The following problems
from the 1995, 1996 and 1997
Written Ph.D. Qualifying Exams
are provided without solutions.

They can be used
as a study aid
to create practice exams, etc.

1997

STATISTICAL MECHANICS

1. A toy model for DNA consists of a zipper-like structure with N pairs of 'teeth' (each pair of teeth corresponding to a base-pair). The bond between the partners in each base-pair can either be closed or open. If a bond is open, the energy associated with it is ϵ, while if a bond is closed the energy associated with it is zero. The zipper can be opened from both ends simultaneously, but it cannot be opened from the center. Thus if the bond i is broken, either all the bonds $1 \ldots i-1$ or all the bonds $i+1 \ldots N$ (or both) must be open. The system is in equilibrium at temperature T. Calculate the Helmholtz free energy and the expectation value for the number of open bonds for $N\epsilon >> k_B T$.

1997

STATISTICAL MECHANICS

2. Consider the spin-1/2 Ising model in a transverse field, whose Hamiltonian is given by

$$\mathcal{H} = -\sum_{\langle i,j\rangle} J_{ij}\sigma_i^z\sigma_j^z - h\sum_i \sigma_i^x ,$$

where the σ_i^α are Pauli spin matrices, and h is the transverse field. Assume that the interactions, J_{ij} act between nearest neighbors and are of strength J. Let the number of nearest neighbors of a given site be z. For sufficiently high temperature or transverse field the system will be in a paramagnetic state and otherwise it will be in a ferromagnetic state.

a.) Find a self-consistent expression for the magnetization $m \equiv \langle\sigma_i^z\rangle$ in the ferromagnetic region, in the mean field approximation. Note: The mean field is a vector.

b.) Find an implicit expression for the critical line separating the paramagnetic and ferromagnetic phases. (Assume that the transition is continuous so this is the line where $m \to 0$). What is the value of the critical temperature when $h = 0$, (i.e. the regular Ising model), and what is the critical value of h at $T = 0$?

c.) Give a rough sketch of the phase diagram, the $h-T$ plane, showing the paramagnetic region, where $m = 0$, and the ferromagnetic region, where $m \neq 0$.

d.) Show that $\langle\sigma_i^x\rangle$ is independent of T below T_c, within this approximation.

1997

STATISTICAL MECHANICS

3. A classical gas of N particles is in thermal equilibrium at temperature T. The particles interact with each other via a potential $U(r)$. Each particle has a mass m.

(a) What is the probability distribution for the x component of the velocity of a particle, $P(v_x)$?

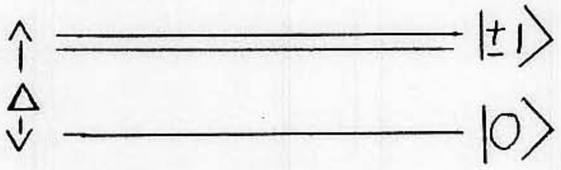
(b) At any given time, one particle has the largest value of $|v_x|$. Call this value $v_{x,max}$. Write down the expression for the probability distribution of $v_{x,max}$. Your answer can involve integrals.

(c) In the limit of very large N, calculate the average value of $v_{x,max}$, to leading order in $\log N$.

1996

STATISTICAL MECHANICS

1. A spin-1 ion in a crystal has its energy levels split by its environment such that the $|S_z = 0>$ state is an energy Δ below the $|S_z = \pm 1>$ states (see sketch).



A magnetic field h in the x direction is added which gives a term in the Hamiltonian

$$-hS_x$$

a) This gives rise to a non-zero expectation value $< S_x >$. Find the susceptibility, χ, as a function of T, where χ is defined by

$$< S_x >= h\chi \quad (h \to 0)$$

I suggest you proceed as follows:
(i) Show that $\chi = \frac{\partial^2 f}{-\partial h^2}|_{h=0}$ where f is the free energy of the ion.
(ii) Calculate the change in the energy of the levels to 2nd order in h.
(iii) Hence, calculate the free energy up to 2nd order in h and so determine χ.

b) Show that for $k_B T \gg \Delta$, $\chi \propto \frac{1}{T}$ (Curie law), and that $\chi \to$ const. as $T \to 0$.

n.b. The non-zero matrix elements of S_x are:

$$\langle 0|S_x| \pm 1\rangle = \langle \pm 1|S_x|0\rangle = \frac{1}{\sqrt{2}}$$

in units where Planck's constant, $\hbar$, is unity.

1996

STATISTICAL MECHANICS

2. One place where it gets very hot is the early universe. Phase transitions probably occurred at various times. We study one.

a. Write down the free energy for a free, non-relativistic spin one particle (Bose-Einstein statistics) as an integral over momenta. Don't evaluate the integral.

b. Write down the free energy for a free, *relativistic* spin one particle by making the replacement

$$\frac{p^2}{2m} \to \sqrt{p^2 + m^2}$$

(use units with $c = 1$). How does this result compare to that for a free photon gas?

c. Assuming that $T \gg m$, expand the integrand in the expression and write out the term which is first order in m^2. In order to get rid of parts which are independent of temperature, subtract from the integrand its value at $T = 0$, and then do the resulting integral.

d. At zero temperature, the ground state energy in the standard model has the form

$$-am^2 + bm^4.$$

Add the temperature dependent contribution you found in part *d*. In the standard model, the mass is dynamical, which means that it will always sit at the minimum value of the free energy. Does this system undergo a phase transition? What is the order?

(Hint:) You need to remember that the free energy for a system of bosons is

$$F = -T \sum_n \ln(1 - e^{-\beta E_n}).$$

You will need the integral

$$\int_0^\infty \frac{x^{n-1}}{e^x - 1} = \Gamma(n)\zeta(n) \quad n > 1$$

1996

STATISTICAL MECHANICS

3. Statistical Mechanics of a Lock. Consider a combination lock with N digits. Each digit takes on the values $0 \ldots 9$. If the correct combination is found, the lock opens and the energy is $-N\epsilon < 0$. Otherwise the energy of the lock is 0. The lock is kept at a temperature T.

(a) Calculate the partition function $Z(T)$, and the free energy.

(b) Calculate the energy, entropy and free energy per digit in the limit of large N. Calculate the specific heat.

(c) The digits are simultaneously flipped randomly with a frequency of ω. Estimate the average time it takes to find the correct combination.

1995

STATISTICAL MECHANICS

1. Consider a (fictional!) one-dimensional non-interacting gas of N particles in a container of length L with the Hamiltonian

$$\mathcal{H} = \sum_j \epsilon(p_j)$$

where the single particle energy $\epsilon(p)$ behaves as $\epsilon(p) \approx p^2$ for small p and $\epsilon(p) \approx \alpha \ln|p| + \gamma \ln\ln|p|$ for large $|p|$.

a) Show that the canonical partition function cannot be defined for $T > T_c$, and find T_c.

b) How does the mean energy per particle diverge as $T \to T_c$ for (i) $\gamma = 0$ and (ii) $\gamma = 3\alpha$.

c) For $\gamma = 3\alpha$, what happens if u, the energy per particle, is large, and the gas is isolated from its surroundings?

1995

STATISTICAL MECHANICS

2. Colloidal spherical particles of radius a and mass M dispersed in a solvent are seen to undergo Brownian motion. The cause is a *fluctuating force*, $F(t)$ that arises from collisions with the solvent molecules. The solvent has a viscosity η, and the system is at a temperature T. The equation of motion of a particle is

$$M\frac{d^2x}{dt^2} + 6\pi\eta a\frac{dx}{dt} = F(t).$$

The average over time of $F(t)$ is zero, and the force at different times is uncorrelated: $\langle F(t)F(t')\rangle \propto \delta(t-t')$, where $\langle\ \rangle$ denote an average over different realizations of $F(t)$.

a) Show that a measurement of the mean square displacement, $\langle \Delta x^2 \rangle$, as a function of time can be used to determine Boltzmann's constant k_B.

b) The system (the solvent and the colloidal particles) is confined between two parallel horizontal plates, with vertical coordinates $z = \pm L$. Due to boundary effects from the plates, the viscosity η felt by a colloidal particle now depends on its height. If $\eta(z) = \eta_0/(1 - z^2/L^2)$, obtain an expression for the mean square horizontal displacement as a function of time, for long times, assuming $a << L$. (Do not forget gravity.) *Hint: For long times, the particle distribution in the z direction comes to thermal equilibrium, calcluate this distribution first. From part (a) we know the diffusion coefficient for the particle in a particular plane. Put these facts together.*

1995

STATISTICAL MECHANICS

3. Consider an Ising antiferromagnet on a square lattice where $S_i, S_j = \pm 1$ and S_i and S_j are the spins on the two sublattices. The exchange interaction is between nearest neighbors only. A uniform field H is applied along the spin ordering direction of one sublattice.

a) Write the Hamiltonian for this system.

b) Write an approximate Hamiltonian in the mean field approximation, where each spin sees only the average behavior of its neighbors. Use this approximation for the remaining calculations.

c) Calculate $< S_i >$. Your answer may be expressed in terms of $< S_j >$.

d) Calculate $< S_j >$ in a similar way.

e) For $H = 0$, calculate the transition temperature T_c.

f) Calculate the susceptibility near T_c.

g) Show that the staggered magnetization $M_s =< S_i > - < S_j >$ goes to zero at T_c to first order in H.

h) For $H = 0$, show that the staggered magnetism near T_c has the behaviour $M_s \sim (\frac{T-T_c}{T_c})^\beta$, and calculate β.

1998

Statistical Mechanics
(do 2 out of 3 problems)

Please do **EACH** problem you attempt on a **SEPARATE** paper.
Put your name on each paper.

STATISTICAL MECHANICS

1. Consider a classical pendulum, weakly coupled to a heat bath, near the surface of the earth, consisting of a mass m on a massless, rigid rod of length L. The mass swings freely in one plane with the angle θ defined as shown in the figure. Although you should check that the solutions that you obtain for calculations below agree with your expectations, you must show your calculations for credit.

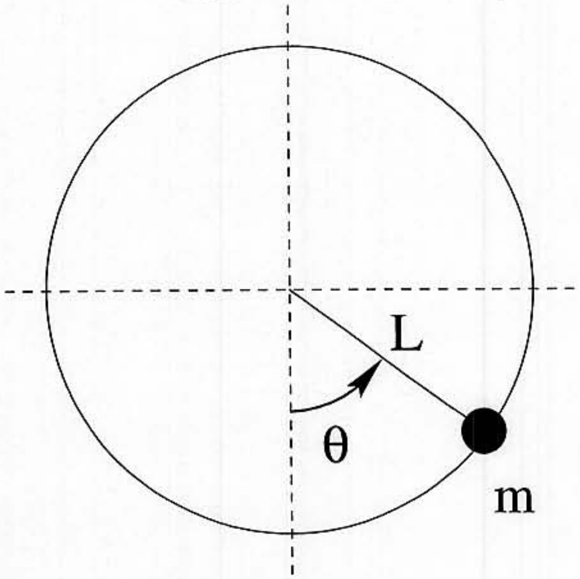
a. Write an expression for the average height of the mass as a function of the temperature T. Although your answer should be expressed in a simple form, you do not need to solve the integral.

b. Calculate from this expression the limiting value of the average height as $T \to \infty$ (you must show your work).

c. Calculate the average height as $T \to 0$. Your answer must include the leading T dependence.

d. Repeat parts a, b and c for the average energy.

e. Sketch the heat capacity for this system.



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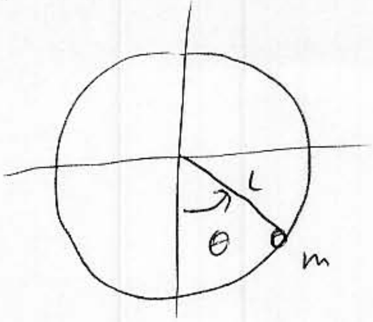

$$h = -L\cos\theta$$

$$E = \tfrac{1}{2} m L^2 \dot{\theta}^2 - mgL\cos\theta$$

a) $$\langle h\rangle = \frac{-L\int_0^{\pi} \cos\theta \, e^{-(\frac{1}{2} m L^2 \dot{\theta}^2 - Lmg\cos\theta)\beta} \, d\dot{\theta}\, d\theta}{\int_0^{\pi} e^{-(\frac{1}{2} m L^2 \dot{\theta}^2 - Lmg\cos\theta)\beta} \, d\dot{\theta}\, d\theta}$$

$$\langle h\rangle = -\frac{L\int_0^{\pi} \cos\theta \, e^{mgL\beta\cos\theta}\, d\theta}{\int_0^{\pi} e^{mgL\beta\cos\theta}\, d\theta}$$

b) for $\beta \to 0$, $T \to \infty$

$$\langle h\rangle \approx \frac{-L\int_0^{\pi}\cos\theta\, d\theta}{\int_0^{\pi} d\theta} = 0$$

c) for $\beta \to \infty$, $T \to 0$

$$E \simeq \tfrac{1}{2} m L^2 \dot{\theta}^2 - mgL + \tfrac{1}{2} mgL\theta^2$$

$$h \simeq -L + \tfrac{1}{2} L\theta^2$$

$$\langle \theta^2\rangle = \frac{\int_0^{\infty} \theta^2 e^{-\frac{1}{2} mgL\beta\theta^2}\, d\theta}{\int_0^{\infty} e^{-\frac{1}{2} mgL\beta\theta^2}\, d\theta} = \frac{kT}{\cancel{2}\, mgL}$$

$$\langle h\rangle \simeq -L + \frac{1}{2}\frac{kT}{mg}$$

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d) $\langle \dot\theta^2 \rangle = \dfrac{\int_0^\infty \dot\theta \, e^{-\frac{1}{2} m L^2 \dot\theta^2 \beta} \, d\dot\theta}{\int_0^\infty e^{-\frac{1}{2} m L^2 \dot\theta^2 \beta} \, d\dot\theta} = \dfrac{kT}{mL^2}$

$$E = \tfrac{1}{2} m L^2 \dot\theta^2 + mgh$$

$$\langle E \rangle = \tfrac{1}{2} kT - mgL \frac{\int_0^\pi \cos e^{mgL\beta\cos\theta} d\theta}{\int_0^\pi e^{mgL\beta\cos\theta} d\theta}$$

for $\beta \to 0$, $T \to \infty$

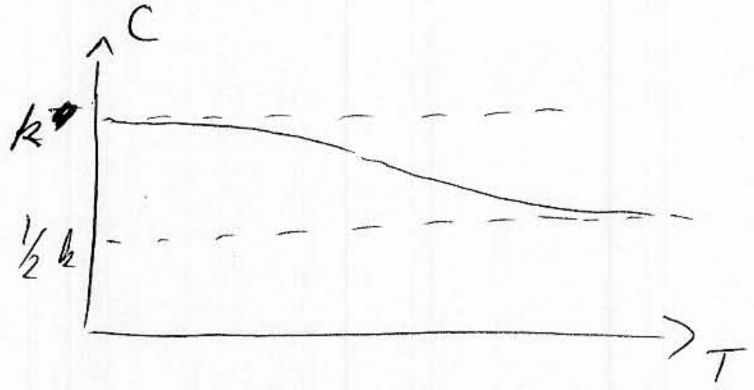
$$\langle E \rangle \simeq \tfrac{1}{2} kT$$

for $\beta \to \infty$, $T \to 0$

$$\langle E \rangle = \tfrac{1}{2} kT - mgL + \tfrac{1}{2} kT$$

$$\langle E \rangle = kT - mgL$$

e)



STATISTICAL MECHANICS

2. A one dimensional system consists of a point mass m attached to a linear spring with spring coefficient k. The other end of the spring is tethered to a wall which is completely impenetrable. Thus the equilibrium position of the spring is at the wall.

a. First consider the system to be classical and calculate the average energy as a function of temperature.

b. Now consider the system to be quantum mechanical and calculate the average energy as a function of temperature.

c. Show that your answer in part (b) goes to your answer in part (a) in the limit of high temperature. Evaluate your answer in part (b) at zero temperature.

SOLUTION Stat Mech #2 1998

(a) The potential energy is $V(x) = V_0(x) + W(x)$, where $V_0 = \frac{1}{2}kx^2$ is the potential of a linear spring, and $W(x)$ represents the potential of the wall which is infinite for $X < 0$ and zero otherwise. The average energy is the sum of the kinetic and potential energy. By the equipartition theorem, the kinetic energy is $K_BT/2$. The average of the potential energy is

$$\frac{\int_0^\infty e^{-\beta V_0(x)} V_0(x) dx}{\int_0^\infty e^{-\beta V_0(x)} dx}$$

By symmetry we can change the limits so as to go from $-\infty$ to ∞. This is identical to the average potential energy of a spring without a wall, which by the equipartition theorem is $k_BT/2$. Thus the sum of the kinetic and potential energies yields k_BT.

(b) The quantum problem with a wall is like the problem without a wall except that the boundary condition at zero is different. We require that the wave function at the wall is zero. Without the wall, the energy is $E_n = \hbar\omega_0(n + \frac{1}{2})$. $\omega_0 = \sqrt{k/m}$ is the oscillation frequency. With the wall, the even n solutions are not allowed since they violate the boundary condition at zero. However the odd n solutions are allowed. Therefore

$$E_n = \hbar\omega_0(\frac{1}{2} + 1 + 2n).$$

for $n = 0, 1, 2, \ldots$. This can be rewritten as

$$E_n = \hbar\omega_2 n + E_0.$$

where $\omega_2 = 2\omega_0 = 2\sqrt{k/m}$, and $E_0 = \frac{3}{2}\omega_0$. The average energy

$$\langle E\rangle = E_0 + \hbar\omega_2\langle n\rangle$$

The term $\langle n\rangle$ is identical to the average occupation of bosons at energy $\hbar\omega_2$ (with zero chemical potential). This is the Bose-Einstein distribution

$$\langle n\rangle = \frac{1}{e^{\beta\hbar\omega_2} - 1}$$

Therefore

$$\langle E\rangle = E_0 + \frac{\hbar\omega_2}{e^{\beta\hbar\omega_2} - 1}$$

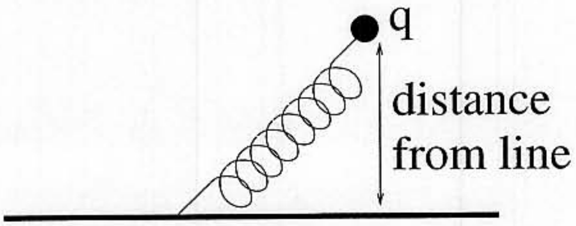
(c) At high temperatures, $\beta \to 0$ so that

$$e^{\beta\hbar\omega_2} - 1 \approx \beta\hbar\omega_2$$

Substituting this into the answer for (b) and ignoring the zero point energy term, which is negligible, we obtain $\langle E\rangle \to k_BT$ as $k_BT \to \infty$. When $T = 0$ we have the zero point energy $E_0 = \frac{3}{2}\omega_0$.

STATISTICAL MECHANICS

3. Consider an infinite line charge with charge per unit length λ, which can either be positive or negative. One end of a massless linear spring is attached to it, and the other side has a charge q and mass m. Call the spring constant k, and treat this system classically at finite temperature T.



a. Write down the partition function for this system.

b. Calculate the average distance between the charge and the line as a function of T and λ.

c. Find the region in the λ-T plane where this average value is zero.

SOLUTION Stat Mech #3 1998

(a) The potential energy of the spring is $U_{sp}(\mathbf{r}) = \frac{1}{2}kr^2$. The potential energy of the line charge can be calculated from the electric field which in turn can be obtained from Gauss's law: $2\pi rE = \lambda/\epsilon_0$ (SI units). Therefore $E = \lambda/2\pi\epsilon_0 r$. Since $\mathbf{E} = -\nabla V$ The electric potential energy is

$$U_{el} = qV = -\frac{q\lambda}{2\pi\epsilon_0}\ln r.$$

Adding these two energies together

$$Z = \int_0^\infty e^{-(\frac{1}{2}k(r^2+z^2)-\frac{q\lambda}{2\pi\epsilon_0}\ln r)/T}2\pi r dr dz \int e^{-(\frac{1}{2}m(v_x^2+v_y^2+v_z^2)/T} dv_x dv_y dv_z$$

(b) The average value of r is

$$\langle r\rangle = \frac{\int e^{-H/T} r 2\pi r dr dz dv_x dv_y dv_z}{\int e^{-H/T} 2\pi r dr dz dv_x dv_y dv_z}$$

The velocities and z integrals cancel leaving

$$\langle r\rangle = \frac{\int_0^\infty e^{-(\frac{1}{2}k(r^2+z^2)-\frac{q\lambda}{2\pi\epsilon_0}\ln r)/T} r^2 dr}{\int_0^\infty e^{-(\frac{1}{2}k(r^2+z^2)-\frac{q\lambda}{2\pi\epsilon_0}\ln r)/T} r dr}$$

Let $u \equiv \frac{1}{2T}kr^2$ and define $K \equiv \frac{q\lambda}{2\pi\epsilon_0 T}$. Then $rdr = \frac{1}{2}d(r^2) = \frac{T}{k}du$. Simplifying,

$$\langle r\rangle = \sqrt{\frac{2T}{k}}\frac{\int_0^\infty e^{-(u-K\ln r)}\sqrt{u}du}{\int_0^\infty e^{-(u-K\ln r)}du}$$

which can be expressed as

$$\frac{\sqrt{\frac{2T}{k}}\int_0^\infty e^{-(u-\frac{K}{2}\ln u)}\sqrt{u}du}{\int_0^\infty e^{-(u-\frac{K}{2}\ln u)}du} = \sqrt{\frac{2T}{k}}\frac{\int_0^\infty e^{-u}u^{\frac{(K+1)}{2}}}{\int_0^\infty e^{-u}u^{\frac{K}{2}}}$$

This can be written in terms of Gamma functions

$$\sqrt{\frac{2T}{k}}\frac{\Gamma(\frac{K}{2}+\frac{3}{2})}{\Gamma(\frac{K}{2}+1)}$$

(c) For sufficiently strong attractive forces, the denominator diverges. The divergence occurs when $u^{K/2}$ diverges faster than u^{-1}, or when $K < -2$. Therefore the region in parameter-space where the the average is zero is

$$\frac{q\lambda}{2\pi\epsilon_0 T} < -2$$

1999

Statistical Mechanics
(do 2 out of 3 problems)

Please do **EACH** problem you attempt on a **SEPARATE** paper.
Put your name on each paper.

STATISTICAL MECHANICS - 1

1. Consider an infinite one-dimensional chain of ferromagnetic Ising spins. Each spin has the value $S = \pm 1$ and interacts only with its immediate neighbors with interaction strength $J > 0$ and the Hamiltonian $H = -J \sum_{<ij>} S_i S_j$.

a. Find the exact partition function of this system.

b. Find the energy of this system as a function of temperature and sketch the result.

c. Find the specific heat of this system as a function of temperature and sketch the result.

d. Does this system have long range order at finite temperature? How do you know this from your solution?

SM#1(1)

Qual Problem #1

$S_i = \pm 1$ $\qquad \mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j$

nearest neighbors

$$Z = \sum_{\substack{\text{all} \\ \text{possible} \\ \text{spin} \\ \text{config}}} e^{J\beta \sum_{\langle ij \rangle} S_i S_j}$$

enumerate possibilities

$\cdots + S_1 S_2 + S_2 S_3 + \cdots$ $\qquad$ each bond acts like spin

11	11	1 1
1 -1	-11	-1 -1
-11	11	-1 1
-1 -1	-11	1 -1
-1 1	1 -1	-1 -1
-1 -1	-1 -1	1 1
1 1	1 -1	1 -1
1 -1	-1 -1	-1 1

each occurs twice

let $z_1 = e^{J\beta} + e^{-J\beta} = 2\cosh J\beta$

$$Z = 2(2\cosh J\beta)^N = 2(2\cosh J\beta)^N$$

for $N \to \infty$

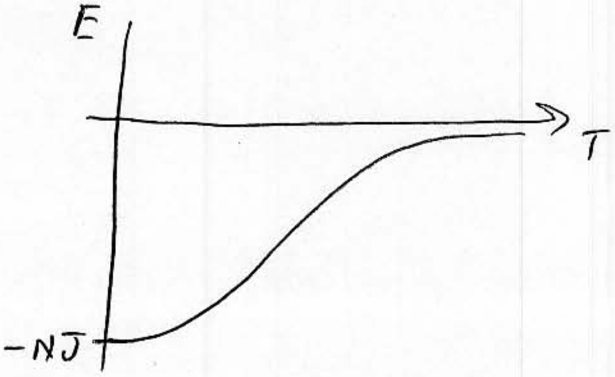
$$Z \approx (2\cosh J\beta)^N = (e^{J\beta} + e^{-J\beta})^N$$

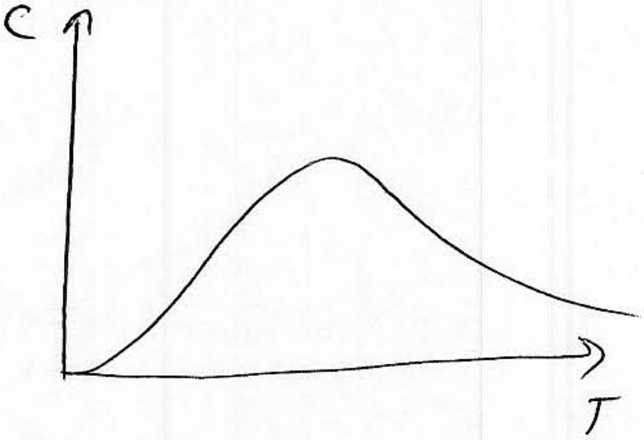
$$E = -\frac{\partial}{\partial\beta}\ln Z = \frac{-JN(e^{J\beta}+e^{-J\beta})^{N-1}(e^{J\beta}-e^{-J\beta})}{(e^{J\beta}+e^{-J\beta})^N}$$

SM#1(2)

$$E = -J_N \tanh(J\beta)$$

$$C = -k\beta^2 \frac{\partial E}{\partial \beta} = Nk\left(\frac{J}{kT}\right)^2 \operatorname{sech}^2\left(\frac{J}{kT}\right)$$





there is no singular behavior, so there is no long range order transition

STATISTICAL MECHANICS - 2

2. Consider a crystal that is formed of two elements, A and B, and has the chemical formula AB_2 [eg, $SrCl_2$]. In this crystal there are N_A A sites and N_B B sites; $N_B = 2\ N_A$. The Gibbs free energy is given by $G = G_0 + U_A n_A + U_B n_B - ST$ for this case.

a. Consider vacancies on both the A and B sites. For this problem assume no other defects are present. The energy to form an A site vacancy is u_A and to form a B site vacancy, u_B. Let there be n_A vacancies on A sites and n_B vacancies on B sites. Write down the Gibbs free energy in terms of the configurational entropy and caculate the equilibrium value of n_A and n_B for a given value of temperature T. What is the ratio n_A/n_B?

b. Next consider only site-antisite disorder in which pairs of atoms are on the opposite site. (Neglect other defects here). Let u_{ex} be the energy to interchange an A and B atom. Let n_b be the number of B atoms on A sites and n_a be the number of A atoms on B sites. ($n_a = n_b = n$). Again use the Gibbs free energy to calculate the equilibrium number of site-antisite defects [ie calculate n] at a temperature T. Assume $n << N_A$ or N_B.

SM#2(1)

Solution.

a) $G = G_0 + u_A n_a + u_B n_b - ST$

$S = k_B \ln W \;;\; W = \frac{N_A!}{(N_A-n_a)!\,n_a!}\,\frac{N_B!}{(N_B-n_b)!\,n_b!}$

use Stirlings approx $\ln N! = n \log N - N$.

$$S = k_B \{ \ln(N_A!N_B!) - \ln(N_A-n_a)! - \ln n_a! - \ln(N_B-n_b)! - \ln n_b! \}$$

Require $\frac{\partial G}{\partial n_a} = \frac{\partial G}{\partial n_b} = 0.$

$$\frac{\partial G}{\partial n_a} = u_A - k_BT \frac{\partial}{\partial n_a}\{-(N_A-n_a)\ln(N_A-n_a) + (N_a-n_a) - n_a \ln(n_a) + n_a\}$$

$$0 = u_A - k_BT\left[\ln(N_A-n_a) - \frac{\cancel{N_A-n_a}(-1)}{\cancel{N_A-n_a}} \cancel{-1} - \ln n_a - \cancel{n_a}/n_a + \cancel{1}\right]$$

$-\frac{u_A}{k_BT} = \ln\frac{n_a}{N_A-n_a} \Rightarrow n_a = (N_A-n_a)\,e^{-u_A/kT}$

$n_a = N_A/(1+e^{+u_A/kT})$

n_b is similar

$n_b = (N_B-n_b)\,e^{-u_B/kT}$

$n_b = \frac{N_b}{1+e^{u_B/kT}}$

$$\frac{n_a}{n_b} = \frac{N_A}{N_B}\,\frac{1+e^{u_B/kT}}{1+e^{u_A/kT}}$$

$\frac{N_A}{N_B} = 1/2.$

If $u/kT \gg 1$, $\frac{n_a}{n_b} \simeq 1/2\, e^{(u_B-u_A)/kT}$

Solutions cont'd.

b) Site - antisite.

$$W = \frac{N_A!}{(N_A - n_B)!\, n_B!} \quad \frac{N_B!}{(N_B - n_A)!\, n_A!}$$

with $n_B = n_A \underset{2}{=} n$,

$$W = \frac{N_A!\, N_B!}{(N_A - n)!\, n!\, (N_B - n)!\, n!}$$

$$G = G_0 + U_{ex}\, n - k_BT \ln W.$$

$$\frac{\partial G}{\partial n} = U_{ex} - k_BT \frac{\partial}{\partial n}\left\{ -\ln (N_A - n)!\ 2\ln n! - \ln(N_B - n)! \right\}$$

$$0 = U_{ex} + k_BT \frac{\partial}{\partial n}\left\{ (N_A - n)\ln(N_A - n) - (N_A - n) + 2(n \ln n - n) + (N_B - n)\ln(N_B - n) - (N_B - n) \right\}$$

$$0 = U_{ex} + k_BT \Big[-\ln(N_A - n) - \frac{\cancel{N_A - n}}{\cancel{N_A - n}} \cancel{+1} + 2\ln n + \cancel{2} - \cancel{2}$$

$$-\ln(N_B - n) - \cancel{1} + \cancel{1} \Big]$$

$$-\frac{U_{ex}}{k_BT} = \ln \frac{n^2}{(N_A - n)(N_B - n)}$$

For n small ($n << N_A, N_B$)

$$n^2 \simeq N_A N_B\, e^{-U_{ex}/k_BT}$$

$$n = \sqrt{N_A N_B}\; e^{-\frac{U_{ex}}{2k_BT}} = \sqrt{2}\, N_A\, e^{-\frac{U_{ex}}{2kT}} \quad (N_B = 2N_A).$$

3. If the energy stored in the rotational and vibrational modes is not too large, we may approximate the Hamiltonian of a diatomic molecule by

$$\mathcal{H} = \mathcal{H}_{transl} + \mathcal{H}_{rot} + \mathcal{H}_{vib}$$

neglecting any effect of the rotation on the vibrational modes and the effect of the vibrational distortions on the moment of inertia, I. In a dilute gas, the density of will be low enough so that the translational motion can be treated classically. The energy of rotation is:

$$E_j = \frac{\hbar^2 j(j+1)}{2I}$$

where $j = 0, 1, 2 \ldots$ is the rotational quantum number. The state with quantum number j has degeneracy $2j+1$ (we have, for simplicity, assumed that the two atoms in the diatomic molecule are different). The vibrational degree of freedom may be taken to be that of a simple harmonic oscillator with frequency ω_v.

a. Find a general expression for the energy at temperature T.

b. Determine the energy and specific heat for the following cases:

(i) $\mathrm{T} \ll \theta_r \ll \theta_v$

(ii) $\theta_r \ll T \ll \theta_v$

(iii) $\theta_r \ll \theta_v \ll T$.

where

$$\theta_r \equiv \frac{\hbar^2}{2Ik_B}, \qquad \theta_v \equiv \frac{\hbar\omega_v}{k_B}\ .$$

Hint: The Euler summation formula,

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x)dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \ldots$$

may be useful.

c. Show that the specific heat per molecule is approximately $\frac{3}{2}k_B$, $\frac{5}{2}k_B$, and $\frac{7}{2}k_B$ respectively in the three ranges.

Statistical Mechanics Questions

Solutions

1 (a) The free energy (and hence the energy and specific heat is a sum of three terms

$$f = f_{trans} + f_{vib} + f_{rot}$$

where f is the free energy per molecule. Hence

$$\underset{\substack{\uparrow \\ \text{energy /mol}}}{u = -\frac{\partial}{\partial\beta}(\beta f)}, \qquad \underset{\substack{\uparrow \\ \text{specific heat /mol.}}}{C = \frac{\partial u}{\partial T}} \qquad (u = u_{trans} + u_{vib} + u_{rot},\ \text{etc.}$$

By equipartition the translational part of the energy is

$$u_{trans} = \frac{3}{2} k_B T, \quad \text{so} \quad C_{trans} = \frac{3}{2} k_B \quad \text{in all 3 regions.}$$

For the vibrational part

$$Z_{vib} = e^{-\frac{1}{2}\beta\hbar\omega_v} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega_v} = \frac{e^{-\frac{1}{2}\theta_v/T}}{1 - e^{-\theta_v/T}} = \frac{1}{2\sinh(\theta_v/2T)}$$

$$u_{vib} = -\frac{\partial}{\partial\beta} \ln Z_{vib} \quad \text{so} \quad \frac{u_{vib}}{k_B} = \frac{\theta_v}{2} \coth\left(\frac{\theta_v}{2T}\right)$$

For the rotational part

$$Z_{rot} = \sum_{j=0}^{\infty} (2j+1) e^{-\hbar^2 j(j+1)/(2k_B T I)} = \sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\theta_r/T}$$

$$u_{rot} = -\frac{\partial}{\partial\beta} \ln Z_{rot}.$$

(b) (i) $T \ll \theta_{rot} \ll \theta_{vib}$

$$\frac{u_{vib}}{k_B} = \frac{\theta_v}{2}\left(1 + 2e^{-\theta_v/T} \cdots\right), \quad \therefore C_{vib} \text{ is exponentially small}$$

$$Z_{rot} = 1 + 3e^{-2\theta_r/T}, \quad u_{rot} = 6 k_B \theta_r \, e^{-2\theta_r/T}$$

$\therefore$ u_{rot} and C_{rot} are exponentially small.

$\therefore$ $C = \frac{3}{2} k_B$ (+ exponentially small corrections) per molecule

1 (b)(ii). U_{trans} and U_{vib} are same as in (i).

For the rotational motion, use the Euler formula

$$Z_{rot} = \int_0^\infty dj\,(2j+1)e^{-j(j+1)\theta_r/T} + \frac{1}{2} - \frac{2}{6} + O\left(\frac{\theta_r}{T}\right)$$

$$= \frac{T}{\theta_r} + \overset{\text{const}}{\cancel{}} + O(\theta_r/T)$$

$$U_{rot} = k_B\left(T - \overset{\text{const.}}{\theta_r} + O\left(\tfrac{1}{T}\right)\right) \qquad \underline{C_{rot} = k_B\left[1 + O\left(\theta_r/T\right)^2\right]}$$

Hence $\underline{C = \frac{5}{2}k_B}$.

b(iii) U_{trans} and U_{rot} are the same as in (ii)

$$U_{vib} = \frac{\theta_v k_B}{2}\left[\frac{2T}{\theta_v} + \frac{1}{3}\frac{1}{2}\left(\frac{\theta_v}{2T}\right) + \cdots\right] = k_B\left[T + O\left(\frac{\theta_v}{T}\right)^2\right]$$

$$\therefore \underline{C_{vib} = k_B\left[1 + O\left(\theta_v/T\right)^2\right]}$$

Hence $\underline{C = \frac{7}{2}k_B}$.