Statistical and Thermal Physics

Second year physics course

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Problem Set 5

Some useful constants

Boltzmann's constant	k_B	$1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Proton rest mass	m_p	$1.6726 \times 10^{-27}\,\mathrm{kg}$
Bohr magneton	μ_B	$9.274 \times 10^{-24}\,\mathrm{JT^{-1}}$
Avogadro's number	N_A	$6.022 \times 10^{23}\,\mathrm{mol^{-1}}$
Standard molar volume		$22.414 \times 10^{-3}\,\mathrm{m^3\,mol^{-1}}$
Molar gas constant	R	$8.315\ \mathrm{J\,mol^{-1}\,K^{-1}}$
1 pascal (Pa)		$1\,\mathrm{N\,m^{-2}}$
1 standard atmosphere		$1.0132 \times 10^{5}\,\mathrm{Pa}\ (\mathrm{N\,m^{-2}})$
1 bar (= 1000 mbar)		$10^{5}\,\mathrm{N\,m^{-2}}$

PROBLEM SET 5: Statistical Mechanics and Thermodynamics of Simple Systems

Problem set 5 can be set partly as vacation work and covered in 2 tutorials (or 1 class and 1 tutorial) held during Weeks 1–2 of Hilary Term

Heat Diffusion Equation

The theory needed for this question was covered in the Mathematical Methods lectures

5.1 One face of a thick uniform layer is subject to a sinusoidal temperature variation of angular frequency ω. Show that damped sinusoidal temperature oscillations propagate into the layer and give an expression for the decay length of the oscillation amplitude.

A cellar is built underground covered by a ceiling which is 3 m thick made of limestone. The outside temperature is subject to daily fluctuations of amplitude 10°C and annual fluctuations of 20°C. Estimate the magnitude of the daily and annual temperature variations within the cellar. Assuming that January is the coldest month of the year, when will the cellar's temperature be at its lowest?

[The thermal conductivity of limestone is $1.6\,\mathrm{Wm^{-1}K^{-1}}$, and the heat capacity of limestone is $2.5 \times 10^6\,\mathrm{JK^{-1}m^{-3}}$.]

Thermodynamics of non p–V systems

5.2 For a stretched rubber band, it is observed experimentally that the tension f is proportional to the temperature T if the length L is held constant. Prove that:

(a) the internal energy U is a function of temperature only;

(b) adiabatic stretching of the band results in an increase in temperature;

(c) the band will contract if warmed while kept under constant tension.

[You may assume that $\left(\frac{\partial L}{\partial f}\right)_T > 0$.]

5.3 A simple microscopic model for rubber and other polymers consists of a chain of links, each of length a, with each link equally likely to be directed to the right or left along the chain. Show that the number of microstates corresponding to a chain of N links of total length L is given by

$$\Omega(L, N) = \frac{2N!}{\left(\frac{N}{2} - \frac{L}{2a}\right)!\left(\frac{N}{2} + \frac{L}{2a}\right)!}.$$

Hence, show that the tension of the system is given by $f = Lk_{\mathrm{B}}T/(Na^2)$ when $L \ll Na$.

[Hint: Show that $\left(\frac{\partial f}{\partial T}\right)_L = -\left(\frac{\partial S}{\partial L}\right)_T$ and integrate assuming $f(T = 0) = 0$.]

5.4 For a fixed surface area, the surface tension of water varies linearly with temperature from $75 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ at 5°C to $70 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ at 35°C. Calculate the surface contributions to the entropy per unit area and the internal energy per unit area at 5°C.
[Ans: $\left(\frac{\partial S}{\partial A}\right)_T = 0.167 \times 10^{-3}\,\mathrm{J\,K^{-1}\,m^{-2}}$, $\left(\frac{\partial U}{\partial A}\right)_T = 121.3 \times 10^{-3}\,\mathrm{J\,m^{-2}}$]

An atomizer produces water droplets of diameter $0.1\,\mu$m. A cloud of droplets at 35° C coalesces to form a single drop of water of mass 1 g. Estimate the temperature of the drop assuming no heat exchange with the surroundings. What is the increase in entropy in this process? (Specific heat capacity of water $c_p = 4,200\,\mathrm{J\,K^{-1}\,kg^{-1}}$.)
[Ans: $\Delta T = 1.73\,\mathrm{K}$, $\Delta S = 13.6 \times 10^{-3}\,\mathrm{J\,K^{-1}}$]

5.5 The magnetization M of a paramagnetic material is given by $M = \chi B/\mu_0$, where B is the magnetic flux density and the susceptibility χ follows Curie's law $\chi = C/T$ with C a constant.

If the heat capacity per unit volume at constant M is $C_M = a/T^2$, show that the heat capacity per unit volume at constant B is

$$C_B = \frac{a}{T^2}\left(1 + \frac{B^2 C}{\mu_0 a}\right).$$

If a sample is initially at temperature T_1 in an applied field of flux density B_1, show that the temperature after adiabatic reduction of the field to zero is

$$T_2 = \frac{T_1}{\left(1 + \frac{B_1^2 C}{\mu_0 a}\right)^{1/2}}.$$

Calculation of thermodynamic quantities from the partition function

5.6 Consider an array of N localised spin-$\frac{1}{2}$ paramagnetic atoms. In the presence of a magnetic field, B, the two degenerate spin states split by $\pm\mu_{\mathrm{B}} B$, where μ_{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

$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = N k_{\mathrm{B}} \left(\frac{\theta}{T}\right)^2 \frac{\mathrm{e}^{\theta/T}}{(\mathrm{e}^{\theta/T} + 1)^2}, \qquad (1)$$

and find the value of the constant θ. Show that C_B has a maximum at a temperature $T_{\max} = A\mu_{\mathrm{B}} B/k_{\mathrm{B}}$ where A is a numerical constant. Determine A.

(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.

(iv) Show that in the limits of high and low temperatures the heat capacity is proportional to $1/T^2$ as $T \to \infty$ and proportional to $\mathrm{e}^{-\theta/T}/T^2$ as $T \to 0$.

5.7 Given that the energy spectrum of a simple harmonic oscillator (SHO) is $E_n = (n+\frac{1}{2})\hbar\omega$, derive an expression for the single-particle partition function. What is the specific heat of an array of N distinguishable SHOs? Find expressions for the high and low temperature limits of C.

5.8 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

$$\frac{S}{Nk_\mathrm{B}} = (1+m)\ln(1+m) - m\ln m. \tag{2}$$

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

5.9 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 $m_J g_J \mu_\mathrm{B} B$, 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_Mag of the magnetic system can be written as

$$Z_\mathrm{Mag} = \frac{\sinh[(J+\frac{1}{2})C]}{\sinh(C/2)}. \tag{3}$$

where $C = g_J \mu_\mathrm{B} B / k_\mathrm{B} T$.

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

$$\chi = \frac{\mu_0 N g^2 \mu_\mathrm{B}^2 J(J+1)}{3k_\mathrm{B}T}. \tag{4}$$

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

(iii) Let us define $Z_\mathrm{SHO}(\hbar\omega)$ to be the partition function of a simple harmonic oscillator with an energy interval $\hbar\omega$ between successive levels. Show that the partition function that you have derived for this magnetic system can be written as the ratio of the two simple harmonic oscillator partition functions:

$$Z_\mathrm{Mag} = \frac{Z_\mathrm{SHO}(g_J \mu_\mathrm{B} B)}{Z_\mathrm{SHO}([2J+1] g_J \mu_\mathrm{B} B)}. \tag{5}$$

Why does this work?

(iv) By considering eqn (5), show that the specific heat of the magnetic system can be written as the difference in the specific heats of two simple harmonic oscillators, one oscillator having effective frequency $g_J \mu_\mathrm{B} B/h$, and the other $[2J+1] g_J \mu_\mathrm{B} B/h$. Plot the specific heat as a function of temperature (in units of $g_J \mu_\mathrm{B} B/k_\mathrm{B}$) for $J = 1/2, 3/2$, and $J \to \infty$. Comment on the form of the specific heat and show that simply by measuring the specific heat of a magnetic system as a function of temperature it is possible to deduce the angular momentum J of the system.

5.10 (i) Show that the thermodynamic properties of an assembly of N three-dimensional harmonic oscillators are the same as those of an assembly of $3N$ one -dimensional oscillators.

(ii) In the Einstein model, each atom in a solid acts acts as a three-dimensional simple harmonic oscillator. An atom in a crystal of copper has a typical vibrational frequency of $\nu = 5.2 \times 10^{12}$ Hz. What is its specific heat at room temperature expressed as a percentage of its maximum specific heat?

(iii) The vibrational frequency of the carbon atoms in diamond is $\nu \approx 3.12 \times 10^{13}$ Hz. What would the Einstein model predict for its heat capacity at room temperature?

Diatomic Gases

5.11 Comment on the following values of molar heat capacity in $\mathrm{J\,K^{-1}\,mol^{-1}}$, all measured at constant pressure at 298 K.

Al	24.35
Ar	20.79
Au	25.42
Cu	24.44
He	20.79
H_2	28.82
Fe	25.10

Pb	26.44
Ne	20.79
N_2	29.13
O_2	29.36
Ag	25.53
Xe	20.79
Zn	25.40

[Hint: express them in terms of R; which of the substances is a solid and which is gaseous?]

5.12 Experimental data for the molar heat capacity of 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 N_2 molecule.

(ii) By making a rough estimate of the separation of the atoms in the molecule, comment on the possibility of reducing the heat capacity of nitrogen to $3R/2$ per mole.

5.13 According to quantum mechanics, the molecules of a diatomic gas have quantized rotational energy levels given by

$$E_J = \frac{\hbar^2}{2I} J(J+1), \qquad J = 0, 1, 2, \ldots,$$

where I is a moment of inertia and the level E_J is $(2J+1)$-fold degenerate. Write down an expression for the partition function of the rotational motion, and hence find the molar rotational heat capacity (i) at low temperature, $k_B T \ll \hbar^2/2I$, and (ii) at high temperature, $k_B T \gg \hbar^2/2I$.

For carbon monoxide (CO) $I = 1.3 \times 10^{-46}\,\mathrm{kg\,m^2}$. What is the molar rotational heat capacity of CO at room temperature?

5.14 Show that for a diatomic molecule at a temperature, T, such that $\theta_{\mathrm{rot}} \ll T \ll \theta_{\mathrm{vib}}$, where θ_{rot} and θ_{vib} are its characteristic temperatures of rotation and vibration respectively, $Z_{\mathrm{sp}} \propto VT^{5/2}$ and thus that along an adiabat $pV^{7/5}$ is a constant.