T} | S_3 \rangle \dots \langle S_N | \hat{T} | S_1 \rangle \quad (58)$$

This reduces to,

$$Z = \text{tr}(T^N) = \lambda_1^N + \lambda_2^N \quad (59)$$

where $\lambda_{1,2}$ are the eigenvalues of the transfer matrix T . The problem is then reduced to diagonalizing a two by two matrix. We find that the eigenvalues of the transfer matrix are,

$$\lambda_1 = 2\text{Cosh}(\beta J); \quad \lambda_2 = 2\text{Sinh}(\beta J) \quad (60)$$

so that,

$$Z = 2^N [\text{Cosh}^N(\beta J) + \text{Sinh}^N(\beta J)] \quad (61)$$

The specific heat can be calculated by using,

$$F = -k_B T \ln(Z) = -k_B T N [\ln(2) + \ln(\text{Cosh}(\beta J))] \quad (62)$$

so that,

$$C_V = T \frac{\partial^2 F}{\partial T^2} = N k_B \left(\frac{J}{k_B T}\right)^2 \text{sech}^2\left(\frac{J}{k_B T}\right) \quad (63)$$

At low temperatures this reduces to,

$$\frac{C_V}{N k_B} \approx \left(\frac{J}{k_B T}\right)^2 \text{Exp}\left[-\frac{2J}{k_B T}\right] \quad \text{as } T \rightarrow 0 \quad (64)$$

while

$$\frac{C_V}{N k_B} \approx \left(\frac{J}{k_B T}\right)^2 \quad \text{as } T \rightarrow \infty \quad (65)$$

The specific heat thus approaches zero exponentially at low temperatures and approaches zero algebraically at high temperatures. There is a peak in the specific heat at around $J = k_B T$. This is typical of systems that have a ‘‘gap’’ of order J between the ground state and the first excited state.

Solution of the two dimensional Ising model is carried out using the transfer matrix method, however the transfer matrix is of dimension $2^L \times 2^L$ where L is the transverse dimension of the square lattice strip. In a spectacular calculation, Onsager found the exact solution and from it found the following results (1944),

$$(\beta J)_c = \frac{1}{2} \ln(1 + \sqrt{2}) \quad \text{or} \quad \left(\frac{k_B T}{J}\right)_c \approx 2.2691\dots \quad (66)$$

and near the critical point the specific heat behaves as, for $T < T_c$,

$$\frac{C_V}{N k_B} \approx \frac{2}{\pi} \left(\frac{2J}{k_B T_c}\right)^2 \left[-\ln\left(1 - \frac{T}{T_c}\right) + \ln\left(\frac{k_B T}{2J}\right) - \left(1 + \frac{\pi}{4}\right)\right] \quad (67)$$

The specific heat thus diverges logarithmically on approach to T_c . The low and high temperature behavior is similar to that in the one dimensional case.

The magnetization can also be calculated. In the one dimensional case the transfer matrix can be extended to treat the hamiltonian,

$$H = -J \sum_i S_i S_{i+1} - h \sum_i S_i \quad (68)$$

The magnetization is found from $\partial \ln(Z) / \partial (h)$, leading to,

$$m(h, T) = \frac{\text{Sinh}(\beta h)}{[\text{Sinh}^2(\beta h) + e^{-4\beta J}]^{1/2}}; \quad \text{1d Ising.} \quad (69)$$

From this expression it is seen that the magnetization is zero for $h = 0$ in one dimension.

In two dimensions an exact result in finite field has not been found, but the magnetization in zero field has been found, with the result that for $T < T_c$ with $h = 0$,

$$m(h = 0, T) = (1 - [\text{Sinh}(2\beta J)]^{-4})^{1/8} \quad 2d \text{ Ising}, \quad T < T_c \quad (70)$$

Near the critical point this reduces to,

$$m(h = 0, T) \propto (T_c - T)^{1/8} \quad T < T_c, \quad h = 0 \quad (71)$$

The critical exponent for the Ising order parameter is thus $1/8$ in two dimensions however this exponent depends on the spational dimension and is $1/2$ above the so-called "upper critical dimension". There is no phase transition in one dimension. What is the behavior in three dimensions?? We shall return to the general issue of phase transitions and critical exponents in Part 3 of the course. Now we show that the behavior above the upper critical dimension is found using mean field theory. In fact, as we shall explore further in Part 3 of the course, systems in high dimensions or with long range interactions are usually well described by mean field theory.

3. Infinite range model of an Ising ferromagnet

The Ising model is very difficult, even in two dimensions where there is an exact solution. However the infinite range model is relatively easy to solve and exhibits an interesting phase transition. The infinite range model is often the same as a mean field model, as is the case for the Ising ferromagnet. Mean field theory in its many forms, and with many different names, is the most important first approach to solving complex interacting many body problems. The Hamiltonian for the infinite range model is,

$$H = -\frac{J}{N} \sum S_i S_j \quad (72)$$

so the partition function is,

$$Z = \left(\prod_i \sum_{S_i \pm 1} \right) e^{\beta \frac{J}{N} \sum_{ij} S_i S_j} = \left(\prod_i \sum_{S_i \pm 1} \right) e^{\beta \frac{J}{N} (\sum_i S_i)^2} \quad (73)$$

Using the Gaussian integral,

$$\int_{-\infty}^{\infty} e^{-x^2 + bx} dx = \frac{\sqrt{\pi}}{\sqrt{a}} e^{b^2/4a} \quad (74)$$

we write,

$$Z = \int_{-\infty}^{\infty} \frac{dx}{\sqrt{\pi}} e^{-x^2} \prod_i \left(\sum_{S_i \pm 1} e^{2x(\beta \frac{J}{N})^{1/2} S_i} \right) \quad (75)$$

Doing the sums gives,

$$Z = \int_{-\infty}^{\infty} \frac{dx}{\sqrt{\pi}} e^{-x^2} 2^N [\text{Cosh}(2x(\beta \frac{J}{N})^{1/2})]^N \quad (76)$$

We write this in the form,

$$Z = \int_{-\infty}^{\infty} \frac{dx}{\sqrt{\pi}} e^{f(x)}; \quad \text{where,} \quad f(x) = -x^2 + N[\ln(2) + \ln(\text{Cosh}(2x(\beta \frac{J}{N})^{1/2}))] \quad (77)$$

Since $f(x)$ contains a large parameter N , it is a sharply peaked function, so we can use the method of steepest descents. This method states that if the function $f(x)$ has a set of maxima, then the integral is dominated by the largest of these maxima, in the thermodynamic limit. At the dominant maximum, x_{max} , the first derivative is zero, so the expansion to quadratic order is,

$$f(x) = f(x_{max}) - \frac{(x - x_{max})^2}{2!} |f''(x_{max})| + \dots \quad (78)$$

where $f''(x_{max}) < 0$ as we are at a maximum. Using this expansion in the integral we find,

$$\int e^{f(x)} dx \rightarrow e^{f(x_{max})} \int_{-\infty}^{\infty} e^{-\frac{(x-x_{max})^2}{2|f''(x_{max})|}} f''(x_{max}) dx = \left(\frac{2\pi}{|f''(x_{max})|} \right)^{1/2} e^{f(x_{max})}. \quad (79)$$

The problem then reduces to finding the maxima of the function $f(x)$, or the minima of the function $-f(x)$. To find the maxima in the case of the Ising model, we take a derivative with respect to x of $f(x)$ in Eq. (77), that leads to,

$$x = N \left(\frac{\beta J}{N} \right)^{1/2} \tanh \left(2 \frac{\beta J}{N} \right)^{1/2} x \quad (80)$$

We define, $y = 2(\beta J/N)^{1/2} x$ to find,

$$y = 2\beta J \tanh(y) \quad (81)$$

For small values of $\beta J < (\beta J)_c$, the only solution to this equation is at $y = 0$, so in that case,

$$Z \rightarrow \left(\frac{\pi}{|f''(x_{max})|} \right)^{1/2} \frac{1}{\sqrt{\pi}} e^{N \ln(2)} \quad (82)$$

The Helmholtz free energy is, $F = -k_B T N \ln(2)$, where we drop the prefactor terms that are much lower order. For large values of $\beta J > (\beta J)_c$, there are three solutions. The behavior in this regime can be treated analytically by expanding to cubic order in y , so that,

$$y = 2\beta J \left(y - \frac{1}{3} y^3 \right) \quad (83)$$

this has three solutions,

$$y = 0; \quad y = \pm [3(2\beta J - 1)]^{1/2} \quad (84)$$

When $2\beta J > 1$, the second pair of solutions is real, while when $2\beta J < 1$ they are imaginary. The critical point is then at $(\beta J)_c = \frac{1}{2}$, and the behavior near the critical point is $y \approx [6(\beta J - (\beta J)_c)]^{1/2}$.

Integration of Eq. (83) or a fourth order expansion of (77) leads to,

$$-f_R(y) \approx a_1(T - T_c)y^2 + a_2y^4, \quad (85)$$

where a_1 and a_2 are positive and constant terms along with higher order terms in y have been dropped. This expression is the same as the Landau free energy for an Ising system, as we shall see in the next section of the course. The function $f(y)$ is a reduced free energy. We then interpret y as the order parameter for the Ising model, so that $y \propto m$, and we find that the order parameter approaches zero as $m \propto (T_c - T)^{1/2}$ which is typical mean field behavior.

The exact solutions above enable us to state some very interesting properties of the Ising model that provide a basis for a more general discussion of phase transitions as a function of dimension and range of interaction. For a discussion of critical behavior we focus only on the magnetization, that behaves as

$$m \approx (T_c - T)^{\beta_I} \quad T \rightarrow T_c \text{ from below.} \quad (86)$$

We have the following results for the Ising model with short range interactions:

- In one dimension there is no phase transition at finite temperature.
- In two dimensions there is a phase transition at finite temperature, $\beta_I = 1/8$.
- In a long range model there is phase transition at finite temperature, $\beta_I = 1/2$.

These results are consistent with some general postulates about phase transitions that we shall return to in Parts 2 and 3 of the course:

1. Below a lower critical dimension, d_{lc} , fluctuations destroy the ordered state at any finite temperature. For the Ising model $d_{lc} = 1 + \delta$.

2. Above an upper critical dimension, d_{uc} , the critical behavior is given by mean field theory, which in turn is equivalent to the behavior of a model with infinite range interactions. For the ferromagnetic Ising model treated above, $\beta_I = 1/2$ in all of these cases.

3. Between the lower and upper critical dimensions the critical behavior is dependent on the spatial dimension. In the case of the short range ferromagnetic Ising model the critical exponent β changes with dimensions and the upper critical dimension is 4.

III. STATISTICAL PHYSICS BY FILLING SINGLE PARTICLE ENERGY LEVELS APPLICATIONS TO QUANTUM AND CLASSICAL GASES

A. Statistics of filling energy levels for Bose, Fermi and Classical gases

A great deal of theoretical physics reduces complex many body problems to single particle problems and in quantum problems this reduces to filling up single particle energy levels. A many body state is then a configuration of occupancies of the single particle energy levels and the statistical physics is based on methods to calculate the thermodynamics for different energy levels and different methods for filling these energy levels. We consider three ways of filling a set of single particle energy levels, $\epsilon_1 \dots \epsilon_M$. We also include the possibility that these single particle energy levels each has its own degeneracy, so the energy levels are characterized by ϵ_i, g_i , where g_i is the degeneracy of energy level i .

We consider three ways of filling these energy levels: Fermi statistics, Bose statistics and Maxwell-Boltzmann statistics. We concentrate on the grand canonical partition function that reduces to a product of single energy level grand partition functions and for the Bose or Fermi cases, we have,

$$\Xi_{B,F} = \prod_i \left(\sum_{n_i} e^{(-\beta\epsilon_i + \beta\mu)n_i} \right)^{g_i} = \prod_i (\Xi_i)^{g_i} \quad (87)$$

Our task is now reduced to filling a single energy level in the correct manner for the cases of Bose, Fermi statistics in order to calculate Ξ_i . In the Bose and Fermi cases we have to fill energy levels in ways that are consistent with the many particle wavefunctions that are constructed for each configuration.

For example, for a two particle Fermi system we construct a wavefunction by placing two fermions in different single particle states. The correct antisymmetric state is given by,

$$\frac{1}{2^{1/2}} (\phi_i(x_1)\phi_j(x_2) - \phi_i(x_2)\phi_j(x_1)) \quad (88)$$

The only way that a correctly antisymmetrized two particle state can be constructed from single particle wavefunctions is to omit any configurations where two fermions are in the same single particle state, because if we set $i = j$ in the expression above we get zero which means we cannot construct a wavefunction for that case. In general antisymmetrized wave functions constructed from single particle states may be found by forming a determinant, called a Slater determinant, which is of the form,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \dots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \dots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \dots & \psi_N(\mathbf{x}_N) \end{vmatrix}. \quad (89)$$

This determinant captures the fact that if any pair of the single particle wavefunctions used in the construction of the determinant are the same, then the determinant is zero so two particles can never be in the same single particle state. It means that for fermions we must restrict the filling of single particle energy levels so that there is only one fermion or no fermions in any energy level. Of course if there are additional quantum numbers such as spin, color or isospin, an energy level also has a specific value for each of these quantities. In the case of spin for example we would assign a degeneracy of $g_i = 2$ to account for the two possible spin orientations. Particles with different spin or other quantum number are considered to be different particles, so it is possible to put an up spin fermion and a down spin fermion in the same spatial wavefunction. The spin wavefunction then provides the distinction between the states and a correct antisymmetrized product wavefunction (product of spatial and spin parts) can be constructed.

In the Bose case we have to construct wavefunctions that are symmetric under exchange. For this reason we can construct wavefunctions with many particles in one energy level, so for example,

$$\phi_i(x_1)\phi_i(x_2) \quad (90)$$

is a good wavefunction for two bosons. This can be generalized to any number of wavefunctions so *we can put any number of Boson particles in a single particle energy level*. To construct a Boson state using different single particle states, we have to add all possible combinations which turns out to be the same structure as a determinant, but with all the signs in the expansion of a determinant changed to positive. This is called a Permanent. Though evaluation of a permanent seems easier than evaluating a determinant, it is not. The reason is that a determinant is equal

to the product of the eigenvalues, while the permanent does not have a simple expression in terms of eigenvalues and cannot be reduced using linear transformations. The determinant has the nice property that $Det(ABC) = Det(A)Det(B)Det(C)$, so the determinant is invariant under non-singular similarity transformations. The permanent does not have this property so we are stuck with a minor expansion which is of order $N!$ where N is the dimension of the single particle basis. This is much worse than diagonalizing a matrix which is at most N^3 . In computational terms evaluating the permanent is in general NP-hard while evaluating the determinant is polynomial.

Now that we know how to fill the single particle energy levels we can write down explicit expressions for the single energy level grand partition functions Ξ_i . For the fermi case we have,

$$\Xi_i^F = \sum_{n_i=0,1} e^{-\beta(\epsilon_i-\mu)n_i} = 1 + e^{-\beta(\epsilon_i-\mu)} = 1 + ze^{-\beta\epsilon_i}. \quad (91)$$

The Bose case is,

$$\Xi_i^B = \sum_{n_i=0,1,\dots,\infty} e^{-\beta(\epsilon_i-\mu)n_i} = \frac{1}{1 - e^{-\beta(\epsilon_i-\mu)}} = \frac{1}{1 - ze^{-\beta\epsilon_i}}. \quad (92)$$

For the Maxwell-Boltzmann (classical) case we can have any number of particles in each energy level, provided we include the Gibbs factor so that,

$$\Xi_i^{MB} = \sum_{n_i=0,1,\dots,\infty} \frac{1}{n_i!} e^{-\beta(\epsilon_i-\mu)n_i} = Exp[e^{-\beta(\epsilon_i-\mu)}] = Exp[ze^{-\beta\epsilon_i}] \quad (93)$$

The thermodynamic properties are found using,

$$\phi_G = -PV = -k_B T \ln(\Xi) = -k_B T \ln\left(\prod_i (\Xi_i)^{g_i}\right) = -k_B T \sum_i g_i \ln(\Xi_i) \quad (94)$$

From this expression we can find the thermodynamics for any of the gases, using,

$$d\phi_G = -SdT - PdV - Nd\mu \quad (95)$$

Further relations that we will use frequently are,

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial \ln(\Xi)}{\partial \epsilon_i}; \quad N = \sum_i \langle n_i \rangle; \quad U = \sum_i \epsilon_i \langle n_i \rangle = -\left(\frac{\partial \ln(\Xi)}{\partial \beta}\right)_z. \quad (96)$$

Carrying out the derivatives we find,

$$\langle n_i \rangle_B = \frac{g_i z e^{-\beta\epsilon_i}}{1 - z e^{-\beta\epsilon_i}}; \quad \langle n_i \rangle_F = \frac{g_i z e^{-\beta\epsilon_i}}{1 + z e^{-\beta\epsilon_i}}. \quad (97)$$

where $z = e^{\beta\mu}$ is the fugacity. $\langle n_i \rangle$ is the occupancy of all g_i degenerate levels with energy ϵ_i . Remove the factor of g_i to find the average occupancy of any one of the degenerate states. These expressions are often summarized as,

$$\langle n \rangle_{\pm} = \frac{1}{e^{\beta(\epsilon-\mu)} \pm 1} \quad (98)$$

which is the occupancy of any one non-degenerate energy level with energy ϵ and the plus(minus) sign refers to fermions (bosons).

B. Energy levels for a particle in a box

To proceed further we need the energy levels and in this course most of the calculations are for ideal gases where the energy levels are those of a particle in a box that are given by,

$$\epsilon_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}, \quad \text{non-relativistic}, \quad (99)$$

$$\epsilon_{\vec{k}} = \hbar kc, \quad \text{ultra-relativistic} \quad (100)$$

and

$$\epsilon_{\vec{k}} = \sqrt{(\hbar kc)^2 + (m_0 c^2)^2}, \quad \text{general} \quad (101)$$

In each case the wavefunction in the box is a standing wave that must have zero amplitude at the edges of the box. If we take the box to be a hypercube, each dimension can be treated independently and if we take the interior of the box to lie on the interval $0 < x < L$ for each direction, then choosing sinusoidal wave functions that for the three dimensional case is,

$$\psi = A \sin(k_x x) \sin(k_y y) \sin(k_z z). \quad (102)$$

Then for each co-ordinate we must have,

$$\sin(k_l L) = 0; \quad \text{so} \quad k_l = \frac{\pi}{L} s_l \quad (103)$$

where n_l is a positive integer. For arbitrary dimensions we then find,

$$\vec{k} = \frac{\pi}{L} (s_1, s_2, \dots, s_d) \quad (104)$$

with n_l positive integers and d the spatial dimension.

To calculate ensemble averages, we need to carry out a sum over all of the energy levels. To do this it is usually convenient to convert the sum to an integral, for example in three dimensions,

$$\sum_{s_x, s_y, s_z} \rightarrow \left(\frac{L}{\pi}\right)^3 \int_0^\infty d^3 k + T_0 = \left(\frac{L}{2\pi}\right)^3 \int_{-\infty}^\infty d^3 k + T_0 = \left(\frac{L}{2\pi}\right)^3 \int_0^\infty 4\pi k^2 dk + T_0 \quad (105)$$

Where the last integral form applies to energy levels that for only depend on the modulus of $k = |\vec{k}|$. The term T_0 is needed in cases of Bose condensation where the ground state occupancy has to be treated separately from the excited states.

C. Photon gas thermodynamics

One of the the most remarkable predictions of quantum statistical physics is the Planck blackbody spectrum. To find the blackbody spectrum and to analyse the thermodynamics of photons gas, we consider energy-momentum dispersion relation $\epsilon_p = pc = \hbar kc = \hbar\omega = h\nu = hc/\lambda$, i.e. the ultrarelativistic case. We set the chemical potential to zero as there can be an infinity of photons at zero energy. Actually the chemical potential of photons is not always zero as there are cases in photochemistry and photovoltaics where photons have a chemical potential that is less than zero. However for the case of photons in a box, i.e. blackbody radiation, the chemical potential is zero. We are actually treating the Bose condensed phase of the photon gas. However we are only interested in the excited state part of the system.

Defining $p = \hbar k$ and using $z = 1$ and equations (96), (97), (100) and (105) we find for the three dimensional ideal photon gas,

$$\ln(\Xi) = -2 \left(\frac{L}{2\pi\hbar}\right)^3 \int_0^\infty 4\pi p^2 dp \ln(1 - e^{-\beta pc}), \quad (106)$$

while the number of excited state photons is,

$$N = 2 \left(\frac{L}{2\pi\hbar}\right)^3 \int_0^\infty 4\pi p^2 dp \frac{e^{-\beta pc}}{1 - e^{-\beta pc}} = V \int d\omega n(\omega) \quad (107)$$

and the internal energy is given by,

$$U = 2 \left(\frac{L}{2\pi\hbar}\right)^3 \int_0^\infty 4\pi p^2 dp (pc) \frac{e^{-\beta pc}}{1 - e^{-\beta pc}} = V \int d\omega u(\omega) \quad (108)$$

where $n(\omega)$ is the number density of photons and $u(\omega)$ is the energy density at angular frequency ω . Notice that the T_0 term has been dropped as it does not contribute to the physics of the ideal photon gas (that we know of).

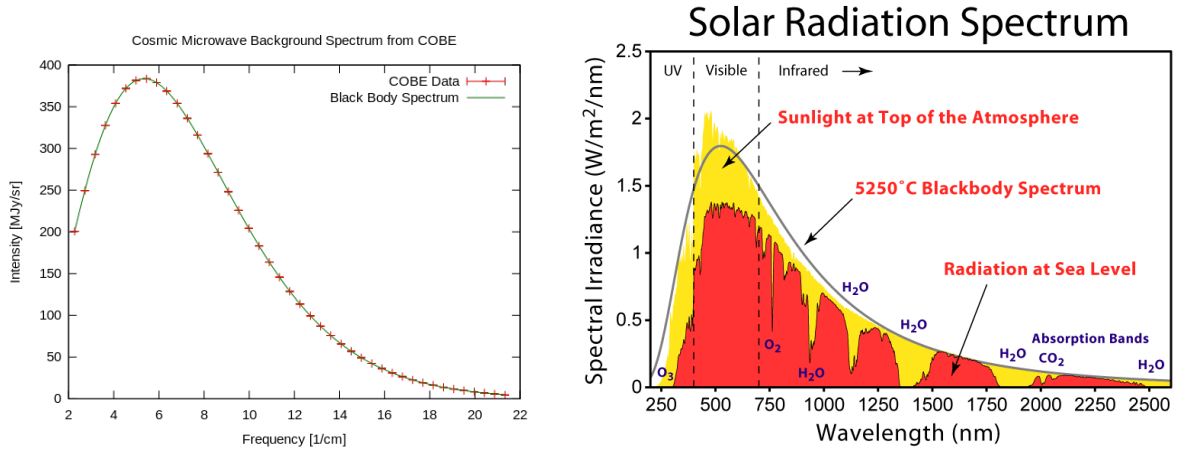


FIG. 4. Comparison of the blackbody photon spectral intensity (Eq. (109) below) with experiments: Left figure: The cosmic microwave background measured by the COBE satellite; Right figure: The solar intensity outside the atmosphere and at the earth's surface.

The additional factor $g_i = 2$ in front of these equations is due to the two polarizations that are possible for photons. These functions characterize the “blackbody spectrum” inside the box confining the photon gas, with temperature T . However measurements of radiation measure radiation spectral intensity, which is related to the energy density by the relation, $i(\omega) = u(\omega)c$. Moreover, the Planck radiation law is often quoted in a slightly different way. It is often defined to be the radiant spectral intensity per unit solid angle, which is related to the spectral energy density by $u(\omega)$ by $i_s(\omega, T) = c u(\omega)/(4\pi)$, where 4π is solid angle of a sphere. Several forms of i_s are common, including:

$$i_s(\omega, T) = \frac{\hbar}{4\pi^3 c^2} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \quad \text{or} \quad i_s(\nu, T) = \frac{2h}{c^2} \frac{\nu^3}{e^{\beta h\nu} - 1}; \quad \text{or} \quad i_s(\nu, T) = \frac{2c^2 h}{\lambda^5} \frac{1}{e^{\beta hc/\lambda} - 1} \quad (109)$$

Blackbody spectra provide a surprisingly good description of many systems (see Figure 4), including the cosmic microwave background, with temperature $T_{CMB} = 2.713K$; and the spectral intensity reaching earth from stars such as our Sun with $T = 5500K$, Antares with $T = 3400K$, Spica with $T = 23,000K$.

The average properties of the photon gas is found by integration, using the integral,

$$\int_0^\infty \frac{x^{s-1} dx}{e^x - 1} = \Gamma(s)\zeta(s), \quad (110)$$

where $\Gamma(s) = (s-1)!$ for s a positive integer, and $\zeta(3) = 1.202\dots$, $\zeta(4) = \pi^4/90$. For $s = 4$, we find $\gamma(s)\zeta(s) = \pi^4/15$.

$$\frac{U}{V} = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} T^4; \quad PV = \frac{1}{3}U; \quad N = V \frac{2\zeta(3)(k_B T)^3}{\pi^2 \hbar^3 c^3} \quad (111)$$

Two other nice relations for the photon gas that can be derived from standard thermodynamic relations are $S = 4U/(3T)$, $C_V = 3S$.

The Stefan-Boltzmann law $I_{SB} = \sigma T^4$, is the power per unit area radiated from a blackbody with emissivity one. The relation I_{SB} and U/V of the photon gas is, are as follows,

$$I_{SB}(T) = \frac{cU}{4V} = \sigma_{SB} T^4; \quad \text{where} \quad \sigma_{SB} = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} \quad (112)$$

where σ_{SB} is the Stefan Boltzmann constant. The factor $c/4$ has two origins, the first factor (c) comes from the relationship between the energy of a travelling wave and its intensity, and the second is a geometric factor due to an assumption of isotropic emission from a small surface element on the surface of the emitter. To understand the first factor, consider a classical EM wave in free space with energy density $u = \epsilon_0 E_0^2/2 + B_0^2/(2\mu_0)$. In the direction of propagation of the wave, the energy crossing a surface of area A per unit time is,

$$\text{Energy per unit time} = \text{Power} = u * A * c \quad \text{so that} \quad I_w = \text{Power}/\text{Area} = uc \quad (113)$$

where I_w is the intensity of the wave. This applies to both the peak and rms intensity of the wave, provided the energy density is the peak or rms value respectively. The geometric factor comes from considering a small flat surface

element that emits radiation in all directions. In the case of blackbody radiation, this element is considered to be at the surface, so it emits half of its radiation back into the black body and half out of the black body. In addition, the radiation in the direction normal to the surface is reduced from the total radiation emitted from the surface element due to the assumption of isotropic emission. The component normal to the surface is found by finding the component of the electric field in the normal direction, $E_0 \cos(\theta)$, then squaring this to get the correct projection of the intensity, and then averaging over angles θ in a hemisphere. The result is that we need to average $\cos^2(\theta)$ over a half period. This leads to a geometric factor of $1/2$. Multiplying these two factors of $1/2$ gives the total geometric factor of $1/4$. In most applications, the Stefan-Boltzmann law needs to be modified to account for the emissivity of the material (e) and the geometry of the surface and the location of the observer with respect to the surface, if the surface is not spherical.

One of the quantities that is measured for a new star is its luminosity. In Astronomy the bolometric luminosity is the total luminosity while the luminosity is the visible part of the radiant energy. The bolometric luminosity, L , is equal to the emitted power, and from the Stefan-Boltzmann law we find,

$$L = 4\pi R^2 e \sigma T^4 \quad (114)$$

For main sequence stars there is also a relation between the mass of a star and the luminosity $L \propto M^{3.9}$. In these stars, the tendency toward gravitational collapse is balanced by the radiation pressure of the photons that are generated primarily by the fusion of hydrogen. Fortunately this is quite a stable process so that stars find an equilibrium state (radius) maintained by the balance of radiation pressure and gravitational forces. This stable state has the relation between mass and energy stated above.

D. Phonons

Phonons are lattice vibrations in crystals. The longitudinal vibrations in a crystal can be described by Hooke's law springs connecting all of the atoms in the crystal. The longitudinal vibrations are called acoustic modes as they are the modes that carry sound waves and the direction of vibration is in the same direction as the wave propagation. Transverse modes also exist and they are called optical modes by analogy with light waves that have EM oscillations that are transverse to the direction of wave propagation.

At low frequencies or long wavelengths, the acoustic phonon modes obey the dispersion relation $\epsilon_p = p v_s$, where v_s is the velocity of sound. The low temperature thermodynamics due to lattice vibrations is dominated by the acoustic modes as the optical modes are much higher in energy. The chemical potential of these modes is zero as there is an infinite set of zero energy modes that are available, as in the photon case.

Two simple models for the thermodynamics of lattice vibrations are the Einstein model and the Debye model. The Einstein model treats the vibrations in a lattice of N_A atoms as N_A independent d-dimensional harmonic oscillators. The Debye model, which is more accurate, treats the phonons as a set of Bose particles in a box with volume $V = L^d$. Accurate calculations of the true phonon modes in crystals may be carried out computationally, and then the thermodynamics can be calculated numerically. Here we analyse the Debye model.

Consider a Debye model for a cubic lattice with N_A atoms. The volume is $V = L^3$. As remarked above, analysis of the acoustic phonons uses the dispersion relation $\epsilon_p = v_s p$ and chemical potential $\mu = 0$, so $z = 1$. So far this model looks exactly the same as the photon model described above, however there is an important difference, the number of available acoustic phonon modes in the model is set to $3N_A$ to ensure a correct crossover to the high temperature limit. This is correct at high temperature as there the optical and acoustic phonons contribute. To enforce a limit on the possible number of phonons, we add a constraint to the calculations,

$$N_A = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi k_D^3}{3} \quad \text{or} \quad k_D = \left(\frac{6\pi^2 N_A}{V}\right)^{1/3}. \quad (115)$$

The expressions for the thermodynamics looks similar to those for photons in a box, with the modification that the upper limit of the integrations over p is now $p_D = \hbar k_D$, so we have,

$$\ln(\Xi) = -3 \left(\frac{L}{2\pi\hbar}\right)^3 \int_0^{p_D} 4\pi p^2 dp \ln(1 - e^{-\beta p v_s}), \quad (116)$$

where the factor of three in front of this expression is to capture the correct number of degrees of freedom in the high temperature limit.

The internal energy is given by,

$$U = 3 \left(\frac{L}{2\pi\hbar}\right)^3 \int_0^{p_D} 4\pi p^2 dp (p v_s) \frac{e^{-\beta p v_s}}{1 - e^{-\beta p v_s}} = V \int d\omega u(\omega) \quad (117)$$

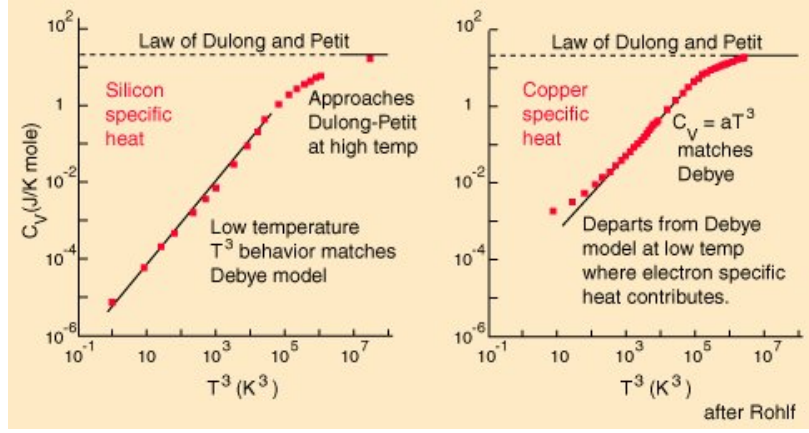


FIG. 5. Fit of the Debye specific heat to measurements

We define the Debye temperature,

$$k_B T_D = p_D v_s; \quad \text{so that} \quad T_D = \frac{h v_s}{2 k_B} \left(\frac{6 N_A}{\pi V} \right)^{1/3} \quad (118)$$

so that,

$$\frac{U}{N k_B} = 9 T \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} dx \frac{x^3}{e^x - 1} \quad (119)$$

The specific heat is the most directly measurable thermodynamic quantity for phonons, so we consider its behavior in the low and high temperature limits. At low temperatures, the upper limit of the integral goes to infinity and the integral is carried out using Eq. (110). In the high temperature limit T_D/T is small, so we take the leading order term in x of Eq. (119), so we replace the denominator by x . The limiting behaviors of the specific heat within the Debye model are then,

$$\frac{C_V}{N k_B} \rightarrow \frac{12 \pi^4}{5} \left(\frac{T}{T_D} \right)^3 \quad \text{for} \quad T \ll T_D \quad (120)$$

and

$$\frac{C_V}{N k_B} \rightarrow \frac{\partial}{\partial T} \left(9 T \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} dx \frac{x^3}{x} \right) = 3 \quad T \gg T_D. \quad (121)$$

The high temperature result may be understood as the equipartition theorem applied to both the spatial and momentum degrees of freedom, when both are harmonic. There are then six modes (3 momentum and 3 position) with internal energy $k_B T/2$ for each mode.

The Debye temperature is an important parameter in materials as it is a rough measure of the elastic properties and melting temperature of the material. A high Debye temperature indicates a stiff material with a high melting temperature (e.g. for diamond $T_D \approx 2200 K$, while a low Debye temperature indicates a soft material with a low melting temperature (e.g. for lead $T_D = 105 K$). Calorimetry measurements of C_V are quite routine and if they are carried out over a temperature range $0 < T < 5 T_D$, they clearly show the crossover between the two regimes of Eqs. (120) and (121) (see Figure 5).

E. The 3-d non-relativistic ideal Bose gas, where $\mu \neq 0$

We consider a Bose gas of massive particles that are in the non-relativistic regime and where $\mu \neq 0$. The formulation has to take into account the possibility of Bose condensation so we have to consider the ground state term T_0 of Eq. (105), so we separate the ground state term from the rest of the integral, to find,

$$\frac{P}{k_B T} = -\frac{\ln(\Xi)}{V} = -\frac{4\pi}{h^3} \int_0^\infty dp p^2 \ln \left(1 - z e^{-\beta p^2/2m} \right) - \frac{1}{V} \ln(1-z) \quad (122)$$

As we shall show later the ground state term in this expression can be ignored, so henceforth we neglect it. However the ground state term in the number of Bosons, so we consider,

$$\frac{N}{V} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 \frac{ze^{-\beta p^2/2m}}{1 - ze^{-\beta p^2/2m}} + \frac{1}{V} \frac{z}{1 - z} \quad (123)$$

and the internal energy is given by,

$$\frac{U}{V} = \frac{4\pi}{h^3} \int_0^\infty dp p^2 \frac{p^2}{2m} \frac{ze^{-\beta p^2/2m}}{1 - ze^{-\beta p^2/2m}}. \quad (124)$$

In the expression for U , we dropped the ground state term, T_0 , as the $p^2/2m$ term in the sum goes to zero sufficiently quickly as $p \rightarrow 0$ that the ground state contribution can no longer be singular. As we shall see later when we treat Bose condensation, the $\ln(1 - z)$ term in the expression for the pressure may also be dropped. However the $z/(1 - z)$ term in the total number of particles is not negligible and provides the description of the Bose condensed fraction of the gas. Using integration by parts it is straightforward to show that,

$$P = \frac{2}{3} \frac{U}{V}. \quad (125)$$

For dispersion relations of the form $\epsilon_k = ck^s$, in d dimensions this generalizes to the same expression as applies to the Bose gas, ie. $P = su/d$.

Using the change of variables $x^2 = \beta p^2/2m$, we find

$$P = -\frac{k_B T}{\lambda^3} \frac{4}{\pi^{1/2}} \int_0^\infty dx x^2 \ln(1 - ze^{-x^2}); \quad \frac{N}{V} = \frac{1}{\lambda^3} \frac{8}{\pi^{1/2}} \int_0^\infty dx x^3 \frac{ze^{-x^2}}{1 - ze^{-x^2}} + \frac{1}{V} \frac{z}{1 - z} \quad (126)$$

The thermodynamic functions are most succinctly stated in terms of the functions $g_{3/2}(z)$ and $g_{5/2}(z)$ so that Eqs. (126) reduce to,

$$P = \frac{k_B T}{\lambda^3} g_{5/2}(z); \quad \frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z) + \frac{1}{V} \frac{z}{1 - z} \quad (127)$$

where,

$$g_{5/2}(z) = -\frac{4}{\pi^{1/2}} \int_0^\infty dx x^2 \ln(1 - ze^{-x^2}) = \sum_{l=1}^\infty \frac{z^l}{l^{5/2}}; \quad g_{3/2}(z) = z \frac{\partial}{\partial z} g_{5/2}(z) = \sum_{l=1}^\infty \frac{z^l}{l^{3/2}}. \quad (128)$$

The series expansion for $g_{5/2}$ is found by expanding the logarithm in the integral form of $g_{5/2}$ and then integrating the Gaussians that remain, using,

$$\ln(1 - y) = -\sum_{l=1}^\infty \frac{y^l}{l}; \quad \int_0^\infty dx x^2 e^{-lx^2} = \frac{\pi^{1/2}}{4} \frac{1}{l^{3/2}}. \quad (129)$$

The expansion for $g_{3/2}$ can be found by differentiation or by expanding $1/(1 - y)$ and carrying out the Gaussian integrals.

F. High temperature limit - the classical ideal gas

First we look at the behavior at high temperatures where we expect to recover the classical, Maxwell-Boltzmann gas. In the high temperature limit, $z = e^{-\beta\mu}$ is small because the chemical potential is large and negative, so we can expand in z to find,

$$\frac{N}{V} = \frac{1}{\lambda^3} g_{3/2}(z) = \frac{1}{\lambda^3} (z + \frac{z^2}{2^{3/2}} + \dots) \quad (130)$$

Keeping only the leading order term in the expansion on the right hand side of this equation we find

$$z = \frac{N\lambda^3}{V}; \quad \text{and using } \beta\mu = \ln(z); \quad (131)$$

we find the chemical potential of the Bose gas in the high temperature limit is,

$$\mu = k_B T \ln\left(\frac{N\lambda^3}{V}\right) \quad (132)$$

which is the same as the chemical potential found in the classical ideal gas (see Eq. (15)) of the lecture notes for Part 2. Note that the chemical potential is large and negative at high temperature, so the fugacity approaches zero. The fugacity is always positive as it is an exponential of real number.

From Eq. (52) using the leading order $g_{5/2} = z$, along with $z = N\lambda^3/V$ as found above, give the ideal gas law and the equipartition result for the internal energy of the classical ideal gas. Problem 4 of the assignment asks that you calculate the next correction to the classical limit. This is achieved by considering the next term in the expansion of Eq. (130).

G. Low temperature limit and Bose Einstein Condensation (BEC)

Now we consider the low temperature limit where BEC can occur. Bose condensation is a very important phenomena that is closely related to superfluidity, superconductivity and other phase coherent phenomena such as lasing. However the Bose condensation of gases has been very difficult to achieve. In most cases Bose condensation occurs in systems made up of *composite* Bosons, such as Helium 4 in superfluidity and cooper pairs in superconductivity. Composite Bosons consist of an even number of Fermions that may be of different types, for example in Helium 4, 2 protons, 2 neutrons and 2 electrons. The hydrogen atom itself can form a composite Boson (one proton and one electron) and any system where the spin adds to an integer is has this possibility. For this reason Wolfgang Ketterle's group focused on achieving Bose Condensation in atomic Hydrogen gases in atom traps. However Bose condensation can only occur if other phase transitions and/or bonding interactions are avoided. In the case of Hydrogen for example formation of Hydrogen molecules and then a hydrogen solid at temperatures around 14K prevent formation of the BEC state. Attempts to form a BEC state in Alkali metal gases were finally successful in 1995 when a group at U. Colorado (Wieman and Cornell) with the observation of BEC in Rubidium 85 at 170 nano Kelvin. This lead to the nobel prize in physics for BEC in 2001 (Cornell, Wieman, Ketterle). Though high densities favor condensation, competing states are also favored so the gases need to be kept quite dilute to allow BEC to occur. The number of atoms involved in the condensates was originally only about 10,000 atoms, though that number has risen significantly since. Though a full description of BEC in atom traps requires treatment of the trap potential, particle-particle scattering and finite size effects, the ideal gas BEC is the starting point about which the more complex effects can be treated perturbatively. Here we concentrate on the ideal gas case.

As noted above, the chemical potential of gases are large and negative at high temperature, so the fugacity approaches zero as $T \rightarrow \infty$. At low temperatures, the chemical potential is dominated by the energy contribution. For a Bose system where the ground state energy is at zero energy, the change in energy on addition of a particle is zero, so the chemical potential approaches zero as $T \rightarrow 0$. In the Bose case, the equation for the number density of particles consists of a ground state part and a finite temperature part,

$$N = \frac{V}{\lambda^3} g_{3/2}(z) + \frac{z}{1-z} = N_1 + N_0 \quad (133)$$

where N_1 is the number of Bose particles in the excited states and N_0 is the number of Bose particles in the ground state. As noted above, the largest value that z can take for a Bose gas is $z = 1$, therefore the largest possible value that N_1 can take is,

$$N_1^{max} = \frac{V}{\lambda^3} g_{3/2}(1) = \frac{V}{\lambda^3} \zeta(3/2) \quad (134)$$

where $\zeta(x)$ is the Reimann zeta function $\zeta(z) = \sum l^{-z}$ and $\zeta(3/2) = 2.612\dots$. Bose condensation occurs when $N_1^{max} < N$ as if this occurs, the remaining Bose particles must be in the ground state. Therefore the condition for Bose condensation is,

$$N = N_1^{max} = \zeta(3/2) \frac{V}{\lambda_c^3}; \quad \text{or} \quad \frac{N\lambda^3}{V} = \frac{N h^3}{V(2\pi m k_B T_c)^{3/2}} = \zeta(3/2) \quad (135)$$

or,

$$T_c = \frac{h^2}{2\pi m k_B} \left(\frac{N}{V \zeta(3/2)} \right)^{2/3}. \quad (136)$$

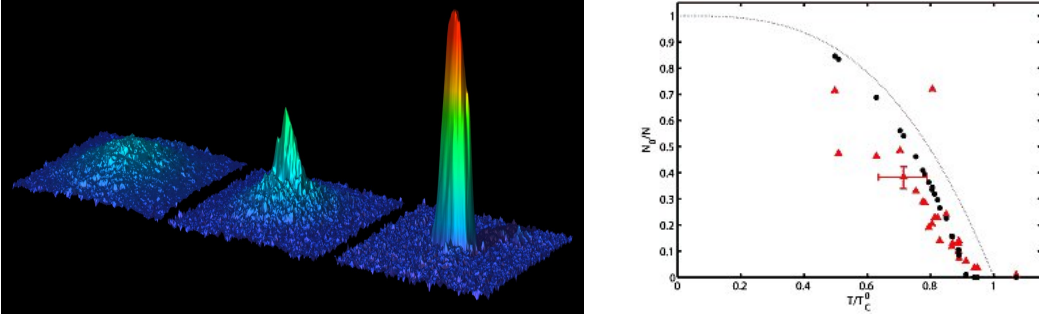


FIG. 6. Left: Phase space density of Strontium atoms released from trap (IQOQI group Austria). Right: Chromium 52 trapped atomic gas condensate fraction as a function of temperature (triangles) compared to the ideal Bose gas (solid). Deviations predicted by theory (solid dots) are due to finite number of atoms and due to interactions (from Pfau group [www page at U. Stuttgart](http://www.pfau.de)).

From this we see that BEC is favored for high density gases consisting of particles with low mass, provided other interactions can be prevented from interfering with the BEC. In alkali metals in gases it turns out the heavier particles are easier to condense despite the fact that their mass is higher.

Using the mass and density of Helium 4 the above equation gives $T_c = 3.13K$. The superfluid transition in Helium 4 is actually at $T_c = 2.18K$ so the BEC theory is not very good for Helium 4, but that is not surprising as Helium 4 is not an ideal gas. However for atom traps the ideal Bose gas BEC transition is a much better model (see Fig. 6). Because $\mu = 0$ and hence $z = 1$ in the Bose condensed state, the thermodynamics can be calculated in terms of ζ functions, for example the fraction of the Bose gas that is in the condensed phase is,

$$f_s = \frac{N_0}{N} = 1 - \frac{N_1}{N} = 1 - \frac{V}{N\lambda^3} \zeta(3/2) = 1 - \left(\frac{T}{T_c}\right)^{3/2} \quad T \leq T_c. \quad (137)$$

where f_s is the condensed or superfluid fraction of the gas. The internal energy is given by,

$$\frac{U}{V} = \frac{3}{2} \frac{k_B T}{\lambda^3} g_{5/2}(1) = \frac{3}{2} \frac{k_B (2\pi m k_B)^{3/2}}{h^3} T^{5/2} g_{5/2}(1) = \frac{3}{2} \frac{N}{V} k_B T \left(\frac{T}{T_c}\right)^{3/2} \frac{g_{5/2}(1)}{g_{3/2}(1)} \quad T \leq T_c \quad (138)$$

The specific heat at constant volume is then (using $\zeta(5/2) = 1.3415$,

$$C_V = \frac{15}{4} \frac{k_B (2\pi m k_B)^{3/2}}{h^3} T^{3/2} g_{5/2}(1) = \frac{15}{4} N k_B \left(\frac{T}{T_c}\right)^{3/2} \frac{g_{5/2}(1)}{g_{3/2}(1)} \quad (139)$$

The specific heat then goes to zero as $T \rightarrow 0$. The peak value of the specific heat is at $T = T_c$, where it takes the value

$$C_V(T_c) = \frac{15}{4} N k_B \frac{g_{5/2}(1)}{g_{3/2}(1)} \approx 1.926 N k_B \quad (140)$$

This can be compared to the ideal gas result $C_v = 1.5 N k_B$ (Dulong-Petit law), which is correct at high temperature. There is a cusp in the specific heat at $T = T_c$ due to the Bose condensation phase transition. This cusp behavior is quite different that that observed in Helium 4 (the λ transition) where there is a much sharper divergence at the transition, so the specific heat measurement clearly shows that the ideal Bose gas is a relatively poor model for superfluid Helium (see Figure 7). Finally, using $PV = 2U/3$, we have,

$$PV = N k_B T \left(\frac{T}{T_c}\right)^{3/2} \frac{g_{5/2}(1)}{g_{3/2}(1)} \quad T \leq T_c \quad (141)$$

In the condensed phase, the pressure is then smaller than that of the ideal classical gas. In writing this expression, we have ignored the term $\ln(1 - z)$, moreover in doing the calculation of N we have also avoided discussing the term $z/(1 - z)$, that is singular as $z \rightarrow 1$. We now discuss these terms. In order to discuss these terms, we have to consider a finite system, so that z is not exactly one, but instead approaches 1 with increasing volume. The dependence of z

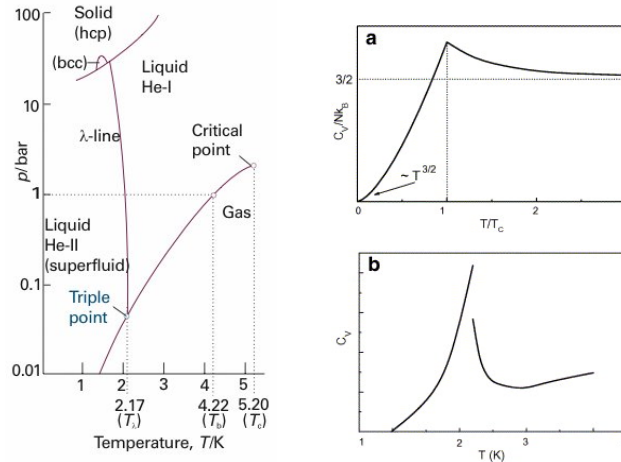


FIG. 7. Left: Phase diagram of Helium 4. Right: Comparison of the specific heat of Helium 4 at the superfluid transition to the ideal Bose gas result. The BEC transition of the ideal gas is also about 50% higher than the observed transition, for the same mass and density parameters.

on volume can be deduced from Eq. 137), so that in the condensed phase we define $z = 1 - \delta$, where δ is small so that,

$$\frac{z}{N(1-z)} \approx \frac{1}{N\delta} = 1 - \frac{V}{N\lambda^3} \zeta(3/2) = f_s, \quad \text{so that} \quad \delta = \frac{1}{Nf_s} \quad (142)$$

so the fugacity approaches zero as $1/N$, provided $f_s > 0$. From this result it is evident that the term

$$\ln(1-z) = \ln\left(\frac{1}{Nf_s}\right) \approx -\ln(Nf_s). \quad (143)$$

In the equation $P = k_B T g_{5/2}(z)/\lambda^3 - \ln(1-z)/V$ (see Eq. (127)), the first term is of order one, however the second term goes to zero rapidly as $|\ln(Nf_s)| \ll V$ and is negligible in comparison to terms of order one. We are thus justified in ignoring it in the evaluation of the equation of state. In a similar way the corrections to the thermodynamics of the BEC phase due to deviations of z from one are of order $1/N$ compared to the leading order terms, so they can be neglected. In the thermodynamic limit the results given above for the equation of state, f_s and C_V are *exact* in the condensate phase.

If we carry through the analysis for the ideal non-relativistic Bose gas in two dimensions, the key difference is that the function $g_{3/2}(z)$ is changed to $g_1(z)$ and this function diverges as $z \rightarrow 1$. The fraction of the gas particles that go into the condensate is then finite for all $T > 0$ so there is no finite temperature BEC phase transition in the ideal Bose gas. We may also carry the calculations through for the ultrarelativistic Bose gas where $\epsilon_k = \hbar kc$. In that case we find that similar relations hold except that the functions $g_d(z)$ apply in d dimensions. From this we deduce that in dimensions two and higher the ideal relativistic Bose gas has a BEC phase transition at finite temperature.

H. The Fermi gas

For the case of Fermi particles, we have,

$$\Xi_F = \prod_l \left(\sum_{n_l} e^{-\beta(\epsilon_l - \mu)n_l} \right)^{g_l} = \prod_l (1 + ze^{-\beta\epsilon_l})^{g_l} \quad (144)$$

where $z = e^{\beta\mu}$ and the sum is over the possibilities $n_l = 0, 1$ as required for Fermi statistics. We then have,

$$\ln(\Xi_F) = \sum_l g_l \ln(1 + ze^{-\beta\epsilon_l}) \quad (145)$$

so that,

$$PV = k_B T \ln(\Xi_F) = k_B T \sum_l g_l \ln(1 + ze^{-\beta\epsilon_l}) \quad (146)$$

The number of particles is found using,

$$N = z \frac{\partial}{\partial z} [\ln(\Xi_F)]; \quad \text{or,} \quad N = \sum_l \langle n_l \rangle, \quad \text{where} \quad \langle n_l \rangle = -\frac{\partial}{\partial \epsilon_l} [\ln(\Xi_F)] = \frac{g_l z e^{-\beta \epsilon_l}}{1 + z e^{-\beta \epsilon_l}} \quad (147)$$

and the internal energy is given by,

$$U = -\frac{\partial}{\partial \beta} (\ln(\Xi_F)), \quad \text{or,} \quad U = \sum_l \epsilon_l \langle n_l \rangle = \sum_l \epsilon_l \frac{g_l z e^{-\beta \epsilon_l}}{1 + z e^{-\beta \epsilon_l}} \quad (148)$$

I. The non-relativistic ideal Fermi gas in three dimensions

High temperature behavior

We take $\epsilon_k = \hbar^2 k^2 / 2m$ and ignore internal degrees of freedom so $g_l = 1$. Since we can derive everything from $\ln(\Xi_F)$ we consider the continuum limit of Eq. (145),

$$\ln(\Xi_F) = \left(\frac{L}{2\pi}\right)^3 \int_0^\infty 4\pi k^2 dk \ln(1 + z e^{-\beta \hbar^2 k^2 / 2m}) \quad (149)$$

substituting $x^2 = \beta \hbar^2 k^2 / 2m$, we find,

$$\ln(\Xi_F) = \left(\frac{L}{2\pi}\right)^3 \left(\frac{2m}{\beta \hbar^2}\right)^{3/2} 4\pi \int_0^\infty x^2 dx \ln(1 + z e^{-x^2}) \quad (150)$$

Now we expand the logarithm using

$$\ln(1 + y) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} y^l}{l} \quad (151)$$

to find,

$$\ln(\Xi_F) = \left(\frac{L}{2\pi}\right)^3 \left(\frac{2m}{\beta \hbar^2}\right)^{3/2} 4\pi \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l} \int_0^\infty x^2 e^{-lx^2} dx \quad (152)$$

The integral is given by,

$$\int_0^\infty x^2 e^{-lx^2} dx = -\frac{\partial}{\partial l} \int_0^\infty e^{-lx^2} dx = \frac{1}{4} \frac{\pi^{1/2}}{l^{3/2}} \quad (153)$$

so we find,

$$\ln(\Xi_F) = \frac{V}{\lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{5/2}} = \frac{V}{\lambda^3} f_{5/2}(z) \quad (154)$$

where we define,

$$f_\alpha(z) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^\alpha}. \quad (155)$$

This is very similar to the function $g_\alpha(z)$ we used in the analysis of the Bose gas and only differs by the fact that $f_\alpha(z)$ has an alternating sign. Using equations (147,148) we then find that the thermodynamics of the 3-d non-relativistic Fermi gas is given by,

$$P = \frac{k_B T}{\lambda^3} f_{5/2}(z); \quad N = \frac{V}{\lambda^3} f_{3/2}(z); \quad P = \frac{2}{3} \frac{U}{V} \quad (156)$$

This formulation is useful at high temperature where a systematic expansion in z is reasonable due to the fact that $z \rightarrow 0$ in the high temperature limit. However at low temperatures the fugacity of the Fermi gas diverges because

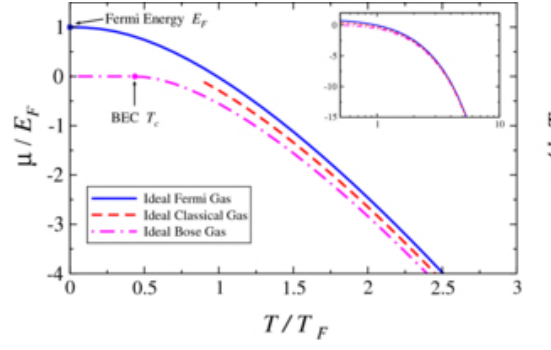


FIG. 8. The chemical potential of ideal gases as a function of temperature. The Fermi gas has a finite positive chemical potential at low temperature so the fugacity diverges in this limit. The Bose gas chemical potential goes to zero so the fugacity goes to one. In the high temperature limit the three ideal gases asymptotically have the same chemical potential $\mu = k_B T \ln(N\lambda^3/V)$, which is negative and approximately linearly decreasing at high T .

$z = \text{Exp}(\beta\mu)$ with μ finite and positive (see Fig. 8), while $\beta = 1/k_B T$ diverges so this expansion is not useful. Below we shall carry out an expansion (the Sommerfeld expansion) for large fugacity.

In the high temperature limit $z \rightarrow 0$ ($T \rightarrow \infty$, $\mu \rightarrow -\infty$, $\beta\mu \rightarrow -\infty$), Fermi case is,

$$\frac{N}{V} = \frac{1}{\lambda^3} f_{3/2}(z) = \frac{1}{\lambda^3} \left(z - \frac{z^2}{2^{3/2}} + \dots \right) \quad (157)$$

Carrying out an expansion to find the second virial coefficient (using the same procedure as in Assigned problem 11), we find,

$$z_1 = z_0 \pm \frac{z_0^2}{2\sqrt{2}} \quad \text{with} \quad z_0 = e^{N\lambda^3/V} \quad (158)$$

where z_0 is the fugacity of the ideal classical gas and where the plus sign is for the Fermi gas and minus sign is for the Bose gas. The pressure is given by,

$$\frac{PV}{Nk_B T} = 1 \pm \frac{1}{4\sqrt{2}} \frac{\lambda^3 N}{V} + \dots \quad (159)$$

This is an example of a virial expansion, that is usually written in the form,

$$\frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots \quad (160)$$

where $\rho = N/V$ is the number density. We shall return to this expansion later when we consider interacting gases. Here we note that the second virial coefficient, which is actually an important parameter in deducing the interactions in gases, for Fermi (+) and Bose (-) gases is given by,

$$B_2(T) = \pm \frac{1}{4\sqrt{2}} \lambda^3 \quad (161)$$

which is a purely quantum statistical interaction term.

1. The ground state

The ground state of the Fermi gas is remarkable as the Fermi statistics leads to the filling of energy states with relatively high kinetic energy. This leads to a very significant degeneracy pressure. For example white dwarf stars are predominantly stabilized by the balance between the degeneracy pressure of electrons and gravity, while neutron stars are stabilized by the balance between the degeneracy pressure of neutrons and gravity. Stars above mass roughly 1.44 the solar mass have a gravitational field that is too strong to be supported by electron degeneracy pressure and they collapse to form either a neutron star or a black hole. The equation of state of neutron stars is not well known so

Some Fermi Energies		
Metal		Fermi Energy, eV
Lithium	Li	4.72
Sodium	Na	3.12
Aluminum	Al	11.8
Potassium	K	2.14
Cesium	Cs	1.53
Copper	Cu	7.04
Zinc	Zn	11.0
Silver	Ag	5.51
Gold	Au	5.54

FIG. 9. The Fermi Energy of some metals

the threshold for a neutron star to form a black hole is not precise. Even in everyday materials the effects of Fermi statistics are profound with the kinetic energy of conduction electrons in copper, even at very low temperature, being around $80,000K$. Due to this, to a good first approximation electrons in materials are very close to the ground state of a Fermi system. We first study this ground state and then consider a systematic expansion in the temperature effects. In the ground state we fill the energy levels until all of the N fermi gas particles are in the box or volume V . Here we assume the Fermions have degeneracy $g_l = g$. The energy required to add another particle is the chemical potential in the ground state, μ_0 . It is also called the Fermi energy, E_f . We then have,

$$U = \left(\frac{L}{2\pi}\right)^3 \int_0^{k_f} g 4\pi k^2 \frac{\hbar^2 k^2}{2m} dk = \frac{gV}{2\pi^2} \frac{\hbar^2}{2m} \frac{k_f^5}{5} \quad (162)$$

where,

$$N = \left(\frac{gV}{2\pi^2}\right) \frac{k_f^3}{3}; \quad E_f = \frac{\hbar^2 k_f^2}{2m} \quad (163)$$

Using these relations, we find,

$$k_f = \left(\frac{6\pi^2 N}{gV}\right)^{1/3}; \quad \frac{U}{N} = \frac{3}{5} E_f. \quad (164)$$

The degeneracy pressure is related to the energy density in the usual way, i.e.

$$P = \frac{s}{d} \frac{U}{V}; \quad \text{so} \quad P = \frac{2}{5} \frac{N}{V} E_f = \frac{2}{5} \frac{N}{V} \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{gV}\right)^{2/3}$$

The equation of state for the non-relativistic Fermi gas may then be written as $P = K_1 \rho^{5/3}$, where $\rho = N/V$. This has applications to the stability of white dwarf stars, as the degeneracy pressure of the electrons in these stars is sufficient to balance the gravitational force which tries to collapse the stars. White dwarf stars are effectively burnt out with relatively low radiation pressure to offset gravity. However an ultrarelativistic calculation finds a modified equation of state $P = K_2 \rho^{4/3}$ and this pressure is slightly smaller than the non-relativistic case. Using the relativistic form Chandrasekar showed that there is a limiting mass beyond which electron degeneracy pressure cannot support white dwarf stars. The current estimate of this "Chandrasekar limit" is 1.44 solar masses. Stars of mass greater than this may collapse to form a neutron star or a black hole, however the mass range over which neutron stars are stable is not well characterized, though they are also supported by degeneracy pressure (of neutrons). The difficulty in this case is treating the strong interactions between neutrons.

Surprisingly the Fermi temperature, that is defined by $k_B T_F = E_F$ is very high. For example, consider conduction electrons in copper where have one conduction electron per atom leading to electron number density $N/V = 8.49 * 10^{28}/m^3$. We take $g = 2$ to account for the spin degeneracy. Using the mass of the electron and converting to energy per electron we find that the Fermi energy is around $7eV$ so the Fermi temperature is around $84,000K$ (using

300K $\approx 0.025eV$). The Fermi energy and temperature are related to the electron density and this varies considerably in metals, as seen in the table. Carrying through the calculations to find the degeneracy pressure, we find that for copper $P \approx 3.8 \times 10^{10} N/m^2 \approx 3.5 * 10^5 Atmospheres$. The high kinetic energy and pressure of the electrons in metals are offset by the binding energy of the material. Given that the Fermi temperature is high, we can consider the ratio T/T_F to be small in most cases of interest and look for an expansion in this variable.

2. Expansion at "low" temperatures - Sommerfeld

At low temperatures, $\beta\mu$ is large so the series expansions in Eq. (69) for $f_{3/2}$ and $f_{5/2}$ are poorly convergent so we need a different approach. Following Somerfeld, it is more convenient to carry out an expansion in $\nu = \beta\mu = \ln(z)$. The procedure is as follows. We work the the integral form of $f_{3/2}(z)$,

$$f_{3/2}(z) = \frac{4}{\pi^{1/2}} \int_0^\infty dx x^2 \frac{ze^{-x^2}}{1 + ze^{-x^2}} \quad (167)$$

We change variables to $y = x^2$, then and integrate by parts to find,

$$f_{3/2}(z) = \frac{2}{\pi^{1/2}} \int_0^\infty dy \frac{y^{1/2}}{e^{y-\nu} + 1} = \frac{4}{3\pi^{1/2}} \int_0^\infty dy \frac{y^{3/2} e^{y-\nu}}{(e^{y-\nu} + 1)^2} \quad (168)$$

The integration by parts leads to an integrand that is cnvergent at large y . Now we expand $y^{3/2}$ in a Taylor series about ν ,

$$y^{3/2} = (\nu + (y - \nu))^{3/2} = \nu^{3/2} + \frac{3}{2}\nu^{1/2}(y - \nu) + \frac{3}{8}\nu^{-1/2}(y - \nu)^2 + \dots \quad (169)$$

so that,

$$f_{3/2}(z) = \frac{4}{3\pi^{1/2}} \int_0^\infty dy \frac{e^{y-\nu}}{(e^{y-\nu} + 1)^2} (\nu^{3/2} + \frac{3}{2}\nu^{1/2}(y - \nu) + \frac{3}{8}\nu^{-1/2}(y - \nu)^2 + \dots). \quad (170)$$

Defining $t = y - \nu$ yields,

$$f_{3/2}(z) = \frac{4}{3\pi^{1/2}} \int_{-\nu}^\infty dt \frac{e^t}{(e^t + 1)^2} (\nu^{3/2} + \frac{3}{2}\nu^{1/2}t + \frac{3}{8}\nu^{-1/2}t^2 + \dots) \quad (171)$$

Now we break the integral up as,

$$\int_{-\nu}^\infty = \int_{-\infty}^\infty - \int_{-\infty}^{-\nu} \quad (172)$$

where the second integral is exponentially small, ie. $O(e^{-\nu})$, so we can ignore it. Finally we have,

$$f_{3/2}(z) = \frac{4}{3\pi^{1/2}} (\nu^{3/2} I_0 + \frac{3}{2}\nu^{1/2} I_1 + \frac{3}{8}\nu^{-1/2} I_2 + \dots); \quad \text{where } I_n = \int_{-\infty}^\infty dt \frac{t^n e^t}{(e^t + 1)^2} \quad (173)$$

$I_0 = 1$, while by symmetry I_n is zero for odd n . For even $n > 0$, I_n is related to the Reimann zeta function, through,

$$I_n = 2n(1 - 2^{1-n})(n-1)! \zeta(n), \quad \text{with } \zeta(2) = \frac{\pi^2}{6}, \quad \zeta(4) = \frac{\pi^4}{90}, \quad \zeta(6) = \frac{\pi^6}{945} \quad (174)$$

At very low temperatures, we take only the leading order term in the expansion so that,

$$\frac{N}{V} = \frac{1}{\lambda^3} \frac{4}{3\pi^{1/2}} (\beta\mu_0)^{3/2} I_0 \quad (175)$$

where μ_0 is the leading order expression for the chemical potential at low temperatures. Solving yields,

$$\mu_0 = \epsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{V} \right)^{2/3} \quad (176)$$

The fermi energy is calculated directly using,

$$\epsilon_F = \hbar^2 k_F^2 / 2m; \quad \text{with} \quad N = \left(\frac{L}{2\pi}\right)^3 \int_0^{k_F} 4\pi k^2 dk \quad (177)$$

that of course leads to the same result. However the Sommerfeld method enables us to also calculate the temperature dependence. To find the first temperature dependent term, we take the next term in the expansion of the chemical potential.

$$\frac{N}{V} = \frac{1}{\lambda^3} \frac{4}{3\pi^{1/2}} [(\beta\mu)^{3/2} I_0 + \frac{3}{8}(\beta\mu)^{-1/2} I_2 + \dots] \quad (178)$$

We define μ_1 to be the next to leading estimate of μ and using $I_2 = \pi^2/3$, find that it is given by,

$$\frac{N}{V} = \frac{1}{\lambda^3} \frac{4}{3\pi^{1/2}} [(\beta\mu_1)^{3/2} + \frac{3}{8} \frac{\pi^2}{6} (\beta\mu_0)^{-1/2}]. \quad (179)$$

which may be written as,

$$(\beta\mu_0)^{3/2} = (\beta\mu_1)^{3/2} + \frac{\pi^2}{8} (\beta\mu_0)^{-1/2} \quad \text{or} \quad (\beta\mu_1)^{3/2} = (\beta\mu_0)^{3/2} [1 - \frac{\pi^2}{8} (\beta\mu_0)^{-2}] \quad (180)$$

Solving and using $\beta\mu_0 = \beta\epsilon_F$ gives,

$$\mu_1 = \epsilon_F [1 - \frac{\pi^2}{8} \left(\frac{k_B T}{\epsilon_F}\right)^2]^{2/3} = \epsilon_F [1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F}\right)^2 + O\left(\left(\frac{k_B T}{\epsilon_F}\right)^4\right)] \quad (181)$$

It is not too difficult to calculate the next term in the expansion of μ ,

$$\mu_2 = \epsilon_F [1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F}\right)^2 - \frac{\pi^4}{80} \left(\frac{k_B T}{\epsilon_F}\right)^4 + O\left(\left(\frac{k_B T}{\epsilon_F}\right)^6\right)] \quad (182)$$

It is then evident that this is a rapidly convergent series for all $kT < \epsilon_F$. For many applications this is well satisfied so the low temperature thermodynamics is deduced from this form of the chemical potential. To find the thermodynamics, we also need an asymptotic expansion for $f_{5/2}(z)$ (see e.g. Pathria and Beale p 236),

$$f_{5/2}(\nu) = \frac{8}{15\pi^{1/2}} (\nu^{5/2} + \frac{5\pi^2}{8} \nu^{1/2} + \dots) = \frac{8}{15\pi^{1/2}} \nu^{5/2} (1 + \frac{5\pi^2}{8} \nu^{-2} + \dots) \quad (183)$$

From Eq. (70) to leading order in the temperature we write,

$$U = \frac{3k_B T V}{2\lambda^3} \frac{8}{15\pi^{1/2}} (\beta\mu_1)^{5/2} (1 + \frac{5\pi^2}{8} (\beta\mu_0)^{-2}) = \frac{3k_B T V}{2\lambda^3} \frac{8(\beta\mu_0)^{5/2}}{15\pi^{1/2}} [(1 - \frac{5\pi^2}{24} (\beta\mu_0)^{-2})] (1 + \frac{5\pi^2}{8} (\beta\mu_0)^{-2}) \quad (184)$$

Using a leading order expansion and some work on the prefactor we find,

$$U = \frac{3}{5} N \epsilon_F [1 + \frac{5}{12} \pi^2 \left(\frac{k_B T}{\epsilon_F}\right)^2] \quad (185)$$

The specific heat is then,

$$\frac{C_V}{N k_B} = \frac{\pi^2}{2} \frac{k_B T}{\epsilon_F} \quad (186)$$

and the equation of state is,

$$PV = \frac{2}{3} U = \frac{2}{5} N \epsilon_F [1 + \frac{5}{12} \pi^2 \left(\frac{k_B T}{\epsilon_F}\right)^2] \quad (187)$$

Note that at the densities typical of metals, and at room temperature, the electrons at the Fermi energy have velocities characteristic of a classical gas with temperatures roughly 10,000K. This is due to the peculiar nature of the exchange interaction, or Pauli principle. For this reason high density Fermi systems become more ideal as their density increases as in that limit, the exchange interaction dominates.

The Fermi factor is the average number of particles in each energy level,

$$\langle n_p \rangle = \frac{1}{\exp(\beta(\epsilon - \mu)) + 1} \quad (188)$$

At low temperatures, this function approaches a step function, where states below the Fermi energy, $\epsilon_p < \epsilon_F$, are fully occupied, while those above the Fermi energy are unoccupied. The width of the step function is given by $k_B T / \epsilon_F$.

IV. MODELING OF THE BEHAVIOR OF METALS

In some metals the electrons near the Fermi energy can be treated as a free Fermi gas. For example, this approximation is very good for Alkali metals that have one electron in an outer s orbital. The free electron model is also a good starting point for more complex metals where band structure effects become important and for strongly correlated systems where Coulomb interactions between the electrons play a key role. In many materials the Debye model provides a useful approximation of the contribution of phonons to the thermodynamic properties. The thermodynamic behavior of metals can therefore, to first approximation, be considered to be a sum of the contribution due to phonons and a contribution due to electrons. For the specific heat this leads to the prediction that at low temperatures,

$$\frac{C_V}{Nk_B} = \frac{\pi^2}{2} \frac{k_B T}{\epsilon_F} + \frac{12\pi^4}{5} \left(\frac{T}{T_D} \right)^3 \quad (189)$$

which is a sum of the electron contribution and the phonon contribution. This provides a good approximation when band structure effects, interaction effects and disorder effects are not important, and provided $T \ll T_D$.

V. GENERALIZED SOMMERFELD EXPANSION

The Sommerfeld expansion is easily generalized to high order in any spatial dimension and for a wide range of dispersion relation. We consider the general dispersion relation $\epsilon_k = c_\epsilon k^s$, which for $s = 1$, $c_\epsilon = \hbar c$ is the ultrarelativistic case, while $s = 2$, $c_{\epsilon_{\text{photon}}} = \hbar^2/2m$ is the non-relativistic case. We carry out the Sommerfeld expansion for N and U in general dimension starting with,

$$N = g \left(\frac{L}{2\pi} \right)^d \int_0^\infty c_d k^{d-1} \frac{z e^{-\beta \epsilon_k}}{1 + z e^{-\beta \epsilon_k}}; \quad U = g \left(\frac{L}{2\pi} \right)^d \int_0^\infty c_d k^{d-1} c_\epsilon k^s \frac{z e^{-\beta \epsilon_k}}{1 + z e^{-\beta \epsilon_k}} \quad (190)$$

where g is the degeneracy. Now we use,

$$x = \beta \epsilon_k = \beta c_\epsilon k^s; \quad k = \left(\frac{x}{\beta c_\epsilon} \right)^{1/s}; \quad dk = \frac{1}{sx} \left(\frac{x}{\beta c_\epsilon} \right)^{1/s} \quad (191)$$

which leads to,

$$N = g \left(\frac{L}{2\pi} \right)^d \frac{C_d}{s} \left(\frac{1}{c_\epsilon \beta} \right)^{d/s} \int_0^\infty dx \frac{x^{d/s-1}}{e^{x-\nu} + 1}; \quad U = g k_B T \left(\frac{L}{2\pi} \right)^d \frac{C_d}{s} \left(\frac{1}{c_\epsilon \beta} \right)^{d/s} \int_0^\infty dx \frac{x^{d/s}}{e^{x-\nu} + 1}; \quad (192)$$

We then carry out the Sommerfeld expansion for the integral,

$$J(\alpha) = \int_0^\infty dx \frac{x^{\alpha-1}}{e^{x-\nu} + 1} = \frac{1}{\alpha} \int_0^\infty dx \frac{x^\alpha e^{x-\nu}}{(e^{x-\nu} + 1)^2} \quad (193)$$

where the last expression is found by integrating by parts. Now we use the expansion,

$$x^\alpha = (\nu + (x - \nu))^\alpha = \sum_{l=0}^{\infty} \frac{\alpha!}{l!(\alpha-l)!} \nu^{\alpha-l} (x - \nu)^l \quad (194)$$

so that,

$$J(\alpha) = \frac{1}{\alpha} \sum_{l=0}^{\infty} \frac{\alpha!}{l!(\alpha-l)!} \nu^{\alpha-l} I_l \quad (195)$$

where,

$$I_l = \int_{-\nu}^\infty dt \frac{t^l e^t}{(e^t + 1)^2} = \int_{-\infty}^\infty dt \frac{t^l e^t}{(e^t + 1)^2} + O(e^{-\nu}) \quad (196)$$

The values for I_l are given in Eq. (174) above. For the N equation we use $\alpha = d/s$, while for the energy equation we use $d/s + 1$.

Assigned problems and sample quiz problems

Sample Quiz Problems

Quiz Problem 1. Write down the equation for the thermal de Broglie wavelength. Explain its importance in the study of classical and quantum gases.

Quiz Problem 2. Why are the factors $1/N!$ and $1/h^{3N}$ introduced into the derivation of the partition function of the ideal classical gas?

Quiz Problem 3. Explain why the heat capacity at constant volume of a nitrogen molecule is roughly $1.5Nk_B$ at $1K$ but $2.5Nk_B$ at room temperature. What are the expressions for the heat capacity at constant pressure for these two cases?

Quiz Problem 4. In modeling the earth's atmosphere using the equilibrium isothermal model, the gas pressure decreases exponentially with altitude. Explain how this is reconciled with the equilibrium condition of constant pressure found in our discussion of thermodynamics in Part 1 of the course.

Quiz Problem 5. Discuss the assumptions used in the isothermal and adiabatic models of the atmosphere.

Quiz Problem 6. What is the Curie law? Derive this law for the spin half Ising paramagnet.

Quiz Problem 7. Paramagnets and also the Ising model in one dimension exhibit a peak in their specific heat, with the low temperature behavior being an approach to zero exponentially and at high temperature an approach to zero as $1/T^2$. What is there a peak in the specific heat in these models. What can't we use the rule $k_B T/2$ per degree of freedom?

Quiz Problem 8. Explain the meaning of negative temperature in the Ising paramagnetic and how it can be used to make a magnetic cooling device.

Quiz Problem 9. What is the meaning of the terms "spontaneous symmetry breaking" (or spontaneous magnetization) and "breaking of ergodicity" in the context of the two dimensional Ising model.

Quiz Problem 10. State and give a physically explanation of the behavior of the chemical potential μ and the fugacity $z = e^{\beta\mu}$ as temperature $T \rightarrow \infty$, for both the Bose gases. Compare the cases of photons, phonons and Helium 4.

Quiz Problem 11. Write down the starting expression in the derivation of the grand partition function, Ξ_B for the ideal Bose gas, for a general set of energy levels ϵ_l . Carry out the sums over the energy level occupancies, n_l and hence write down an expression for $\ln(\Xi_B)$, and the average occupancy of each energy level $\langle n_l \rangle$.

Quiz Problem 12. In the condensed phase superfluids are often discussed in terms of a two fluid model. Based on the analysis of the ideal Bose gas, explain the physical basis of the two fluid model.

Quiz Problem 13. Why is the chemical potential of photons in a box, and also acoustic phonons in a crystal, taken to be zero?

Quiz Problem 14. Write down the blackbody energy density spectrum.

Quiz Problem 15. Write down and explain the relationship between the intensity of radiation emitted by a blackbody (Stefan-Boltzmann law) and the energy density of a photon gas in the blackbody.

Quiz Problem 16. Explain the physical origin of the cosmic microwave background (CMB) blackbody spectrum of the universe. It is currently at a temperature of $T_{CMB} = 2.713K$. If the universe is expanding at a constant rate $L(t) = H_0 t$, where H_0 is a constant what is the expected behavior of the temperature $T_{CMB}(t)$.

Quiz Problem 17. Derive or write down the spectral energy density for blackbody radiation in a universe with two spatial dimensions.

Quiz Problem 18. Derive or write down the Debye theory for the internal energy for phonons in a square lattice. Derive the low and high temperature limits of the internal energy and specific heat for this system.

Quiz Problem 19. On a graph, illustrate the behavior of the chemical potential μ and the fugacity $z = e^{\beta\mu}$ as a function of temperature. What is the chemical potential and fugacity of the the Fermi and Bose gases as temperature $T \rightarrow \infty$ and as $T \rightarrow 0$.

Quiz Problem 20. Write down the starting expression in the derivation of the grand partition function, Ξ_F for the ideal Fermi gas, for a general set of energy levels ϵ_l . Carry out the sums over the energy level occupancies, n_l and hence write down an expression for $\ln(\Xi_F)$.

Quiz Problem 21. White dwarf stars are stable due to electron degeneracy pressure. Explain the physical origin of this pressure.

Assigned problems

Assigned Problem 1. From the density of states for an ideal monatomic gas $\Omega(E)$ given in Eq. (26) of the notes, find the Sackur-Tetrode equation for the entropy, Eq. (27) of the notes.

Assigned Problem 2. Using the canonical partition function for the ideal gas, show that,

$$(\delta E)^2 = k_B T^2 C_v \quad (197)$$

Assigned Problem 3. Using the grand partition function of the ideal classical gas show that,

$$(\delta N)^2 = N k_B T \rho \kappa_T \quad (198)$$

Assigned Problem 4

Consider a gas of N atoms in volume V . Each atom has one unpaired electron in its outer energy level that is a zero angular momentum state, i.e. the ground state is $l = 0$ and has an unpaired electron. A magnetic field is applied to this gas. Write down the canonical and grand canonical partition functions of this system taking into account center of mass and spin degrees of freedom, assuming that the magnetic interaction is paramagnetic with no spin-orbit coupling.

Assigned Problem 5.

Consider a gas where each atom can have one of two energy levels ϵ_0 and ϵ_1 . Find the average energy per particle taking into account the ideal monatomic gas behavior and the two internal energy levels. Find the specific heat of the system in the limits $T \rightarrow 0$ and $T \rightarrow \infty$.

Assigned Problem 6.

Consider a dissociating system at thermal equilibrium, where,



Ignore the internal degrees of freedom of both species and take the mass of an A particle to be twice that of a B particle. Given that $N = 2N_A + N_B$ is fixed, that the volume is fixed, and that the binding energy of A is ϵ , find the temperature dependence of N_A and N_B and find a simple expression for the ratio $\langle N_B \rangle^2 / \langle N_A \rangle$.

Assigned Problem 7.

Calculate the specific heat of the model defined by the Hamiltonian Eq. (51) of the text. Is there a peak in the specific heat? Why or why not?

Assigned Problem 8.

Generalize the transfer matrix method for the one dimensional Ising model to the case of an applied field (i.e. combine the Hamiltonians in Eq. (41) and (55)) and calculate the magnetic susceptibility at low field. Does it obey a Curie law?

Assigned Problem 9.

Consider the Peierls argument for the two dimensional spin half Ising model on a square lattice, where the topological excitation is a flat domain wall dividing a domain of up spins and down spins. Does this argument suggest

that finite temperature spontaneous symmetry breaking is possible in the two dimensional Ising model?

Assigned Problem 10.

By using the Maxwell-Boltzmann statistics to fill the energy levels of a particle in a box, show that the grand partition function found in this way is the same as that found by carrying out the classical phase space integrals.

Assigned Problem 11. At high temperatures we found that the ideal Bose gas reduces to the ideal classical gas. Derive the next term in the expansion of the equation of state of the ideal Bose gas at high temperatures, and verify that,

$$\frac{PV}{Nk_B T} = 1 - \frac{1}{2^{5/2}} \frac{\lambda^3 N}{V} + \dots \quad (200)$$

The pressure of the ideal Bose gas is lower than that of the classical gas at the same temperature and volume. Why?

Assigned Problem 12. Using the general forms of the Bose gas equations, discuss the behavior of the Bose gas at low temperatures in one and two dimensions for the case of a non-relativistic gas. Is a finite temperature Bose condensation predicted? Show that at high temperatures the equation of state reduces to the ideal classical gas? Explain your reasoning.

Assigned Problem 13. For the 3-D non-relativistic case: a) Find the entropy of the ideal Bose gas in the condensed phase $T < T_c$. Is this entropy higher or lower than the classical ideal gas under the same conditions? Explain your result.

Assigned Problem 14. Show that a d - dimensional Bose gas with dispersion relation $\epsilon_p = cp^s$ obeys the relation,

$$P = \frac{s}{d} \frac{U}{V} \quad (201)$$

Assigned Problem 15. Find the entropy of a photon gas in d dimensions. Show that the entropy per photon is independent of temperature - explain your result.

Assigned Problem 16. Find the thermodynamic properties, PV , U , S , C_V of the Debye phonon model in d dimensions.

Assigned Problem 17. Carry through the analysis of the Bose gas for the case of massive ultrarelativistic particles where $\mu \neq 0$. What is the lower critical dimension for a BEC transition in this case?

Assigned Problem 18. At high temperatures we found that the ideal quantum gases reduce to the ideal classical gases. Derive the next term in the expansion of the equation of state of the ideal Fermi gas at high temperatures, and verify that,

$$\frac{PV}{Nk_B T} = 1 + \frac{1}{2^{5/2}} \frac{\lambda^3 N}{V} + \dots \quad (202)$$

The pressure of the ideal Fermi gas is higher than that of the classical gas at the same temperature and volume. Why? Carry out a similar expansion for the Bose gas. Is the pressure higher or lower than the ideal classical gas at the same values of T, V ? Why?

Assigned Problem 19. By expanding the denominator of the integral, $1/(1-y)$ for small $y = ze^{-x^2}$ show that,

$$f_{3/2}(z) = \frac{4}{\pi^{1/2}} \int_0^\infty dx x^2 \frac{ze^{-x^2}}{1+ze^{-x^2}} = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{3/2}} \quad (203)$$

Assigned Problem 20. Derive expressions for Z , Ξ , PV , μ and U for the classical gas in one and two dimensions. Are the results what you expect? How do they compare with the result in three dimensions. Write general expressions that are valid in any dimension.

Assigned Problem 21. Derive expressions for Ξ , PV , N/V and U for the Fermi gas in one and two dimensions. Write general expressions that are valid in any dimension. Find the leading order terms in the high temperature expansions for these quantities. Are the results what you expect? How do they compare with the result in three dimensions, and with the classical gas.

Assigned Problem 22. Show that a d - dimensional Fermi gas with dispersion relation $\epsilon_p = cp^s$ obeys the relation,

$$P = \frac{s}{d} \frac{U}{V} \quad (204)$$

Quiz Problem 23. Find the first two terms in the low temperature behavior of the internal energy an ultrarelativistic Fermi gas at low temperature. From your expression for the internal energy, find the specific heat of the gas. Compare the pressure of the gas to that of a non-relativistic gas with the same density.