

# Statistical Physics



## Second year physics course

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(with thanks to Prof. S. J. Blundell)

## Problem Set 6: Statistical Mechanics

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### Some useful constants

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Boltzmann's constant	$k_B$	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Stefan-Boltzmann constant	$\sigma$	$5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
Avogadro's number	$N_A$	$6.022 \times 10^{23} \text{ mol}^{-1}$
Standard molar volume		$22.414 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$
Molar gas constant	$R$	$8.315 \text{ J mol}^{-1} \text{ K}^{-1}$
1 pascal (Pa)		$1 \text{ N m}^{-2}$
1 standard atmosphere		$1.0132 \times 10^5 \text{ Pa (N m}^{-2}\text{)}$
1 bar (= 1000 mbar)		$10^5 \text{ N m}^{-2}$

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## PROBLEM SET 6: Statistical Mechanics of Simple Systems

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*This Problem Set can be attempted during Weeks 4 and 5 of Hilary Term, with the tutorial or class on this material held at the end of Week 5 or later.*

### Calculation of thermodynamic quantities from the partition function

6.1 Consider an array of  $N$  localised spin- $\frac{1}{2}$  paramagnetic atoms. In the presence of a magnetic field of flux density  $B$ , the two degenerate spin states split by  $\pm\mu_B B$ , where  $\mu_B$  is the Bohr magneton.

- (i) Derive the single-particle partition function for the system.  
(ii) Show that the heat capacity  $C_B$  can be written as

$$C_B = \left( \frac{\partial U}{\partial T} \right)_B = Nk_B \left( \frac{\theta}{T} \right)^2 \frac{e^{\theta/T}}{(e^{\theta/T} + 1)^2}. \quad (1)$$

Show that  $C_B$  has a maximum at a temperature  $T_{\max} = A\mu_B B/k_B$  where  $A$  is a numerical constant. Determine  $A$ , and sketch  $C_B$  as a function of  $\theta/T$ .

(iii) Given that the largest static magnetic field that can easily be produced in the laboratory is of order 10 Tesla, estimate the temperature at which the magnetic heat capacity of such a system will be largest.

6.2 An array of  $N$  1D simple harmonic oscillators is set up with an average energy per oscillator of  $(m + \frac{1}{2})\hbar\omega$ . Show that the entropy per oscillator is given by

$$\frac{S}{Nk_B} = (1 + m) \ln(1 + m) - m \ln m. \quad (2)$$

Comment on the value of the entropy when  $m = 0$ .

6.3 An assembly of  $N$  particles per unit volume, each having angular momentum  $J$ , is placed in a magnetic field. The field splits the level into  $2J + 1$  different energies, given by  $m_J g_J \mu_B B$ , where  $m_J$  runs from  $-J$  to  $+J$ .  $g_J$  is known as the Landé g-factor, which you will presently meet in atomic physics.

(i) Show that the single-particle partition function  $Z_{\text{mag}}$  of the magnetic system can be written as

$$Z_{\text{mag}} = \frac{\sinh[(J + \frac{1}{2})y]}{\sinh(y/2)}. \quad (3)$$

where  $y = g_J \mu_B B/k_B T$ .

(ii) Show that the susceptibility,  $\chi$ , (defined as  $\mu_0 M/B$  as  $B \rightarrow 0$ ) is given by

$$\chi = \frac{\mu_0 N g^2 \mu_B^2 J(J + 1)}{3k_B T}. \quad (4)$$

Prove that this is consistent with the result derived in lectures for a spin- $\frac{1}{2}$  paramagnet. [N.B. In the limit of small  $x$ ,  $\coth x \approx 1/x + x/3$ ]

## Diatomic gases and the equipartition theorem

6.4 Comment on the following values of molar heat capacity at constant pressure  $C_p$  in  $\text{JK}^{-1} \text{mol}^{-1}$ , all measured at 298 K.

Al	24.35	Pb	26.44
Ar	20.79	Ne	20.79
Au	25.42	$\text{N}_2$	29.13
Cu	24.44	$\text{O}_2$	29.36
He	20.79	Ag	25.53
$\text{H}_2$	28.82	Xe	20.79
Fe	25.10	Zn	25.40

[Hint: express them in terms of  $R$ . Which substance is a solid and which is gaseous?]

6.5 Experimental data for the molar heat capacity of  $\text{N}_2$  as a function of temperature are shown in the table below.

$T$ (Kelvin)	170	500	770	1170	1600	2000	2440
$C_V/R$	2.5	2.57	2.76	3.01	3.22	3.31	3.4

(i) Estimate the frequency of vibration of the  $\text{N}_2$  molecule.

(ii) By making a rough estimate of the moment of inertia of the molecule, comment on the possibility of quenching the rotational degrees of freedom and hence reducing the heat capacity of nitrogen to  $3R/2$  per mole.

6.6 Show that for a diatomic molecule at a temperature,  $T$ , such that  $\theta_{\text{rot}} \ll T \ll \theta_{\text{vib}}$ , where  $\theta_{\text{rot}}$  and  $\theta_{\text{vib}}$  are its characteristic temperatures of rotation and vibration respectively, the partition function satisfies  $Z \propto VT^{5/2}$ . Hence show that  $pV^{7/5}$  is a constant along an adiabat.

## Grand canonical ensemble and chemical potential

6.7 *Classical Ideal Gas.*

a) Starting from the grand canonical distribution, prove that the equation of state for a classical ideal gas is  $P = nk_B T$ , where  $n = \bar{N}/V$  is the mean number density.

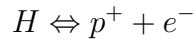
b) Find the chemical potential  $\mu$  as a function of pressure  $P$  and temperature  $T$  for a diatomic classical ideal gas whose rotational levels are excited but vibrational ones are not. The mass of each of the two atoms in the molecule is  $m$ , the separation between them is  $r$ .

6.8 *Rotating Gas.* A cylindrical container of radius  $R$  is filled with ideal gas at temperature  $T$  and rotating around the axis with angular velocity  $\Omega$ . The molecular mass is  $m$ . The mean density of the gas without rotation is  $\bar{n}$ . Assuming the gas is in isothermal equilibrium, what is the gas density at the edge of the cylinder,  $n(R)$ ? Discuss the high and low temperature limits of your result.

6.9 *Particle Number Distribution.* Consider a volume  $V$  of classical ideal gas with mean number density  $n = \bar{N}/V$ , where  $\bar{N}$  is the mean number of particles in this volume. Starting from the grand canonical distribution, show that the probability to find exactly  $N$  particles in this volume is a Poisson distribution (thus, you will have recovered the result you proved in PS-3 by a different method).

### Multispecies systems

6.10 *Ionisation-Recombination Equilibrium.* Consider hydrogen gas at high enough temperature that ionisation and recombination are occurring (i.e., we are dealing with a partially ionised hydrogen plasma). The reaction is



(hydrogen atom becomes a proton + an electron or vice versa). Our goal is to find, as a function of density and temperature (or pressure and temperature), the degree of ionisation  $\chi = n_p/n$ , where  $n_p$  is proton number density,  $n = n_H + n_p$  is total number density of hydrogen, ionised or not, and  $n_H$  is the number density of the un-ionised  $H$  atoms. Note that  $n$  is fixed (conservation of nucleons). Assume overall charge neutrality of the system.

- What is the relation between chemical potentials of the  $H$ ,  $p$  and  $e$  gases if the system is in chemical equilibrium?
- Treating all three species as classical ideal gases, show that in equilibrium

$$\frac{n_e n_p}{n_H} = \left( \frac{m_e k_B T}{2\pi \hbar^2} \right)^{3/2} e^{-R/k_B T},$$

where  $R = 13.6$  eV (1 Rydberg) is the ionisation energy of hydrogen. This formula is known as the Saha Equation.

*Hint.* Remember that you have to include the internal energy levels into the partition function for the hydrogen atom. You may assume that only the ground state energy level  $-R$  matters (i.e., neglect all excited states).

- Hence find the degree of ionisation  $\chi = n_p/n$  as function of  $n$  and  $T$ . Does  $\chi$  go up or down as density is decreased? Why? Consider a cloud of hydrogen with  $n \sim 1 \text{ cm}^{-3}$ . Roughly at what temperature would it be mostly ionised? These are roughly the conditions in the so called “warm” phase of the interstellar medium — the stuff that much of the Galaxy is filled with (although the law of mass action is not thought to be a very good approximation for interstellar medium, because it is not exactly in equilibrium).
- Now find an expression for  $\chi$  as a function of total gas pressure  $p$  and temperature  $T$ .

## Other Ensembles

6.11 *Microcanonical Ensemble Revisited.* Derive the grand canonical distribution starting from the microcanonical distribution (i.e., by considering a small subsystem exchanging particles and energy with a large, otherwise isolated system).

*Hint.* This is a generalisation of the derivation in Lecture Notes 12. If you can't figure it out on your own, you will find the solution in Blundell & Blundell's or Kittel's books.

6.12 (\*) *Pressure Ensemble.* Throughout this course, we have repeatedly discussed systems whose volume is not fixed, but allowed to come to some equilibrium value under pressure. Yet, in both canonical and grand canonical ensembles, we treated volume as an external parameter, not as a quantity only measurable in the mean. In this question, your objective is to construct an ensemble in which the volume is not fixed.

a) Consider a system with (discrete) microstates  $\alpha$  to each of which corresponds some energy  $E_\alpha$  and some volume  $V_\alpha$ . Maximise Gibbs entropy subject to measured mean energy being  $U$  and the mean volume  $\bar{V}$ , whereas the number of particles  $N$  is exactly fixed and find the probabilities  $p_\alpha$ . Show that the (grand) partition function for this ensemble can be defined as

$$\mathcal{Z} = \sum_{\alpha} e^{-\beta E_{\alpha} - \sigma V_{\alpha}},$$

where  $\beta$  and  $\sigma$  are Lagrange multipliers. How are  $\beta$  and  $\sigma$  determined?

b) Show that if we demand that the Gibbs entropy  $S_G$  for those probabilities be equal to  $S/k_B$ , where  $S$  is the thermodynamic entropy, then the Lagrange multiplier arising from the mean-volume constraint is  $\sigma = \beta P = P/k_B T$ , where  $P$  is pressure. Thus, this ensemble describes a system under pressure set by the environment.

c) Prove that  $dU = TdS - Pd\bar{V}$ .

d) Show that  $-k_B T \ln \mathcal{Z} = G$ , where  $G$  is the Gibbs free energy defined in the usual way. How does one calculate the equation of state for this ensemble?

e) Calculate the partition function  $\mathcal{Z}$  for classical monatomic ideal gas in a container of changeable volume but impermeable to particles (e.g., a balloon made of inelastic material). You will find it useful to consider microstates of an ideal gas at fixed volume  $V$  and then sum up over all possible values of  $V$ . This sum (assumed discrete) can be converted to an integral via  $\sum_V = \int_0^\infty dV/\Delta V$ , where  $\Delta V$  is the "quantum of volume." You will also need to use the formula  $\int_0^\infty dx x^N e^{-x} = N!$

f) Calculate  $G$  and find what conditions  $\Delta V$  must satisfy in order for the resulting expression to coincide with the standard formula for the ideal gas (derived in the lectures and Q6.7) and be independent of  $\Delta V$  (assume  $N \gg 1$ ).

g) Show that the equation of state is  $P = nk_B T$ , where  $n = N/\bar{V}$ .