

August, 2006: Thermodynamics & Statistical Mechanics Solutions

SA

Let T_e be the equilibrium temperature. Heat is given out by the pump at the rate $Q_1 = W/\eta$, where $\eta = 1 - T_0/T_e$. At equilibrium $Q_1 = \alpha(T_e - T_0)$, so that

$$W = \frac{\alpha}{T_e}(T_e - T_0)^2,$$

from which we get

$$T_e = T_0 + \frac{W}{2\alpha} + \sqrt{T_0 \frac{W}{\alpha} + \left(\frac{W}{2\alpha}\right)^2}$$

SB

(a) The mean magnetic moment for a dipole is

$$\langle \mu \rangle = \frac{\int \mu \cos \theta \exp(x \cos \theta) d\Omega}{\int \exp(x \cos \theta) d\Omega} = \frac{\mu \int_{-1}^1 \cos \theta \exp(x \cos \theta) d \cos \theta}{\int_{-1}^1 \exp(x \cos \theta) d \cos \theta} = \mu \left[\coth x - \frac{1}{x} \right],$$

where $x = \mu H/kT$. Then the induced magnetization in the system is

$$\langle M \rangle = N \langle \mu \rangle = N \mu \left(\coth x - \frac{1}{x} \right)$$

(b)

$$c = \frac{\partial \langle u \rangle}{\partial T} = -H \frac{\partial \langle M \rangle}{\partial T} = Nk \left(1 - \frac{x^2}{\sinh^2 x} \right)$$

SC1

(a Version 1) On the basis of the equation of state of an ideal gas, we introduce the constant b when considering the volume of a real gas to allow for the finite volumes of the molecules and we introduce the constant a to allow for mutual attraction between molecules of the gas. Now we discuss why the pressure correction term is inversely proportional to V^2 .

Each of the molecules of the gas has a certain interaction region. For the molecules near the center of the volume, the forces on them are isotropic because of the uniform distribution of molecules around them. For the molecules near the walls (the distances from which are smaller than the interaction distance of molecules), they will have a net attractive force directing inwards because the distribution of molecules there is not uniform. Thus the pressure on the wall must have a correction Δp . If Δk denotes the decrease of a molecule's momentum perpendicular to the wall due to the net inward attractive force, $\Delta p = (\text{The number of molecules colliding with unit area of the wall in unit time}) \times 2\Delta k$. As Δk is proportional to the attractive force, the force is proportional to the number of molecules in unit volume, n , and the number of molecules colliding with unit area of the wall in unit time is proportional to n too, we have

$$\Delta p \propto n^2 \propto 1/V^2.$$

(a Version 2) The Van der Waal's equation of state is a modification of the ideal gas equation for which $a = b = 0$. A non-zero constant a represents two-body interactions between molecules. Effects of two-body interactions depend on the rate of two-body collisions which is proportional to the number density squared, n^2 . To lowest order, the number density is proportional to the inverse volume, $n \propto 1/V$. So to lowest order, corrections due to two-body interactions are proportional to $1/V^2$. Now the pressure of a gas is a measure of the total energy. For an ideal gas this is entirely kinetic. But for a non-ideal gas this also receives contributions from molecular interactions. Two-body interactions therefore modify the pressure of the gas as

$$P = P_{\text{eff}} - \frac{a}{V^2}$$

where P_{eff} is the effective or kinetic pressure. Attractive interactions lower the energy of the gas and therefore pressure, so that $a > 0$ in this case. [Note that corrections for n -body interactions would be proportional to $1/V^n$].

A non-zero constant b represents the finite volume of molecules, or equivalently a hard core repulsion between molecules. This reduces the effective volume in which the molecules can move,

$$V_{\text{eff}} = V - b$$

The ideal equation of state for the effective pressure and volume, $P_{\text{eff}}V_{\text{eff}} = RT$ then yields the Van der Waal's equation of state.

(b) The equation of state can be written as

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

In the isothermal process, the change of the Helmholtz free energy is

$$\begin{aligned} \Delta F &= - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \left(\frac{RT}{V - b} - \frac{a}{V^2} \right) dV = \\ &= -RT \ln \left(\frac{V_2 - b}{V_1 - b} \right) + a \left(\frac{1}{V_1} - \frac{1}{V_2} \right) \end{aligned}$$

(c) We can calculate the change of internal energy in terms of T and V :

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

For the isothermal process, we have

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV$$

The theory of thermodynamics gives

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p.$$

Use of the equation of state then gives

$$dU = \frac{a}{V^2} dV$$

Integrating, we find

$$\Delta U = \int_{V_1}^{V_2} \frac{a}{V^2} dV = a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

SC2

(a) The chemical potential of the photon gas is zero. Since the number of photons is not conserved at a given temperature and volume, the average photon number is determined by the expression

$$\left(\frac{\partial F}{\partial \bar{N}}\right)_{T,V} = 0,$$

then

$$\mu = \left(\frac{\partial F}{\partial \bar{N}}\right)_{T,V} = 0$$

(b) The density of states is $V\omega^2 d\omega/\pi^2 c^3$. Then the number of photons is

$$\begin{aligned}\bar{N} &= \int \frac{V}{\pi^2 c^3} \omega^2 \frac{1}{e^{\hbar\omega/kT} - 1} d\omega \\ &= \frac{V}{\pi^2 c^3} \left(\frac{kT}{\hbar}\right)^3 \int_0^\infty \frac{\alpha^2 d\alpha}{e^\alpha - 1} \propto T^3\end{aligned}$$

(c) and (d)

$$\begin{aligned}\frac{\bar{E}}{V} &= \int \frac{\omega^2}{\pi^2 c^3} \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} d\omega \\ &= \frac{(kT)^4}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{\xi^3 d\xi}{e^\xi - 1}\end{aligned}$$

Hence

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/kT} - 1},$$

and $\bar{E} \propto T^4$.

SD1 (a) The probability to have j particles in a state with energy ϵ is proportional to $e^{j(\mu-\epsilon)/\tau}$. The occupancy of the state is

$$n(\epsilon) = \langle j \rangle = \frac{\sum_{j=0}^{\infty} j e^{j(\mu-\epsilon)/\tau}}{\sum_{j=0}^{\infty} e^{j(\mu-\epsilon)/\tau}} = \frac{e^{(\mu-\epsilon)/\tau} + 2e^{2(\mu-2\epsilon)/\tau}}{1 + e^{(\mu-\epsilon)/\tau} + e^{2(\mu-2\epsilon)/\tau}} \quad (1)$$

Suppose the gas is cold, $\tau \rightarrow 0$. For states above the chemical potential $\epsilon > \mu$ and $(\mu - \epsilon)/\tau = -\infty$, for states below $\epsilon < \mu$ and $(\mu - \epsilon)/\tau = +\infty$, for states at the chemical potential $\epsilon = \mu$ and $(\mu - \epsilon)/\tau = 0$. We have

$$n(\epsilon > \mu) = 0 \quad n(\epsilon < \mu) = 2 \quad n(\epsilon = \mu) = 1$$

(b) The number of states with momenta between p and $p + dp$ is $dpL/(2\pi\hbar)$. Using $p = \sqrt{2m\epsilon}$, we obtain for the density of states $\nu(\epsilon)$ (number of states per unit energy as a function of energy)

$$\begin{aligned}\nu(\epsilon)d\epsilon &= \frac{dpL}{2\pi\hbar} = \frac{L\sqrt{2m}}{4\pi\hbar\sqrt{\epsilon}} d\epsilon \\ \nu(\epsilon) &= \frac{L\sqrt{2m}}{4\pi\hbar\sqrt{\epsilon}}\end{aligned}$$

At zero temperature each state below the chemical potential μ_0 is doubly occupied, states above the chemical potential are empty. The total number of weirdons is

$$N = \int_0^{\mu_0} 2\nu(\epsilon)d\epsilon = \int_0^{\mu_0} 2 \frac{L\sqrt{2m}}{4\pi\hbar\sqrt{\epsilon}} d\epsilon = \frac{L\sqrt{2m\mu_0}}{\pi\hbar}$$

We obtain

$$\mu_0 = \frac{\pi^2 \hbar^2 (N/L)^2}{2m}$$

The total energy is

$$E = \int_0^{\mu_0} 2\epsilon \nu(\epsilon) d\epsilon = \int_0^{\mu_0} 2 \frac{L\sqrt{\epsilon}\sqrt{2m}}{4\pi\hbar} d\epsilon = \frac{L\sqrt{2m}}{3\pi\hbar} \mu_0^{3/2}$$

$$\frac{E}{L} = \frac{(\pi\hbar)^2 (N/L)^3}{6m}$$

(c) One can understand the low temperature behavior of the specific heat quite simply from the temperature dependence of the distribution function $n(\epsilon, \tau)$. For $|\mu - \epsilon| \gg \tau$ we obtain from Eq. (1)

$$n(\epsilon, \tau) - n(\epsilon, 0) \approx \text{sgn}(\epsilon - \mu_0) e^{-|\epsilon - \mu_0|/\tau},$$

where $\text{sgn } x = 1$ for $x > 0$ and $\text{sgn } x = -1$ for $x < 0$.

The increase in energy of the weirdons when the temperature is raised from $\tau = 0$ comes about entirely because some weirdons with energies within τ below μ_0 have been excited to an energy range τ above μ_0 . The number of weirdons that have been so excited is the width, τ , of the energy interval times the density of levels $\nu(\mu_0)$. Furthermore, the excitation energy is of order τ , and hence the total thermal energy is $\Delta U \propto \nu(\mu_0)\tau^2$ above the ground state. Thus,

$$C = \frac{d\Delta U}{d\tau} \propto \tau, \quad \alpha = 1.$$

Further, using $C = \tau \partial S / \partial \tau$, we obtain $S \propto \tau$, i.e. $\beta = 1$.

SD2

(a) We have

$$\ln Z = \sum_{np_z} \ln(1 + e^{\beta\mu} e^{-\beta E_{np_z}}) = \int_{-\infty}^{\infty} \frac{L dp_z}{2\pi\hbar} \sum_{n=0}^{\infty} \frac{L^2 eB}{2\pi\hbar c} \ln \left(1 + \lambda \exp \left\{ -\beta \left[2\mu_B B \left(n + \frac{1}{2} \right) + \frac{p_z^2}{2m} \right] \right\} \right),$$

where Z is the grand partition function, $\lambda = e^{\beta\mu}$, $\beta = 1/T$, and μ is the chemical potential. Note that the temperature units are such that the Boltzman constant $k_B = 1$.

In the high temperature limit $\lambda \ll 1$, hence

$$\ln Z = \frac{eBV}{(2\pi\hbar)^2 c} \lambda \int_{-\infty}^{\infty} dp_z \sum_{n=0}^{\infty} \exp \left\{ -\beta \left[2\mu_B B \left(n + \frac{1}{2} \right) + \frac{p_z^2}{2m} \right] \right\} = \frac{\lambda V}{\lambda_T^3} \frac{\mu_B B}{T \sinh x},$$

where $V = L^3$ is the volume of the box, $\lambda_T = 2\pi\hbar/\sqrt{2\pi m T}$ and $x = \mu_B B/T$.

(b) The magnetization is

$$M = -\frac{\partial F}{\partial B} = T \left(\frac{\partial \ln Z}{\partial B} \right)_{\mu, T, V},$$

where F is the free energy of the system. Hence

$$M = \frac{\lambda V}{\lambda_T^3} \mu_B \left[\frac{1}{\sinh x} - \frac{x \cosh x}{\sinh^2 x} \right]$$

By

$$\bar{N} = \left(\lambda \frac{\partial}{\partial \lambda} \ln Z \right)_{B, T, V} = \frac{\lambda V}{\lambda_T^3} \frac{x}{\sinh x}$$

we have $M = -\bar{N} \mu_B L(x)$, where $L(x) = \coth x - 1/x$.

At high temperatures, $T \gg \mu_B B$ or $x \ll 1$. Therefore,

$$L(x) = \frac{1}{3}x - \frac{1}{45}x^3 + \dots,$$

$$\bar{N} \approx \frac{\lambda V}{\lambda_T^3},$$

$$M \approx -\bar{N} \frac{\mu_B^2 B}{3T}$$

The magnetic susceptibility at high temperatures is

$$\chi_\infty = \frac{M}{VB} = \frac{-n_e \mu_B^2}{3T},$$

where $n_e = \bar{N}/V$ is the electron number density.