Statistical Physics

Φxford
hysics

Second year physics course
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Problem Set 8: Thermodynamics of Real Gases and Phase Equilibria
++ Statistical Mechanics Revision Questions
(vacation work)

Some useful constants

Boltzmann's constant	k_{B}	$1.3807 \times 10^{-23} \, \mathrm{J\,K^{-1}}$
Stefan–Boltzmann constant	σ	$5.67 \times 10^{-8} \ \mathrm{Wm^{-2}K^{-4}}$
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		$1.0132 \times 10^5 \, \mathrm{Pa\,(N\,m^{-2})}$
1 bar (= 1000 mbar)		$10^5 \, \mathrm{N\,m^{-2}}$

PROBLEM SET 8: Real Gases, Expansions and Phase Equilibria

Problem set 8 can be covered in 1 tutorial. The relevant material will be done in lectures by the end of week 8 of Hilary Term. Starred questions (*) are harder. Revision questions are designed to build on the understanding of Statistical Mechanics developed in the two previous problem sets.

Real gases

8.1 A gas obeys the equation $p(V - b) = RT$ and has C_V independent of temperature. Show that (a) the internal energy is a function of temperature only, (b) the ratio $\gamma = C_p/C_V$ is independent of temperature and pressure, (c) the equation of an adiabatic change has the form $p(V - b)^\gamma = \text{constant}$.

8.2 Dieterici's equation of state for 1 mole is

$$p(V - b) = RT \mathrm{e}^{-a/RTV}. \tag{1}$$

(a) Show that the critical point is specified by

$$T_c = a/4Rb; \qquad V_c = 2b; \qquad p_c = a/4e^2b^2.$$

(b) Show that equation (1) obeys a *law of corresponding states*, i.e. show that it can be written in reduced units as

$$\tilde{p}(2\tilde{V} - 1) = \tilde{T} \exp\left[2\left(1 - \frac{1}{\tilde{T}\tilde{V}}\right)\right],$$

where $\tilde{p} = p/p_\mathrm{c}$, $\tilde{T} = T/T_\mathrm{c}$, $\tilde{V} = V/V_\mathrm{c}$.

Real gas expansions

8.3 Explain why enthalpy is conserved in a Joule–Kelvin process. Show that the Joule–Kelvin coefficient may be written

$$\mu_{\mathrm{JK}} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right].$$

The equation of state for helium gas may be expressed as a virial expansion

$$pV = RT\left(1 + \frac{B}{V} + \cdots\right)$$

in which B is a function of temperature only. The table below gives some values of B for 1 mole of helium. Determine the Boyle temperature and the inversion temperature.

Temperature (K)	10	20	30	40	50	60	70
B $(\mathrm{cm^3\,mol^{-1}})$	-23.3	-4.0	2.4	5.6	7.6	8.9	9.8

8.4 For a van der Waals gas, show that

$$\lim_{p\to 0} \mu_{\mathrm{JK}} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right) \quad \text{and} \quad T_{\mathrm{i}}^{\max} = \frac{2a}{Rb},$$

where $T_{\mathrm{i}}^{\max}$ is the maximum inversion temperature.

8.5* Prove that the equation of the inversion curve of a Dieterici gas is, in reduced units,

$$\tilde{p} = (8 - \tilde{T})\exp\left(\frac{5}{2} - \frac{4}{\tilde{T}}\right),$$

and sketch it in the $\tilde{p}$–$\tilde{T}$ plane. Hence, show that the maximum inversion temperature is $T_{\mathrm{i}}^{\max} = 2a/(Rb)$.

Phase equilibria

8.6 When lead is melted at atmospheric pressure the melting point is $327.0°C$, the density decreases from 11.01×10^3 to 10.65×10^3 $\mathrm{kg\,m^{-3}}$ and the latent heat is 24.5 $\mathrm{kJ\,kg^{-1}}$. Estimate the melting point of lead at a pressure of 100 atm.

8.7 Some tea connoisseurs claim that a good cup of tea cannot be brewed with water at a temperature less than $97°C$. Assuming this to be the case, is it possible for an astronomer, working on the summit of Mauna Kea in Hawaii (elevation 4194 m) where the air pressure is 615 mbar, to make a good cup of tea without the aid of a pressure vessel?

[Latent heat of vaporisation of water $= 40.7\,\mathrm{kJ\,mol^{-1}}$.]

8.8 (a) Show that the temperature dependence of the latent heat of vapourisation L of an incompressible liquid is given by the following expression:

$$\frac{\mathrm{d}L}{\mathrm{d}T} = \frac{L}{T} + \Delta C_p - \frac{L}{V_{\mathrm{vap}}}\left(\frac{\partial V_{\mathrm{vap}}}{\partial T}\right)_p,$$

where $\Delta C_p = C_{p,\mathrm{vap}} - C_{p,\mathrm{liq}}$.

(b) Treating the vapour as an ideal gas, and assuming ΔC_p is independent of temperature, show that $L = \Delta C_p T + L_0$.

(c) Show further that when the saturated vapour is expanded adiabatically, some liquid condenses out if

$$C_{p,\mathrm{liq}} + T\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{L}{T}\right) < 0.$$

[Hint: For condensation, what is the condition on $\left(\frac{\partial p}{\partial T}\right)_S$ in relation to the gradient of the liquid–vapour phase boundary in the p–T plane?]

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REVISION QUESTIONS on Statistical Mechanics

R.1 *Heat Capacity of Metals.* The objective of this question is to find at what temperature the heat capacity of the electron gas in a metal dominates over the heat capacity associated with the vibrations of the crystal lattice.

(a) Calculate the heat capacity of electrons in aluminium as a function of temperature for $T \ll T_F$.

(b) To estimate the heat capacity due to the vibrations of the lattice, you will need to use the so-called Debye model. Derive it from the results you obtained in PS-7 via the following assumptions.

The vibrations of the lattice can be modelled as sound waves propagating through the metal. These in turn can be thought of as massless particles ("phonons") with energies $\varepsilon = \hbar\omega$ and frequencies $\omega = c_s k$, where c_s is the speed of sound in a given metal and k is the wave number (allowed wave numbers are set by the size of the system, as usual). Thus, the statistical mechanics for the phonons is the same as for photons, with two exceptions: (i) they have 3 possible polarisations in 3D (1 longitudinal, 2 transverse) and (ii) the wave number cannot be larger, roughly, than the inverse spacing of the atoms in the lattice (do you see why this makes sense?).

Given these assumptions,

— calculate the density of states $g(\varepsilon)$ (or $g(\omega)$);

— calculate the mean energy of a slab of metal of volume V;

— figure out the condition on temperature T that has to be satisfied in order for it to be possible to consider the maximum wave number effectively infinite;

— calculate the heat capacity in this limit as a function of T (you may need to use the fact that $\int_0^\infty dx\, x^3/(e^x - 1) = \pi^4/15$)

Hint. You already did all the required maths in Q7.1, so all you need is to figure out how to modify it to describe the phonon gas.

(c) Roughly at what temperature does the heat capacity of the electrons in aluminium become comparable to that of the lattice?

[You may need the density of atoms and alectrons in Al — see Q7.3(b). The speed of sound in Al is $c_s \approx 6000$ m/s. You may find it convenient to define the Debye temperature $\Theta_D = \hbar c_s (6\pi^2 n)^{1/3}/k_B$, where n is the number density of the metal. This is the temperature associated with the maximal wave number in the lattice, which Debye defined by stipulating that the total number of possible phonon modes was equal to 3 times the number of atoms: $\int_0^{k_{\max}} dk\, g(k) = 3N$. For Al, $\Theta_D = 394$ K.]

R.2 *Low Energy Levels in Degenerate Bose Gas.* In a degenerate Bose gas, the lowest energy level (particle energy $\varepsilon_0 = 0$) is macroscopically occupied, in the sense that its occupation number $\bar{n}_0$ is comparable with the total number of particles N. Is the first energy level

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(particle energy ε_1, the next one above the lowest) also macroscopically occupied? In order to answer this question, estimate the occupation number of the first level and show that $\bar{n}_1 \propto N^{2/3}$. Comment on the significance of this result: do the particles in the first level require special consideration as a condensate the same way the zeroth-level ones did?

R.3 *Paramagnetism of Degenerate Bose Gas.* Consider bosons with spin 1 in a weak magnetic field, with energy levels

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} - 2\mu_B s_z B, \quad s_z = -1, 0, 1,$$

where $\mu_B = e\hbar/2m_e c$ is the Bohr magneton (in cgs-Gauss units).

(a) Derive an expression for the magnetic susceptibility of this system. Show that Curie's law ($\chi \propto 1/T$) is recovered in the classical limit.

(b) What happens to $\chi(T)$ as the temperature tends to the critical Bose-Einstein condensation temperature from above ($T \to T_c + 0$)? Sketch $\chi(T)$.

(c) At $T < T_c$ and for a given B, which quantum state will be macroscopically occupied? Taking $B \to +0$ (i.e., infinitesimally small), calculate the spontaneous magnetisation of the system, $M_0(n, T) = \lim_{B \to 0} M(n, T, B)$, as a function of n and T. Explain why the magnetisation is non-zero even though B is vanishingly small. Does the result of (b) make sense in view of what you have found?

R.4 *Creation/Annihilation of Matter.* When the number of particles N in an ideal gas is fixed, its chemical potential μ is determined implicitly from an equation that relates N to μ, the gas volume V, its temperature T, and the spin s and mass m of the particles. Now, instead of fixing the number of particles, let us include them into the energy budget of our system (energy cost of making a particle is mc^2). How must the formula for N be modified?

Using the equation you have obtained, calculate the number density of an ideal gas in equilibrium, at room temperature. Does this result adequately describe the room you are sitting in? If not, why do you think that is?

R.5 (*) *Entropy of Fermi and Bose Gases out of Equilibrium.* In this question, we will learn how to construct the statistical mechanics for quantum ideal gases directly in terms of occupation numbers. In the spirit of Gibbs, consider an ensemble of $\mathcal{N}$ copies of our system (gas in a box). Let N_i be the number of particles that are in the single-particle microstate i across this entire set of copies. Then the average occupation number of i per copy is $\bar{n}_i = N_i/\mathcal{N}$. The (Boltzmann) entropy of the whole ensemble of copies associated with a given assignment $(N_1, N_2, \ldots, N_i, \ldots)$ of particles to microstates is $S_B = \ln \Omega_{\mathcal{N}}(N_1, N_2, \ldots)$, where $\Omega_{\mathcal{N}}$ is the number of ways in which such an assignment can be achieved. Then the Gibbs entropy of the set of occupation numbers $(\bar{n}_1, \bar{n}_2, \ldots, \bar{n}_i, \ldots)$ will be $S_G(\bar{n}_1, \bar{n}_2, \ldots) = S_B/\mathcal{N}$ in the limit $\mathcal{N} \to \infty$ and all $N_i \to \infty$ while keeping $\bar{n}_i$ constant. This is very similar to the construction in the Lectures of the Gibbs entropy of a set of probabilities of microstates, except we now have different rules about how many particles can be in any given microstate i:

— for fermions, each copy of the system in the ensemble can have only one or none of the N_i particles available for each state i;

— for bosons, the N_i particles in each state i can be distributed completely arbitrarily between the $\mathcal{N}$ copies.

(a) Prove that the Gibbs entropy, as defined above, will be

$$S_G = -\sum_i \left[\bar{n}_i \ln \bar{n}_i \pm (1 \mp \bar{n}_i)\ln(1 \mp \bar{n}_i)\right],$$

where the upper sign is for fermions and the lower for bosons.

Hint. Observe that $\Omega_{\mathcal{N}}(N_1, N_2, \ldots) = \Pi_i \Omega_i$, where Ω_i is the number of ways to asign the N_i particles available for the microstate i to the $\mathcal{N}$ copies in the ensemble.

Note that this formula certainly holds for Fermi and Bose gases *in equilibrium* as derived in the Lectures (convince yourself that this is the case), but you have shown now is that it also holds *out of equilibrium*, i.e., for arbitrary occupation numbers.

(b) Considering a system with fixed average energy and number of particles and maximising S_G, derive from the above the Fermi-Dirac and Bose-Einstein formulae for the mean occupation numbers in equilibrium.

(c) Devise a way to treat a classical gas by the same method.