Exam solutions
Statistical Mechanics
20 December 2016, 14:00-18:00

Problem 1 (6 points)

The van der Waals equation of state has the following form

$$P = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2} \ . \tag{1}$$

a) Calculate from it the critical pressure, temperature and volume P_c, T_c, and V_c.

b) Show that in rescaled units the above equations takes the following from

$$\tilde{p} = \frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2} \ , \tag{2}$$

where the critical point corresponds to $\tilde{p} = \tilde{T} = \tilde{v} = 1$.

c) Obtain from the rescaled equation the exponent γ describing the divergence of the isothermal compressibility

$$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_{N,T} \ , \tag{3}$$

when the critical point is approached from above $T \to T_c^+$.

Solution: We start with the relation

$$P = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2} \ . \tag{4}$$

The critical pressure, volume and temperature are calculated using the relations

$$\frac{\partial P}{\partial V} = 0 \ , \qquad \frac{\partial^2 P}{\partial V^2} = 0 \ . \tag{5}$$

Using these two equations and the relation

$$P_c = \frac{Nk_BT_c}{V_c - Nb} - \frac{aN^2}{V_c^2} \ , \tag{6}$$

one finds

$$V_c = 3Nb \ , \qquad T_c = \frac{8a}{27bk_B} \ , \qquad P_c = \frac{a}{27b^2} \ . \tag{7}$$

Now one can define

$$\tilde{p} \equiv \frac{P}{P_c} \,, \qquad \tilde{T} \equiv \frac{T}{T_c} \,, \qquad \tilde{v} \equiv \frac{V}{V_c} \,, \tag{8}$$

and use (4) and (7) to find

$$\tilde{p} = \frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2} \,, \tag{9}$$

Finally use

$$\left.\frac{\partial \tilde{p}}{\partial \tilde{v}}\right|_{\tilde{v}\to 1} \to 6(1 - \tilde{T}) = 6\frac{T_c - T}{T_c} \,, \tag{10}$$

to find

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_{N,T} = -\frac{1}{P_c \tilde{v}}\left.\frac{\partial \tilde{v}}{\partial \tilde{p}}\right|_{N,T} \to -\frac{1}{P_c}\frac{T_c}{6(T_c - T)} \sim \frac{1}{(T - T_c)^{\gamma}} \,, \tag{11}$$

with from the last equation we conclude that the critical exponent is $\gamma = 1$.

Problem 2 (3 points)

Consider a system of three quantum particles. Each of them can be in one of three states with energies 0, 2ϵ and 5ϵ. The particles are in equilibrium with temperature T.

a) Compute the canonical partition function and internal energy of the system assuming that the particles obey the Bose-Einstein statistics. Discus the low and high temperature limits.

b) Now assume that the particles obey Fermi-Dirac statistics. What is the canonical partition function and the internal energy? Discuss again the low and high temperature limits.

Solution: Let us label the available energy states by the value of the energy $\{0, 2\epsilon, 5\epsilon\}$. With the notation (p, q, r) we will mean that one particle occupies state p, the second state q and the third state r.

Consider the case of two indistinguishable bosons first. The particles are indistinguishable so possible configurations are $(0,0,0)$, $(0,0,2\epsilon)$, $(0,0,5\epsilon)$, $(0,2\epsilon,2\epsilon)$, $(0,2\epsilon,5\epsilon)$, $(0,5\epsilon,5\epsilon)$, $(2\epsilon,2\epsilon,2\epsilon)$,$(2\epsilon,2\epsilon,5\epsilon)$, $(2\epsilon,5\epsilon,5\epsilon)$, $(5\epsilon,5\epsilon,5\epsilon)$ Thus the total partition functions is

$$Z_B = 1 + e^{-2\beta\epsilon} + e^{-5\beta\epsilon} + e^{-4\beta\epsilon} + e^{-7\beta\epsilon} + e^{-10\beta\epsilon} + e^{-6\beta\epsilon} + e^{-9\beta\epsilon} + e^{-12\beta\epsilon} + e^{-15\beta\epsilon} \,, \tag{12}$$

where $\beta^{-1} \equiv k_B T$.

Now let us study the fermionic system. The particles are again indistinguishable. Due to the Pauli exclusion principle there cannot be two fermions occupying the same quantum state. Thus there is only one possible configuration $(0, 2\epsilon, 5\epsilon)$. Therefore the partition function is

$$Z_F = e^{-7\beta\epsilon} \,. \tag{13}$$

At low temperatures we have $\beta \gg 1$ and thus

$$Z_B \approx 1 + e^{-2\beta\epsilon} \,, \qquad Z_F \approx e^{-7\beta\epsilon} \,. \tag{14}$$

At high temperatures we have $\beta \ll 1$ and thus

$$Z_B \approx 10 \,, \qquad Z_F \approx 1 \,, \tag{15}$$

as expected both partition functions approach a constant.

Problem 3 (4 points)

Consider a system of two non-interacting one-dimensional quantum harmonic oscillators of frequencies $\omega_1 \equiv \alpha\omega$ and $\omega_2 \equiv \frac{1}{\alpha}\omega$. The energy levels of the systems are given by

$$\varepsilon = \hbar\omega_1 \left(n_1 + \frac{1}{2}\right) + \hbar\omega_2 \left(n_2 + \frac{1}{2}\right) ,$$

where $n_{1,2} = 0, 1, 2, 3 \ldots$.

a) Calculate the canonical partition function of the system, Z, and the average energy, E, as a function of the temperature T.

b) Analyze the low and high temperature behavior of E. Discuss the relation between your results at high temperature and the equipartition theorem.

c) Use the leading term in your expansion of E at low temperatures to find the value of the parameter α for which E is minimized for fixed ω.

Solution:
The partition function of the system is (where we use the geometric series)

$$\begin{aligned} Z &= \sum_{n_{1,2}=0}^{\infty} \exp\left[-\beta\hbar\omega_1\left(n_1+\frac{1}{2}\right) - \beta\hbar\omega_2\left(n_2+\frac{1}{2}\right)\right] , \\ &= \frac{1}{4\sinh(\frac{\beta\hbar\alpha\omega}{2})\sinh(\frac{\beta\hbar\omega}{2\alpha})} . \end{aligned} \tag{16}$$

For the average energy one finds

$$E = -\frac{\partial}{\partial\beta}\log Z = \frac{\hbar\omega}{2\alpha}\left[\coth\left(\frac{\beta\hbar\omega}{2\alpha}\right) + \alpha^2\coth\left(\frac{\beta\hbar\alpha\omega}{2}\right)\right) . \tag{17}$$

At high temperatures we have

$$E \approx 2k_BT + \frac{\hbar}{12k_BT}(\omega_1^2 + \omega_2^2) . \tag{18}$$

The leading terms in this expression reproduce exactly the expected result from the equipartition theorem.

At low temperatures one finds

$$E \approx \frac{\hbar\omega}{2\alpha}[1 + 2e^{-\frac{\beta\hbar\omega}{\alpha}} + \alpha^2(1 + 2e^{-\beta\hbar\alpha\omega})] = \frac{\hbar}{2}[\omega_1(1 + 2e^{-\beta\hbar\omega_1}) + \omega_2(1 + 2e^{-\beta\hbar\omega_2})] . \tag{19}$$

The leading term in the energy at low temperatures is

$$E \approx \frac{\hbar\omega}{2}\frac{1+\alpha^2}{\alpha} . \tag{20}$$

For a fixed frequency ω this expression has a local minimum at $\alpha = 1$. Thus we can conclude that the energy at low temperature is minimized when the two harmonic oscillators have equal frequency.

Problem 4 (7 points)

An average number, N, of bosons of spin $S = 0$ is confined to a two-dimensional domain with surface A. The gas is ultrarelativistic with a single particle energy $\varepsilon = cp$, where c is the speed of light in vacuum and p is the absolute value of the momentum.

a) Define $z \equiv e^{\beta\mu}$, with μ the chemical potential[1] and $\beta \equiv \frac{1}{k_B T}$, and compute N as a function of z. Assume that the system is at high temperature T. Your answer should give $N(z, A, T)$ and you should expand it up to terms quadratic in z.

b) Compute the pressure, P, of this system as a function of z, A and T. While still being in the high-temperature regime, use the result for $N(z, A, T)$ from a). above to find $P(N, A, T)$ (keep up to quadratic terms in N). Discuss your results and the relation to the ideal gas law.

Hint: Throughout your calculations you may use the following identity

$$n! = \int_0^\infty e^{-t} t^n dt \ .$$

Solution: The average number of particles is

$$N = \frac{2\pi A}{h^2} \int_0^\infty \frac{p}{e^{\beta(pc-\mu)} - 1} dp \ , \tag{21}$$

Setting $z \equiv e^{\beta\mu}$ and $x \equiv \beta pc$ we can write this as

$$N = \frac{2\pi A}{(hc\beta)^2} \int_0^\infty \frac{z x e^{-x}}{1 - z e^{-x}} dx \ . \tag{22}$$

Now use that $\mu < 0$ and assume that the temperature is high and expand in a Taylor series in z (up to quadratic terms in z) to find

$$N \approx \frac{2\pi A}{(hc\beta)^2} \left[z \int_0^\infty x e^{-x} dx + z^2 \int_0^\infty x e^{-2x} dx \right] = \frac{2\pi A}{(hc\beta)^2} \left(z + \frac{z^2}{4} \right) \ . \tag{23}$$

Now we use the relation

$$\frac{PV}{k_B T} = \log \Xi \ , \tag{24}$$

where Ξ is the partition function in the grand canonical ensemble to find (below we use the series expansion of $\log(1-y)$ for small y, interchange the sum and the integral, and define $x = \beta cp$)

$$\begin{aligned} \frac{PV}{k_B T} &= -\frac{2\pi A}{h^2} \int_0^\infty p \log\left(1 - z e^{-\beta pc}\right) dp = \frac{2\pi A}{h^2} \int_0^\infty \sum_{k=1}^\infty dp p \frac{z^k e^{-k\beta pc}}{k} \\ &= \frac{2\pi A}{(h\beta c)^2} \sum_{k=1}^\infty \frac{z^k}{k^3} \int_0^\infty x e^{-x} dx = \frac{2\pi A}{(h\beta c)^2} \sum_{k=1}^\infty \frac{z^k}{k^3} \ . \end{aligned} \tag{25}$$

Keeping only the first two terms in this series in z and expressing z in terms of N one finds

$$P \approx \frac{N k_B T}{A} \left(1 - \frac{1}{8} \frac{N (h\beta c)^2}{2\pi A} \right) \ . \tag{26}$$

As expected, since we are dealing with bosons, the leading order correction to the ideal gas law has a negative sign.

[1] Remember that for free bosonic systems the chemical potential is negative.