5. Consider a solid consisting of a lattice of N atoms. If an atom is knocked slightly out of its proper position in the lattice, this is called a *point defect*. Assume that the energy of a point defect is ϵ, and that if there is no defect, the energy at that site is zero. Assume further that the defects are distinguishable, and do not interact with each other.

(a) Determine the number of ways to place n point defects within the N lattice sites. From this show that the entropy associated with their configuration is approximately

$$S(N,n) \sim k\left[N \ln N - n \ln n - (N - n)\ln(N - n)\right]$$

(3 points).

(b) Derive a (simple) expression for the internal energy, U, of the system as a function of n. From this result, write the entropy above, $S(N,n)$ as function of U and N, obtaining $S(U,N)$. (2 points).

(c) Using the expression for $S(U,N)$ above, calculate the chemical potential for changes in N. (3 points).

(d) In thermal equilibrium we know

$$T = \left[\frac{\partial S}{\partial U}\right]^{-1}$$

Use the approximate results above to calculate this temperature as a function of U and N. From this result to find the number of defects, $n(N,T)$. (2 points).

a) $S = k \ln \Omega$

$\Omega = $ multiplicity $= \binom{N}{n} = \frac{N!}{n!(N-n)!}$

$S = k \ln \frac{N!}{n!(N-n)!} = k\left[\ln N! - \ln n! - \ln(N-n)!\right]$

Stirling's approx: $\ln N! \approx N \ln N - N$

$S = k\left[N\ln N - \cancel{N} - n\ln n + \cancel{n} - (N-n)\ln(N-n) + \cancel{(N-n)}\right]$

$S = k\left[N\ln N - n\ln n - (N-n)\ln(N-n)\right]$ ✓

b) $E = n\epsilon$ since only defect pts have energy, ϵ.

$n = E/\epsilon$

$S = k\left[N\ln N - \frac{E}{\epsilon}\ln\frac{E}{\epsilon} - \left(N-\frac{E}{\epsilon}\right)\ln\left(N-\frac{E}{\epsilon}\right)\right]$

$= k\left[N\ln N - \frac{E}{\epsilon}\ln\frac{E}{\epsilon} - \left(\frac{N\epsilon - E}{\epsilon}\right)\ln\left(\frac{N\epsilon-E}{\epsilon}\right)\right]$

$= k\left[N\ln\left(\frac{N\epsilon}{N\epsilon-E}\right) + \frac{E}{\epsilon}\ln\left(\frac{N\epsilon-E}{E}\right)\right]$

c) $\frac{\partial S}{\partial N} = -\frac{\mu}{T} = k\left[\ln N + \frac{N}{N} - 0 - \ln(N\epsilon - E) - \frac{N\epsilon}{N\epsilon-E} + \ln\epsilon + \frac{\frac{E}{\epsilon}\epsilon}{N\epsilon-E} - 0\right]$

$= k\left[\ln N + 1 - \ln(N\epsilon-E) - \frac{N\epsilon}{N\epsilon-E} + \ln\epsilon + \frac{E}{N\epsilon-E}\right]$

$\frac{E - N\epsilon}{N\epsilon-E} = -1$ cancels the $+1$

$= k\left[\ln N - \ln(N\epsilon-E) + \ln\epsilon\right] = k\ln\left(\frac{N\epsilon}{N\epsilon-E}\right)$

$\mu = kT\ln\left(\frac{N\epsilon-E}{N\epsilon}\right)$

d) $\frac{1}{T} = \frac{\partial S}{\partial E} = k\left[-\frac{1}{\epsilon}\ln E - \frac{1}{\epsilon} + \frac{N}{N\epsilon-E} + \frac{1}{\epsilon}\ln(N\epsilon-E) - \frac{E}{\epsilon(N\epsilon-E)}\right]$

$= k\left[\frac{1}{\epsilon}\ln\left(\frac{N\epsilon-E}{E}\right) + \frac{N\epsilon - N\epsilon + E - E}{\epsilon(N\epsilon-E)}\right]$

$\frac{1}{T} = \frac{k}{\epsilon}\ln\left(\frac{N\epsilon-E}{E}\right)$

$e^{\beta\epsilon} = \frac{N\epsilon-E}{E} = \frac{N\epsilon}{E} - 1$

$e^{\beta\epsilon} + 1 = \frac{N\epsilon}{E} \qquad E = \frac{N\epsilon}{1+e^{\beta\epsilon}}$

Problem 5 (10 Points):

A system consists of N identical non-interacting particles in equilibrium with a heat bath. The total number of individual states available to each particle is 2 N. Of these states, N are degenerate with energy 0 and N are degenerate with energy ϵ. It is found by observation that the total energy of the system is $N\epsilon/3$.

a. What is the average number of particles in the excited state? (1.5 Points)

Find the temperature of the system under the following three different assumptions.

b. The particles are bosons. (2 Points)

c. The particles are fermions. (2 Points)

d. The particles obey a Boltzmann distribution. (2 Points)

e. Are the temperatures you found in (b.), (c.) and (d.) the same? Why or why not? Explain your answer. (2.5 Points)

heat baths are allowed to be different for the different types of particles

a) $\frac{N\epsilon}{3} = E$ so $\langle n \rangle = \frac{N}{3}$

b) Use $f_B(\epsilon_i) = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} - 1}$

$\frac{N}{3} = \frac{N}{e^{\beta(\epsilon - \mu)} - 1}$ and $\frac{2}{3}N = \frac{N}{e^{-\beta\mu} - 1}$

Solve together:

$T_B = \frac{\epsilon}{k \ln 8/5} \approx 2.2 \frac{\epsilon}{k}$

c) Use $f_f(\epsilon_i) = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} + 1}$

$\frac{N}{3} = \frac{N}{e^{\beta(\epsilon - \mu)} + 1}$ and $\frac{2}{3}N = \frac{N}{e^{-\beta\mu} + 1}$

Solve together:

$T_f = \frac{\epsilon}{k \ln 4} \approx 0.72 \frac{\epsilon}{k}$

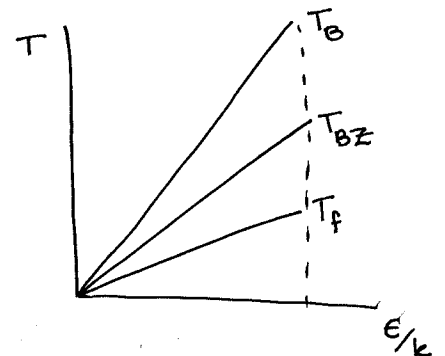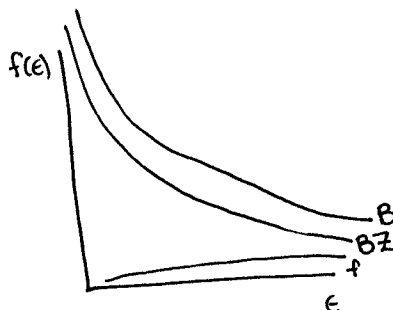d) Use $f_{BZ}(\epsilon_i) = \frac{g_i}{e^{\beta(\epsilon_i - \mu)}}$

$\frac{N}{3} = \frac{N}{e^{\beta(\epsilon - \mu)}}$ and $\frac{2}{3}N = \frac{N}{e^{-\beta\mu}}$

Solve together:

$T_{BZ} = \frac{\epsilon}{k \ln 2} \approx 1.44 \frac{\epsilon}{k}$

e) $T_B > T_{BZ} > T_f$

Because of their distributions, it takes more heat to get them to the same energy the more states they can share.

5. A particular solid is made up of N distinguishable spin 1 atoms each on a fixed position in a lattice. The energy of each atom is given by:

$$E(\sigma_i) = -V_0\sigma_i^2 - \mu_0\sigma_i B$$

$$d\left(\frac{N}{D}\right) = \frac{DN' - ND'}{D^2}$$

where V_0 arises from an internal field in the crystal, B is the applied external magnetic field and μ_0 is the Bohr magneton. The z-component of the spin of an atom can take on values $\sigma_i \in \{0, \pm1\}$

(a) Calculate the free energy, $F(T, B, N)$. (2 pts.)

(b) Calculate the specific heat. (4 pts.)

(c) Calculate the magnetic susceptibility, $\chi(T, B, N)$ when $B = 0$. (4 pts.)

a) Use CE since N, V are fixed but E is not

$$Z = z^N = \left(\sum_n e^{-\beta E_n}\right)^N \quad \text{where } E = 0, -V_0 - \mu_0 B, -V_0 + \mu_0 B \rightarrow Z = \left(1 + e^{\beta V_0 + \beta\mu_0 B} + e^{\beta V_0 - \beta\mu_0 B}\right)^N$$

$$F = -\frac{1}{\beta}\ln Z = -\frac{N}{\beta}\ln\left(1 + e^{\beta V_0}(2\cosh\beta\mu_0 B)\right) = -NkT\ln\left(1 + e^{V_0/kT}\left(2\cosh\frac{\mu_0 B}{kT}\right)\right)$$

b) Use $E = -\frac{\partial}{\partial\beta}\ln Z$ and $C_v = \frac{\partial E}{\partial T} = -k\beta^2\frac{\partial E}{\partial\beta} = k\beta^2\frac{\partial^2}{\partial\beta^2}\ln Z$

$$C_v = Nk\beta^2\frac{\partial}{\partial\beta}\left[\frac{V_0 e^{\beta V_0}(2\cosh\beta\mu_0 B) + e^{\beta V_0}\mu_0 B\, 2\sinh\beta\mu_0 B}{1 + e^{\beta V_0}(2\cosh\beta\mu_0 B)}\right] = Nk\beta^2\frac{\partial}{\partial\beta}\left[\frac{2e^{\beta V_0}(V_0\cosh\beta\mu_0 B + \mu_0 B\sinh\beta\mu_0 B)}{1 + e^{\beta V_0}(2\cosh\beta\mu_0 B)}\right]$$

$$C_v = \frac{Nk\beta^2\, 2}{\left(e^{-\beta V_0} + 2\cosh\beta\mu_0 B\right)^2}\left[\left(e^{-\beta V_0} + 2\cosh\beta\mu_0 B\right)\left(V_0\mu_0 B\sinh\beta\mu_0 B + \mu_0^2 B^2\cosh\beta\mu_0 B\right) - \left(V_0\cosh\beta\mu_0 B + \mu_0 B\sinh\beta\mu_0 B\right)\left(-V_0 e^{-\beta V_0} + 2\mu_0 B\sinh\beta\mu_0 B\right)\right]$$

Use $\xi = \beta\mu_0 B$

$$C_v = \frac{2Nk\beta^2}{\left(e^{-\beta V_0} + 2\cosh\xi\right)^2}\left[V_0\mu_0 B e^{-\beta V_0}\sinh\xi + \mu_0^2 B^2 e^{-\beta V_0}\cosh\xi + 2V_0\mu_0 B\sinh\xi\cosh\xi + 2\mu_0^2 B^2\cosh^2\xi + V_0^2 e^{-\beta V_0}\cosh\xi - 2V_0\mu_0 B\sinh\xi\cosh\xi + V_0\mu_0 B e^{-\beta V_0}\sinh\xi - 2\mu_0^2 B^2\sinh^2\xi\right]$$

Use $\cosh^2 - \sinh^2 = 1$

$$C_v = \frac{2Nk\beta^2}{\left(e^{-\beta V_0} + 2\cosh\xi\right)^2}\left[2V_0\mu_0 B e^{-\beta V_0}\sinh\xi + (V_0^2 + \mu_0^2 B^2)e^{-\beta V_0}\cosh\xi + 2\mu_0^2 B^2\right]$$

See other side for c.

c) $\chi = \frac{\partial M}{\partial B}$ where $M = \frac{1}{\beta}\frac{\partial}{\partial B}\ln Z = -\frac{\partial F}{\partial B}$ so $\chi = \frac{\partial}{\partial B}\left(-\frac{\partial F}{\partial B}\right) = -\frac{\partial^2 F}{\partial B^2}$

$$F = -\frac{N}{\beta}\ln\left(1 + e^{\beta V_0}2\cosh\beta\mu_0 B\right)$$

$$\chi = \frac{N}{\beta}\frac{\partial^2}{\partial B^2}\ln\left(1 + e^{\beta V_0}2\cosh\beta\mu_0 B\right)$$

$$\chi = \frac{N}{\beta}\frac{\partial}{\partial B}\left[\frac{2e^{\beta V_0}\beta\mu_0\sinh\beta\mu_0 B}{1 + e^{\beta V_0}2\cosh\beta\mu_0 B}\right] = \frac{2\beta\mu_0 e^{\beta V_0}N}{\beta}\frac{\partial}{\partial B}\left[\frac{\sinh\beta\mu_0 B}{1 + e^{\beta V_0}2\cosh\beta\mu_0 B}\right]$$

$$\chi = 2N\mu_0 e^{\beta V_0}\left[\frac{(1 + e^{\beta V_0}2\cosh\beta\mu_0 B)(\beta\mu_0\cosh\beta\mu_0 B) - \sinh\beta\mu_0 B(2e^{\beta V_0}\beta\mu_0\sinh\beta\mu_0 B)}{(1 + e^{\beta V_0}2\cosh\beta\mu_0 B)^2}\right]$$

$$\chi = 2N\beta\mu_0^2 e^{\beta V_0}\left[\frac{\cosh\beta\mu_0 B + 2e^{\beta V_0}}{(1 + e^{\beta V_0}2\cosh\beta\mu_0 B)^2}\right]$$

Evaluate at $B = 0$: $\cosh 0 = 1$ $\sinh 0 = 0$

$$\chi = 2N\beta\mu_0^2 e^{\beta V_0}\left[\frac{1 + 2e^{\beta V_0}}{(1 + 2e^{\beta V_0})^2}\right] = \underline{\underline{\frac{2N\beta\mu_0^2 e^{\beta V_0}}{1 + 2e^{\beta V_0}}}} = \underline{\underline{\frac{2N\beta\mu_0^2}{e^{-\beta V_0} + 2}}}$$

5. By shining an intense laser beam on a semiconductor, one can create a metastable collection of electrons (charge $-e$ and effective mass m_e) and holes (charge $+e$ and effective mass m_h). These oppositely charged particles may pair up to form an *exciton*, or they may dissociate into a plasma. This problem considers a simple model of this process. In this problem the densities of electrons and holes are so low that you can ignore their fermionic nature and treat them as classical particles in three dimensions.

(a) Calculate the free energy $F(T, V, N)$ of a gas of N_e electrons and N_h holes at temperature T, treating them as classical, non-interacting, ideal gas particles in a 3D volume V. (2 pts.)

(b) By pairing into an exciton, each electron-hole pair lowers its energy by ΔE. Calculate the free energy of a gas of N_p excitons, treating them as classical, non-interacting, ideal gas particles. (2 pts.)

(c) Calculate the chemical potentials μ_e, μ_h, and μ_p of the electrons, holes, and exciton pairs respectively. What is the condition of equilibrium between excitons and eletrons and holes? (3 pts.)

(d) Consider the case where the numbers of electrons and holes are equal, so that $n_h = n_e \equiv n_0$. Determine the approximate density of excitons as a function of n_0 in the high temperature limit (when the exciton population is low). (3 pts.)

d) use the equil. condition and plug in μ values

$$\frac{1}{\beta}\ln\left(\frac{\lambda_{Tp}^3 N_p}{V}\right) = \frac{1}{\beta}\ln\left(\frac{\lambda_{Te}^3 \lambda_{Th}^3 n_0^2}{V^2}\right)$$

$$\frac{N_p}{V} = \left(\frac{2\pi\hbar \, m_p}{kT \, m_e m_h}\right)^{3/2} \frac{n_0^2}{V^2}$$

For high energies:

n as derived now goes to ~~zero~~ for $T \gg 0$

So makes sense physically — at high T, the e & h are too excited to combine.

a) First find partition functions, where $Z = Z_e Z_h$

$$Z_e = z^N = \frac{1}{N!}\left[\int e^{-\beta E}\right]^N = \frac{1}{N!}\left[\int \frac{d^3x \, d^3p}{(2\pi\hbar)^3} e^{-\frac{\beta p^2}{2m}}\right]^N \quad \text{where } E = \frac{p^2}{2m}$$
for noninteracting ideal gas

$$= \frac{1}{N!}\left[\frac{V 4\pi}{(2\pi\hbar)^3}\int_0^\infty p^2 e^{-\frac{\beta}{2m}p^2} dp\right]^N \quad \text{use integral relation given } \alpha = \beta/2m$$

$$= \frac{1}{N!}\left[\frac{V_e}{\lambda_{Te}^3}\right]^{N_e} \quad \text{where } \lambda_{Te} = \left(\frac{2\pi\hbar\beta}{m}\right)^{1/2} \text{ de Broglie wavelength}$$

$$\therefore Z = Z_e Z_h = \frac{1}{N_e! N_h!}\left[\frac{V_e}{\lambda_{Te}^3}\right]^{N_e}\left[\frac{V_h}{\lambda_{Th}^3}\right]^{N_h}$$

$$F = -\frac{1}{\beta}\ln Z = -\frac{1}{\beta}\left[N_e\ln\left(\frac{V_e}{\lambda_{Te}^3}\right) + N_h\ln\left(\frac{V_h}{\lambda_{Th}^3}\right) - N_e\ln N_e + N_e - N_h\ln N_h + N_h\right]$$

$$\boxed{F = -\frac{1}{\beta}\left[\ln\left[\left(\frac{V_e}{\lambda_{Te}^3 N_e}\right)^{N_e}\left(\frac{V_h}{\lambda_{Th}^3 N_h}\right)^{N_h}\right] + N_e + N_h\right]}$$

b) $Z_p = \frac{1}{N_p!}\left[\frac{V_p}{\lambda_{Tp}^3}\right]^{N_p}$ $\quad F = -\frac{1}{\beta}\ln Z_p = -\frac{1}{\beta}\left[N_p\ln\left(\frac{V_p}{\lambda_{Tp}^3}\right) - N_p\ln N_p + N_p\right]$

$$\boxed{F_p = -\frac{1}{\beta}\left[\ln\left(\frac{V_p}{\lambda_{Tp}^3 N_p}\right)^{N_p} + N_p\right]}$$

c) Condition is $\boxed{\mu_e + \mu_h = \mu_p}$

$$\mu = \frac{dF}{dN} \rightarrow \mu_p = \frac{\partial F_p}{\partial N_p} = \frac{1}{\beta}\frac{\partial}{\partial N_p}\left[N_p\ln\left(\frac{\lambda_{Tp}^3 N_p}{V_p}\right) - N_p\right]$$

$$\boxed{\mu_p = \frac{1}{\beta}\ln\left(\frac{\lambda_{Tp}^3 N_p}{V_p}\right)}$$

Should be able to find μ_e & μ_h the same way since nothing is interacting. Then:

$$\boxed{\mu_e = \frac{1}{\beta}\ln\left(\frac{\lambda_{Te}^3 N_e}{V_e}\right)} \qquad \boxed{\mu_h = \frac{1}{\beta}\ln\left(\frac{\lambda_{Th}^3 N_h}{V_h}\right)}$$

5. Consider a classical ideal gas in 3D that feels a linear gravitational potential,

$$V(z) = mgz$$

where m is the mass of a single gas atom and $0 < z < \infty$. This is not an interaction between gas atoms, it is simply their gravitational potential energy near the surface of the Earth.

The gas is in a box of dimensions L_x, L_y, and L_z, so that:

$$0 < z < L_z$$
$$0 < x < L_x$$
$$0 < y < L_y$$

(a) Calculate the partition function in the canonical ensemble. (3 points)

(b) Determine the internal energy of the gas. (3 points)

(c) Calculate the specific heat c_v. (3 points)

(d) Explain the behavior of the specific heat when $\beta mgL_z >> 1$ and when $\beta mgL_z << 1$. (The approximation for the gravitational potential may or may not be valid for large L_z. Don't worry about that.) (1 point)

a) Use $E_n = \frac{p^2}{2m} + mgz$ and $Z = \frac{z^N}{N!} = \frac{1}{N!}\left[\int \frac{d^3x\, d^3p}{(2\pi\hbar)^3} e^{-\beta\frac{p^2}{2m} - \beta mgz}\right]^N = \frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^3}\right)^{3N/2}\beta^{-5N/2}\left(\frac{1-e^{-\beta mgL_z}}{mgL_z}\right)^N$ where $V = L_x L_y L_z$

b) Use $E = -\frac{d}{d\beta}\ln Z = -\left[-\frac{5N}{2\beta} + \frac{N(-mgL_z)(-e^{-\beta mgL_z})}{1 - e^{-\beta mgL_z}}\right] = \frac{5N}{2\beta} - \frac{NmgL_z}{e^{\beta mgL_z} - 1} = \frac{5N}{2\beta} - NmgL_z\left(e^{\beta mgL_z} - 1\right)^{-1}$

c) Use $C_v = \frac{\partial E}{\partial T} = -k\beta^2\frac{\partial E}{\partial \beta} = -k\beta^2\left[-\frac{5N}{2\beta^2} - NmgL_z(-1)\left(e^{\beta mgL_z} - 1\right)^{-2}(mgL_z)e^{\beta mgL_z}\right] = \frac{5}{2}Nk - \frac{Nk(\beta mgL_z)^2 e^{\beta mgL_z}}{\left(e^{\beta mgL_z} - 1\right)^2}$

d) For $\beta mgL_z >> 1$, $e^{\beta mgL_z} - 1 \approx e^{\beta mgL_z}$

So $C_v \Rightarrow \frac{5}{2}Nk - Nk(mgL_z\beta)^2 e^{-\beta mgL_z}$

2nd term dominates— v. low C_v b/c gravity "freezes out" any thermal excitation.

For $\beta mgL_z << 1$, $e^{\beta mgL_z} \approx 1 + \beta mgL_z + \frac{(\beta mgL_z)^2}{2} + \cdots$

(keeping up to the linear term is enough, has β in answer)

$C_v \Rightarrow \frac{5}{2}Nk - \frac{Nk(\beta mgL_z)^2(1 + \beta mgL_z)}{(1 + \beta mgL_z - 1)^2} = \frac{5}{2}Nk - \frac{Nk(\beta mgL_z)^2(1 + \beta mgL_z)}{(\beta mgL_z)^2}$

use $(1+x)^{-2} \approx 1 - 2x$ for small x.

$C_v \Rightarrow \frac{5}{2}Nk - Nk(1 + \beta mgL_z) \Rightarrow \frac{3}{2}Nk - \beta mgL_z Nk$

Gravity has v. little effect, goes to $\frac{3}{2}Nk$ for free gas.

Statistical Mechanics

4. Consider a certain hard sphere model of a gas of N particles in which we have an "excluded volume term." The entropy in this case can be given as:

$$S(U, V, N) = Nk \ln \left[(V - Nb) \frac{U}{\epsilon_0 N^2} \right]$$

Here b represents the volume of one gas particle, V is the volume of the container, U is the internal energy of the gas, and k is Boltzmann's constant. The constant ϵ_0 has dimensions of energy × volume, and is included to keep the argument of the logarithm dimensionless.

(a) Does this system satisfy the third law of thermodynamics (i.e. does the entropy of the system go to zero as the temperature goes to zero)? Prove your answer. (3 points)

(b) What is the specific heat at constant volume for this gas? (2 points)

(c) A gas with N_1 particles with total energy U_1 in a volume V_1 has an excluded volume/particle of b_1. It is separated by a moveable, insulating piston from a second gas of N_2 particles with total energy U_2 in a volume V_2 and an excluded volume/particle of b_2. The piston is allowed to move so that $V_{tot} = V_1 + V_2$ is a constant, but V_1 and V_2 can change. What is the value of V_1 in equilibrium? (5 points)

a) makes sense because classical results don't usually work for low temperatures— then we have to consider qm effects. ↓

a) Use $dE = TdS - \mu dN + PdV$

For fixed N & V, $\frac{\partial S}{\partial E} = \frac{1}{T}$

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

→ $T = \frac{U}{Nk}$ So as $T \to 0$,

$U \to 0$, $S \to \ln(0)$

S does not go to zero.

b) $C_v = \frac{\partial E}{\partial T}$ and we have $U = NkT$

$C_v = \frac{d}{dT}(NkT) = \underline{\underline{Nk}}$

c) Pressures should be equal

$P_1 = P_2$ So $T_1 \frac{\partial S_1}{\partial V_1} = T_2 \frac{\partial S_2}{\partial V_2}$

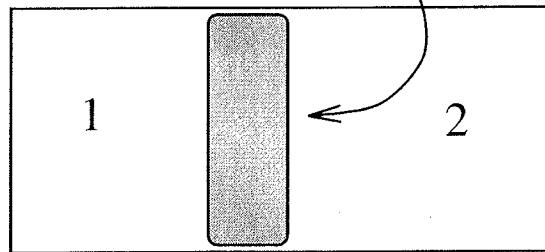$\frac{N_1 kT_1}{V_1 - N_1 b_1} = \frac{N_2 kT_2}{V_2 - N_2 b_2}$

$V_1 - N_1 b_1 = (V_2 - N_2 b_2) \frac{N_1 T_1}{N_2 T_2}$ write $V_2 = V - V_1$

$V_1 = (V - N_2 b_2) \frac{N_1 T_1}{N_2 T_2} - V_1 \frac{N_1 T_1}{N_2 T_2} + N_1 b_1$

$V_1 \left(1 + \frac{N_1 T_1}{N_2 T_2} \right) = (V - N_2 b_2) \frac{N_1 T_1}{N_2 T_2}$

$V_1 = \frac{(V - N_2 b_2) N_1 T_1 + N_1 b_1 N_2 T_2}{N_1 T_1 + N_2 T_2}$

Insulating piston

6

5. A crystalline solid contains N similar, immobile, statistically independent defects. Each defect has 5 possible states $s_1, s_2, \ldots s_5$. The energies of the states are given by $E_1 = E_2 = 0$, and $E_3 = E_4 = E_5 = \Delta$.

(a) Find the partition function for the defects as a function of their number, and the temperature T. (3 points)

(b) Find the defect contribution to the entropy of the crystal as a function of Δ and the temperature T. (4 points)

(c) Without doing a detailed calculation state the contribution to the internal energy due to the defects in the limit $kT \gg \Delta$. Explain your reasoning. (3 points)

a) $Z = \left(\sum_n e^{-\beta E_n} \right)^N = \left(2e^0 + 3e^{-\beta \Delta} \right)^N = \underline{\underline{\left(2 + 3e^{-\beta \Delta} \right)^N}} = \underline{\underline{\left(2 + 3e^{-\Delta/kT} \right)^N}}$

b) $S = \frac{-\partial F}{\partial T} = k\beta^2 \frac{\partial F}{\partial \beta}$ where $F = -\frac{1}{\beta} \ln Z = -\frac{N}{\beta} \ln \left(2 + 3e^{-\beta \Delta} \right)$

$S = -k\beta^2 N \frac{\partial}{\partial \beta} \left[\frac{1}{\beta} \ln \left(2 + 3e^{-\beta \Delta} \right) \right] = \underline{\underline{Nk \ln \left(2 + 3e^{-\beta \Delta} \right) + \frac{3Nk\beta \Delta}{2e^{\beta \Delta} + 3}}} = \underline{\underline{Nk \ln \left(2 + 3e^{-\Delta/kT} \right) + \frac{3Nk\Delta}{kT \left(2e^{\Delta/kT} + 3 \right)}}}$

c) $E = -\frac{\partial}{\partial \beta} \ln Z = \frac{3N\Delta}{2e^{\beta \Delta} + 3}$ For high T, we expect the system to be in its most random state. So each of the 5 states has equal probability of being filled. So our energy contribution should be:

$E_{def} = \left(\frac{1}{5}(0) + \frac{1}{5}(0) + \frac{1}{5}(\Delta) + \frac{1}{5}(\Delta) + \frac{1}{5}\Delta \right) N$

$= \underline{\underline{\frac{3}{5} N \Delta}}$

We can also find that rigorously: 7

$e^{+\beta \Delta} \approx 1 + \beta \Delta \rightarrow E \approx \frac{3N\Delta}{2(1 + \beta \Delta) + 3} \rightarrow \frac{3N\Delta}{5(1 + \frac{\beta \Delta}{5})} \rightarrow \frac{3}{5} N\Delta \left(1 - \frac{\beta \Delta}{5} \right)$ $\beta \rightarrow 0$ so

$E \rightarrow \underline{\underline{\frac{3}{5} N \Delta}}$ which is what we predicted. ✓

Statistical Mechanics

4. A certain system can be modelled as an ideal gas of point particles, but the point particles have two internal states, with energies 0 and Δ.

   (a) Show that in the canonical ensemble the partition function $Z(T, V, N)$ for the gas can be written as

$$Z(T, V, N) = Z_0 \left(1 + e^{-\Delta/kT}\right)^N \frac{\left(VT^{3/2}\right)^N}{N!}$$

   where Z_0 is a multiplicative constant that has no effect on the equation of state. (**2 points**)

   (b) Calculate the specific heat at constant volume for the gas. (**2 points**)

   (c) Assume further that we have *two* such gases, A and B, and that each has an internal state, but that $\Delta_A \neq \Delta_B$. Determine $Z(T, V, N_A, N_B)$, where N_A and N_B are the number of gas atoms of type A and B, respectively. (**1 point**)

   (d) Finally, if gas particles of type A can convert into type B and vice versa, calculate N_A/N_{tot} in equilibrium, where $N_{\text{tot}} = N_A + N_B$. (**5 point**)

a) $Z = Z_{int} Z_{trans}$ $Z_{int} = \left(\sum_n e^{-\beta E_n}\right) = \left(1 + e^{-\beta\Delta}\right)$ $Z_{trans} = \int \frac{d^3x d^3p}{(2\pi\hbar)^3} e^{-\beta p^2/2m} = \frac{V 4\pi}{(2\pi\hbar)^3} \frac{1}{4}\sqrt{\frac{\pi(2m)^3}{\beta^3}} = \frac{V}{2\pi^2\hbar^3} \frac{1}{4}\sqrt{\frac{\pi(2m)^3}{\beta^3}}$

$\left(\begin{array}{l}\text{there will be one}\\\text{factor of } N!\end{array}\right)$

$Z = \frac{1}{N!}\left(Z_{int} Z_{trans}\right)^N = \frac{1}{N!}\left[\left(1 + e^{-\beta\Delta}\right) V T^{3/2} \underbrace{\frac{\sqrt{\pi(2m)^3 k^3}}{8\pi^2\hbar^3}}_{Z_0}\right]^N = Z_0 \left(1 + e^{-\beta\Delta}\right)^N \frac{\left(VT^{3/2}\right)^N}{N!}$ ✓

b) $C_v = \frac{dE}{dT} = -k\beta^2 \frac{\partial E}{\partial \beta} = -k\beta^2 \frac{d}{d\beta}\left[-\frac{\partial}{\partial \beta} \ln Z\right] = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z$

$C_v = k\beta^2 \frac{d}{d\beta}\left[\frac{N e^{-\beta\Delta}(-\Delta)}{1 + e^{-\beta\Delta}}\right] = \frac{k\beta^2 N\Delta^2 e^{\beta\Delta}}{\left(e^{\beta\Delta} + 1\right)^2}$

c) Since we know A & B are linearly independent, $Z = Z_A Z_B$

$Z = Z_{0A} Z_{0B} \left(1 + e^{-\beta\Delta_A}\right)^{N_A} \left(1 + e^{-\beta\Delta_B}\right)^{N_B} \frac{\left(VT^{3/2}\right)^{N_A + N_B}}{N_A! N_B!}$

d) As usual, find μ_A & μ_B and use $\mu_A = \mu_B$ at equil:

$\mu = \frac{\partial F}{\partial N} = -\frac{1}{\beta} \frac{\partial}{\partial N} \ln Z$ so $\mu_A = -\frac{1}{\beta} \ln\left[\left(1 + e^{-\beta\Delta_A}\right)\left(VT^{3/2}\right) N_A\right]$ and $\mu_B = -\frac{1}{\beta}\ln\left[\left(1 + e^{-\beta\Delta_B}\right)\left(VT^{3/2}\right) N_B\right]$

Setting $\mu_A = \mu_B$, I get $\frac{N_B}{N_A} = \frac{\left(1 + e^{-\beta\Delta_A}\right)}{\left(1 + e^{-\beta\Delta_B}\right)}$

$\frac{N_A}{N_A + N_B} = \left(\frac{N_A + N_B}{N_A}\right)^{-1} = \left(1 + \frac{N_B}{N_A}\right)^{-1} = \left(1 + \frac{1 + e^{-\beta\Delta_A}}{1 + e^{-\beta\Delta_B}}\right)^{-1} = \frac{1 + e^{-\beta\Delta_B}}{2 + e^{-\beta\Delta_A} + e^{-\beta\Delta_B}}$

5. A gas of N distinguishable classical non-interacting atoms is held in a neutral atom trap by a potential of the form $V(\vec{r}) = a\,r$ where $r = \sqrt{x^2 + y^2 + z^2}$. The gas is in thermal equilibrium at a temperature T.

   (a) Find the single particle partition function Z_1 for a trapped atom. Express your answer in the form $Z_1 = A T^\alpha a^{-\eta}$. Find the prefactor A and the exponents α and η. (3 points)

   (b) Find the entropy of the gas in terms of N, k, and $Z_1(T, a)$. Do not leave any derivatives in your answer. (4 points)

   (c) The gas can be cooled if the potential is lowered reversibly (by decreasing a) while no heat is allowed to be exchanged with the surroundings, $dQ = 0$. Under these conditions, find T as a function of a and the initial values T_0 and a_0. (4 points)

a) $Z = \int \dfrac{d^3x\, d^3p}{(2\pi\hbar)^3} e^{-\beta p^2/2m - \beta a r} = \dfrac{(4\pi)^2}{(2\pi\hbar)^3} \int p^2 e^{-\beta p^2/2m}\, dp \int r^2 e^{-\beta a r}\, dr = \dfrac{1}{\pi\hbar^3}\cdot\dfrac{1}{4}\sqrt{\dfrac{\pi(2m)^3}{\beta^3}}\cdot\dfrac{2}{(\beta a)^3} = \underbrace{\left[\dfrac{2mk^3}{\pi^{1/3}\hbar^2}\right]^{3/2}}_{A} T^{9/2} a^{-3}$

$\underline{\underline{\eta = 3}}, \quad \underline{\underline{\alpha = 9/2}}$

b) Set $A a^{-3} = \xi$, $\quad Z = \left(\xi T^{9/2}\right)^N$

$F = -kT \ln Z = -NkT \ln\left(\xi T^{9/2}\right)$ $\qquad S = -\dfrac{\partial F}{\partial T} = \left[Nk\ln\left(\xi T^{9/2}\right) + \dfrac{NkT}{\xi T^{9/2}}\xi T^{7/2}\left(\dfrac{9}{2}\right)\right] = \underline{\underline{Nk\ln Z + \dfrac{9}{2}Nk}}$

c) Reversible, so $dS = 0$. Take deriv of S and set to zero, then can do separation of vars.

$dS = d\left(Nk\ln\left(AT^{9/2}a^{-3}\right) + \dfrac{9}{2}Nk\right)$ $\qquad$ ex. $d(x^2 y^2) = 2x\,dx\,y^2 + x^2 2y\,dy$

$dS = \dfrac{Nk\,Aa^{-3}\left(\tfrac{9}{2}T^{7/2}\right)dT}{AT^{9/2}a^{-3}} + \dfrac{Nk\,AT^{9/2}(-3a^{-4})\,da}{AT^{9/2}a^{-3}} = 0$

$\dfrac{Nk\,Aa^{-3}\tfrac{9}{2}T^{7/2}\,dT}{AT^{9/2}a^{-3}} = \dfrac{Nk\,Aa^{-4}T^{9/2}(3)}{AT^{9/2}a^{-3}}$

$\displaystyle\int_{T_0}^{T} \dfrac{9}{2T}\,dT = \int_{a_0}^{a} \dfrac{3}{a}\,da$

$3\cdot\dfrac{3}{2}\ln\left(\dfrac{T}{T_0}\right) = 3\ln\left(\dfrac{a}{a_0}\right)$

$\left(\dfrac{T}{T_0}\right)^{3/2} = \left(\dfrac{a}{a_0}\right)$

$\underline{\underline{T = T_0\left(\dfrac{a}{a_0}\right)^{2/3}}}$ $\qquad$ tricky question!

Problem 6 (10 Points):

The partition function for an ideal gas of molecules in a volume V can be written as, $\qquad Z = \frac{1}{N!}(V\zeta)^N$,

where $V\zeta$ is the partition function for a single molecule (involving its kinetic energy plus internal energy if it is not monotonic) and ζ is a function that depends only on the absolute temperature.

When these molecules are condensed to form a liquid, the crudest approximation consists of treating the liquid as if the molecules still formed a gas of molecules moving independently provided that,

1. each molecule is assumed to have a constant potential energy $-\eta$ due to its average interaction with the rest of the molecules.

2. each molecule is assumed to move throughout a volume $N\nu_0$, where ν_0 is the constant volume available per molecule in the liquid phase.

a. With these assumptions and the equation given in the above text, write down the partition function for a liquid consisting of N_L molecules. (2 Points)

b. Using the equation in the above text, write down the chemical potential μ_G for N_G molecules of the vapor in a volume V_G at temperature T. Treat the system as an ideal gas. (1 Points)

c. Write down the chemical potential μ_l for N_l of the molecules of the liquid at the temperature T using the result from (a.). (1 Points)

d. Using your results in b and c, find an expression relating the vapor pressure to the temperature T where the gas is in equilibrium with the liquid. (2 Points)

e. Use the Clausius-Clapeyron equation and the fact that the gas can be considered ideal to show that $P = P_0\, e^{-L/RT}$, where L in the latent heat of vaporization per mole. (2 Points)

f. Calculate the molar entropy difference between the gas and liquid in equilibrium at the same temperature and pressure. (2 Points)

Left margin handwritten work

$$\left(\zeta_\ell = e^{\beta\eta}\zeta_G\right)$$

$$\nearrow \quad Z = \frac{1}{N_\ell!}\left(N\nu_0\zeta_\ell\right)^{N_\ell}$$

a) $Z = \frac{1}{N_L!}\, \bar{z}^{N_L}$ where $\bar{z} = \int \frac{d^3x\, d^3p}{(2\pi\hbar)^3} e^{-\frac{\beta p^2}{2m}+\beta\eta}$

$$Z = \frac{1}{N_L!}\left(\frac{N_\ell\nu_0\, e^{\beta\eta}\, m^{3/2}}{\hbar^3(2\pi\beta)^{3/2}}\right)^{N_L}$$

b) Use $Z_G = \frac{1}{N_G!}\left(V_G\zeta\right)^{N_G}$

$F = -kT\ln Z_G$

$\mu_G = \frac{\partial F}{\partial N_G} = kT\ln\left(\frac{N_G}{V_G\zeta}\right)$

c) $\mu_\ell = -kT\frac{d}{dN_\ell}\ln Z_\ell$

$= -kT\frac{d}{dN_\ell}\left[N_\ell\ln\left(N_\ell\nu_0\zeta_\ell\right) - N\ln N + N\right]$

$\mu_\ell = -kT\left[\ln\left(\nu_0\zeta_\ell\right) + 1\right]$

d) At equil, $\mu_\ell = \mu_G$

$-kT\left[\ln\left(\nu_0\zeta e^{\beta\eta}\right) + 1\right] = -kT\ln\left(\frac{V_G\zeta}{N_G}\right)$

$\frac{V_G}{N_G} = \nu_0 e^{\beta\eta+1}$

$P_G = -\frac{\partial F_G}{\partial V_G} = \frac{kT}{\nu_0}e^{\beta\eta+1}$

Bottom handwritten work

e) C-C eq: $\frac{dP}{dT} = \frac{L}{T(V_G-V_L)}$ Set $V_L = 0$, $V_G = \frac{nRT}{P}$, $n=1$ (so we get P per 1 mole)

$$\int_{P_0}^P \frac{1}{P}dP = \int \frac{L}{RT^2}dT \;\rightarrow\; \ln\left(\frac{P}{P_0}\right) = -\frac{L}{RT} \;\rightarrow\; P = P_0 e^{-L/RT} \;\checkmark$$

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

$S_{G\,molar} = n_G R\left(\ln\left(\frac{V_G\zeta k}{n_G R}\right) + 1 + T\dot\zeta\right)$

$S_{\ell\,molar} = n_\ell R\left(\ln\left(\nu_0\zeta e^{\beta\eta}\right) + 1 - \eta\beta + T\dot\zeta\right)$

$\left.\right\}$ where $S_{mol\,diff} = S_{G\,molar} - S_{\ell\,molar}$

Right margin handwritten work

f) Alternately, would be easier to see

$\frac{dP}{dT} = \frac{S_G - S_\ell}{V_G - V_\ell}$ at equil

take $\frac{dP}{dT}$ from part d,

plug in V_G from equil cond'n in part d

must plug in equil cond'n from d!

$$S_{diff\,molar} = R(n_G - n_\ell)\ln\left(\frac{V_G\zeta k}{n_G R}\right) + R(n_G + n_\ell\eta\beta) + RT\dot\zeta(n_G - n_\ell)$$