## 統計力學

1. Consider a binary mixture that consists of $n_1$ moles of component 1 and $n_2$ mole of component 2. The total mass of the mixture is M, given by

$$M=n_1m_1+ n_2m_2,$$

where $m_1$ and $m_2$ are the molecular weights of component 1 and 2, respectively. Einstein's fluctuation theory gives the probability density for the fluctuation of the entropy of the system from its equilibrium value $\Delta S_T$ as

$$P(\Delta S_T)=(\text{constant}) \exp(\Delta S_T/k_B)$$

where

$$\Delta S_T= -(\Delta T\Delta S-\Delta P\Delta V+\Delta\mu_1\Delta n_1+\Delta\mu_2\Delta n_2)/2T$$

a) Define s=S/M, $v$=V/M, $m = (m_1 / m_1 - m_2 / m_2)$, and x=$m_1$ $n_1$/M (the mass fraction of component 1), show that

$$\Delta S_T=\frac{M}{2T}[\frac{C_{v,x}}{T}(\Delta T)^2 - 2a(\Delta v\Delta x) + (vc_T)^{-1}(\Delta v)^2 + (\frac{\partial m}{\partial x})_{T,P}(\Delta x)^2]$$

where $C_{v,x}$ is the specific heat at constant volume. $c_T$ is the isothermal compressibility, and $a = (\bar{v}_1 / m_1 - \bar{v}_2 / m_2)/(vc_T)$; here $\bar{v}_i$ is the partial molar volume of component i.

b) Evaluate $\langle(\Delta T)^2\rangle$, $\langle(\Delta v)^2\rangle$, $\langle(\Delta x)^2\rangle$, and $\langle(\Delta v)(\Delta x)\rangle$.

2. A container contains N non-interacting, distinguishable, two level atoms. Each atom can exist in one of two energy levels, $\varepsilon_0=0$ and $\varepsilon_1=\varepsilon$. The number of atoms in energy level $\varepsilon_0$ is $n_0$ and in energy level $\varepsilon_1$ is $n_1$. The total energy E of the system is

$$E = n_0\varepsilon_0 + n_1\varepsilon_1$$

a) Compute the entropy of the system
b) Find the temperature T of the system. Under what condition can the temperature become negative?
c) What is the behavior of the heat capacity when $T\to 0$ and when $T\to\infty$.

3. For a two component solution with components A and B coexisting in the liquid and gas phases in equilibrium, show that the Clausius-Clapeyron equation for the coexistence curve between liquid and vapor phase when the mole fraction of component A in the liquid phase is held fixed is given by

$$\left(\frac{dP}{dT}\right)_{x_A^l} = \frac{x_A^g(s_A^g - s_A^l) + x_B^g(s_B^g - s_b^l)}{x_A^g(v_A^g - s_A^l) + x_B^g(v_B^g - v_B^l)}$$

where $s_i$ *and* $v_i$ are partial molar entropy and partial molar volume, respectively.

4. In describing order-disorder transitions, a very useful model often used is the Ising model, with the Hamiltonian of a d-dimensional spin lattice with N lattice sites in a magnetic field *B* given by

$$H = \sum_{\{i,j\}} e_{ij} s_i s_j - mB\sum_j s_j$$

where $e_{ij}$ is the coupling constant between spins $i$ and $j$, and $\{ij\}$ indicates the $ij$ pair. Both $s_i$ and $s_j$ can take the value of +1 or –1. Unfortunately, an exact solution to a statistical thermodynamic problem using this Hamiltonian can only be obtained in a one-, and, with great difficulty, a two-dimension lattice. Therefore, in practice, one often makes recourse to approximations. Using the mean field approximation, one can simplify the above Hamiltonian as

$$H = -\sum_{i=1}^{N} E(e,B)s_i$$

where $E(e,B) = \frac{1}{2}ne < s > + mB$.

a). What is the meaning of <*s*>? Obtain an expression that can be used to calculate <*s*>.

b). Show the fluctuation in the total magnetic moment is given by

$$< M^2 > - < M >^2 = \frac{Nm^2}{\cosh^2[\frac{1}{2}e < s > + mB]}$$

Here $M = \sum_i m_i = m\sum_i s_i$

c) For *B*=0, show that for T in the vicinity of $T_c$ but below $T_c$,

$$< s^2 > = \frac{1 + < s >^2}{1 + (\frac{Tc}{T}) < s >^2} = \frac{1 + 3(T/T_c)^2[1-(T/T_c)]}{1 + 3(T/T_c)[1-(T/T_c)]}$$

5. The canonical partition function for a solid consisting of N-atoms undergoing harmonic oscillation is given by

$$Z_N(V,T) = \exp\{-\frac{u_0(V,N)}{kT}\}\prod_{j=1}^{3N}(\frac{e^{-\hbar w_j/2kT}}{1-e^{-\hbar w_j/kT}})$$

where $u_0$ is the potential energy of the solid when all atoms are at the equilibrium position. Using Debye's approximation and also assuming the volume of the solid is negligible compared with the volume of the container V, show that the heat of sublimation $\Delta H_s$ is at low temperature is given by

$$\Delta H_s = N_g[5kT/2 - (f_0 + 9kq_D/8) - 3p^4kT^4/(5q_D^3)],$$

where $N_g$ is the number of gas molecules, and $f_0 = (\frac{\partial u_0}{\partial N})_{V,T}$, $q_D$ is the Debye temperature

6. Show that the electric polarization *P* of an ideal gas consisting of *N* diatomic

molecules having a constant electric dipole moment $m$ is given by

$$P = \frac{N}{V} m \left\{ \coth\left( \frac{mE}{kT} \right) - \frac{kT}{mE} \right\},$$

where $V$ is the volume of the gas and $E$ is the external electric field. Prove that if $|mE| <<< kT$, the dielectric constant of the gas is given by

$$e = 1 + 4p \frac{N}{V} \frac{m^2}{kT}$$

(The induced polarization in the molecules is disregarded, and the electric field acting on the molecules is assumed to be equal to the external field $E$.)

7. Show that the energy fluctuation in a canonical distribution is given by

$$\overline{(E - \bar{E})^2} = kT^2 C_v$$

where $T$ is the absolute temperature and $C_v$ is the heat capacity at constant volume. Prove the following relation in a similar manner:

$$\overline{(E - \bar{E})^3} = k^2 \left\{ T^4 \left( \frac{\partial C_v}{\partial T} \right)_v + 2T^3 C_v \right\}.$$

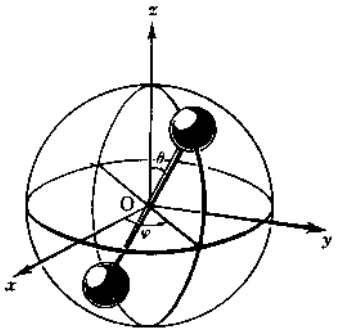
Show that, in particular, for an ideal gas consisting of $N$ monatomic molecules ( disregard the internal structure) these equations can be reduced to

$$\frac{\overline{(E - \bar{E})^2}}{(\bar{E})^2} = \frac{2}{3N} \quad \text{and} \quad \frac{\overline{(E - \bar{E})^3}}{(\bar{E})^3} = \frac{8}{9N^2}$$

8. An evacuated box of volume $V$ is in contact with a heat bath at $\boldsymbol{T}$. Show that the pressure exerted on the vessel wall by thermal radiation prevailing in this empty box is equal to $\frac{1}{3}$ of the energy density $u$ of thermal radiation.
9. Consider equilibrium between a solid and a vapor made up of monatomic molecules. It is assumed that the energy ε is required per atom for transforming the solid into separate atoms. For simplicity, take the Einstein model for the vibration of atoms in the solid, i.e. assume that each atom is represented by a three-dimensional harmonic oscillator performing vibration with a frequency ω about its equilibrium position independently of others. Evaluate the vapor pressure as a function of temperature.
10. Two rigid dipoles are in thermal equilibrium, with the distance between their centers equal to $R$. Calculate the mean force acting between these dipoles. Examine this case at high temperatures.

11. The Hamiltonian of an electron in a magnetic field $\boldsymbol{H}$ is given by $H = -m_B s.H$, where $s$ is Paul's spin operator and $m_B$ stands for the Bohr magneton. Evaluate (i) the density matrix in the diagonalized representation of $s_z$, (ii) the density matrix in the diagonalized representation of $s_x$, and (iii) the average values of $s_z$ in these representations the z-axis being taken along the field direction.

16. The rotational motion of a diatomic molecule is specified by two angular variables $q, j$ and the corresponding canonical conjugate momenta $P_q, P_j$.




Assuming the form of the kinetic energy of the rotational motion to be

$$e_{rot} = \frac{1}{21} p_q^2 + \frac{1}{2I \sin^2 q} P_q^2,$$

Derive the classical formula for the rotational partition function

$$r(T) = \frac{2IKT}{\hbar^2}$$

and calculate the corresponding entropy and specific heat.

12. The rate of ortho-para conversion of hydrogen molecules is so slow that ortho-hydrogen and para-hydrogen can be separated as though they are different kinds of gases. Calculate the specific heat at low temperatures and show that para-hydrogen gas has the larger specific heat.

13. We consider a two-component, two-phase liquid-vapor system. We assume that phase 1, the liquid, and phase 2, the vapor , are ideal.

(a) Show

$$\left(\frac{\partial T}{\partial x_2}\right)_p = \left(\frac{x_2 - y_2}{x_1 x_2}\right) \frac{RT^2}{y_1 \Delta h_1 + y_2 \Delta h_2}$$

and

$$\left(\frac{\partial T}{\partial y_2}\right)_p = \left(\frac{x_2 - y_2}{y_1 y_2}\right)\frac{RT^2}{x_1\Delta h_1 + x_2\Delta h_2}$$

where $x_i$ and $y_i$ are the mole fractions of component i (i=1, 2) in phase 1 and phase 2 , respectively.

(b) From above show that at constant p

$$\frac{\partial \ln\left(\frac{y_2}{x_2}\right)}{\partial\left(\frac{1}{RT}\right)} = -\Delta h_2 \qquad \text{and} \qquad \frac{\partial \ln\left(\frac{y_1}{x_1}\right)}{\partial\left(\frac{1}{RT}\right)} = -\Delta h_2$$

(c) Assuming that $\Delta h_1$ and $\Delta h_2$ are independent of temperature, then show

$$\frac{y_2}{x_2} = \exp\left[\frac{\Delta h_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)\right]$$

and

$$\frac{y_1}{x_1} = \exp\left[\frac{\Delta h_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

where $T_1$ and $T_2$ are the boiling point of pure liquids component 1 and component 2, respectively.

Hint: The chemical potential of component i in an ideal solution (liquid) is

$$m_i = m_i^0 + RT \ln p_i \ , \quad p_i = p_i^0 x_i$$

$p_i^0$ is the vapor pressure of pure liquid i .

14. It can be shown that due to fluctuations the probability density for a system having energy E but its temperature and pressure deviated from equilibrium values by $\Delta T$ and $\Delta P$ is given by

$$P_E(\Delta T, \Delta P) = A\exp\left\{-\frac{1}{2kT}\left[\frac{C_p}{T}(\Delta T)^2 - 2a_p V(\Delta T \Delta P) + c_T V(\Delta P)^2\right]\right\}$$

where $C_p$, $a_p$ and $c_T$ are the heat capacity at constant p, thermal expansion coefficient, and isothermal compressibility, respectively.

(d) Show that in order for $P_E$ to be a normalized probability density, A must be equal to $\frac{(Vc_T C_v / T)^{1/2}}{2pkT}$

(e) From the above, find the average values of $(\Delta T)^2$, $(\Delta T \Delta P)$, and $(\Delta P)^2$.

15. The free energy density of a system that undergoes phase transition at Tc is given by

$$f = f_0 + \frac{1}{3}Ah^2 + \frac{1}{9}Ch^4$$

where $h$ is the order parameter. Assume $A=A_0(T-Tc)$ for $T>Tc$ and $A=A_0(Tc-T)$ for $T<Tc$.

(a) find the entropy difference between the high temperature phase ( where $h$ =0 ) and the low temperature phase ( where $h$ is finite) at Tc

(b) Find the heat capacity difference between the two phase at Tc.

(c) If the system is subject to an external force f that couples to the order parameter. Find the susceptibility difference above and below Tc.

16. Assume that the Gibbs free energy of mixing for a binary system with $n_1$ moles of component 1 and $n_2$ moles of component 2 at temperature T and pressure P is given by

$$\Delta G_m = n_1 RT \ln x_1 + n_2 RT \ln x_2 + a(n_1 + n_2)x_1 x_2$$

a. Drive the expressions for chemical potentials $m_1$ and $m_2$

b. Show that the solution is homogeneous (i.e. it cannot be phase separated) if $\frac{2RT}{a} > 1$, and the system is heterogeneous if $\frac{2RT}{a} < 1$

17. An electron in a magnetic field H has an energy $\pm m_B H$ according to whether the spin magnetic moment is parallel or anti-parallel to the field, $H$ .
Calculate the spin paramagnetic susceptibility of a system of free electrons at 0 K.

18. Show that the spin paramagnetic susceptibility of a system of electrons at arbitrary temperature is given by

$$c = 2m_B^2 \int^{\infty} D'(e) f(e) de$$

where D is the density of states for one electron per unit volume without the spin degeneracy. Derive the susceptibility at low temperature where the degeneracy is very strong.

19. Show that a two-dimensional ideal Bose gas does not exhibit a Bose-Einstein condensation.

20. Consider an ideal Bose gas composed of particles, which have internal degrees of freedom. It is assumed for simplicity that only the first excited level $e_1$ of those internal levels has to be taken into account besides the ground state level $e_0 = 0$ . Determine the Bose-Einstein condensation temperature of this gas as a function of the energy $e_1$ .

21. The canonical partition function for a solid consisting of N-atoms undergoing harmonic oscillation is given by

$$Z_N(V,T) = \exp\{-\frac{u_0(V,N)}{kT}\}\prod_{j=1}^{3N}(\frac{e^{-\hbar w_j/2kT}}{1-e^{-\hbar w_j/kT}})$$

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where $N_g$ is the number of gas molecules, and $f_0 = (\frac{\partial u_0}{\partial N})_{V,T}$, $q_D$ is the Debye temperature

22. A two dimensional solid at temperature T has $N_s$ lattice sites. Assume that there are $N_a$ atoms adsorbed on the surface, so that each lattice site can either have zero or one adsorbed atom. An adsorbed atom has energy E=-$e$, where $e$>0. Assume that the adsorbed atoms do not interact with each other; both $N_a$ and $N_s$ are very large but $N_a << N_s$.

a) Find the chemical potential of the adsorbed atoms as a function of T, $e$, and $N_a/N_s$.

b) If the surface is in equilibrium with an ideal gas of similar atoms at the same temperature having a density ρ, calculate the ratio $N_a/N_s$ as a function of pressure.

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where $E(e, B) = \frac{1}{2} ne < s > + mB$.

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c) For $B$=0, show that for T in the vicinity of $T_c$ but below $T_c$,

$$< s^2 > = \frac{1 + < s >^2}{1 + (\frac{Tc}{T}) < s >^2} = \frac{1 + 3(T / T_c)^2 [1 - (T / T_c)]}{1 + 3(T / T_c)[1 - (T / T_c)]}$$

24. In relativistic mechanics, the energy of a free particle is equal to $e = c\sqrt{m^2 c^2 + p^2}$ . Here *c* and *p* are the velocity of light and the particle's linear momentum, respectively. For an extreme relativistic particle (i.e. for an extremely large energy particle), we may put $e = cp$ .
Consider a system of N such high-energy particles that do not have internal degrees of freedom nor do they interact with each other. If the system is at equilibrium with temperature T, use Boltzmann statistics, find the Helmholtz free energy *A*, internal energy *U*, entropy *S*, Gibbs free energy *G*, and enthalpy *H*. Comment on the difference and similarity in the thermodynamic properties between this high energy ideal gas and that of a classical non-relativistic ideal gas.

25. Electrons are fermions with spin quantum number equal to 1/2 and –1/2. Thus, in the presence of a magnetic field, depending on whether the spin magnetic moment is parallel or anti-parallel to the field, the spin dipole moment of an electron is equal to $m_e$ or $-m_e$. Including the effect of the magnetic filed, one

finds the grandpartition function of the electron as

$$\Xi(b, H, m) = \prod_k \prod_{s_k = \pm 1} \{1 + e^{-b(e_k - m + m_e s_k H)}\}$$

a) Using the Gibbs-Duhem equation and the grandpartition function

$$-SdT + VdP - MdH = \overline{N}dm$$

where M is the total magnetic moments; show that the magnetization is given by

$$m = \frac{M}{V} = \frac{kT}{V}\left(\frac{\partial \ln \Xi}{\partial H}\right)_{T,V,m}$$

$$= \frac{m_e}{V}\sum_k \left\{\frac{1}{e^{b(e_k + m_e H - m)}} - \frac{1}{e^{b(e_k - m_e H - m)}}\right\} = -\left(\frac{m_c^{\ 2}}{V}\right)\int_0^\infty \left\{\frac{\partial W(e)}{\partial e}\right\} f(e)de$$

Here we have assumed that $m_e H$ is much less than μ. $W(e)$ is the density of states given by $2pV\left(\frac{2m}{h^2}\right)^{3/2} e^{1/2}$, and $f(e)$ is the Fermi-distribution function given by $f(e) = \frac{1}{e^{b(e-m)} + 1}$.

b) Show at 0 K the susceptibility $c_0$ is given by: $c_0 = -\frac{m_e^2}{V} W(m_0)$

where $m_0$ is the Fermi-energy.

c) At high temperature such that to the second order in density, show that

$$c = -(m_e^2 r / kT)\left(1 - \frac{1}{2^{3/2}} r\Lambda^3 + ...\right)$$

where $r = \overline{N}/V$ is the number density and $\Lambda = \left[\frac{\hbar^2}{2pmkT}\right]^{1/2}$ is the thermal de-Broglie wavelength