Physics 3410 Homework #8
3 problems
Solutions

▷ **1.**

Consider the van der Waals equation

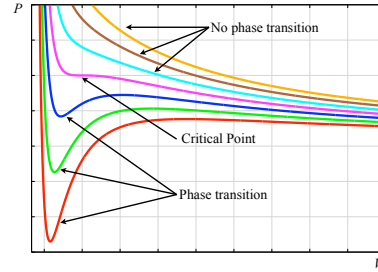$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NkT$$

If we plot $P(V)$ for this equation, the *critical point* occurs where the first and second derivatives of $P(V)$ are both zero. The critical point occurs where

$$V_c = 3Nb \quad \text{and} \quad P_c = \frac{a}{27b^2} \quad \text{and} \quad kT_c = \frac{8a}{27b}$$

Rewrite the van der Waals equation in terms of *reduced variables*:

$$v = \frac{V}{V_c} \quad \text{and} \quad p = \frac{P}{P_c} \quad \text{and} \quad t = \frac{T}{T_c}$$

and show that the reduced version of the equation is independent of a and b. (This means that the two parameters of the model are determined entirely by the location of the critical point.)
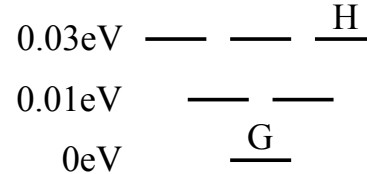
Answer:

Substitute $V = vV_c$, $P = pP_c$, and $T = tT_c$ into the equation.

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NkT$$

$$\left(pP_c + a\frac{N^2}{v^2V_c^2}\right)(vV_c - Nb) = NktT_c$$

$$\left(p\frac{a}{27b^2} + a\frac{N^2}{v^2(9N^2b^2)}\right)(v(3Nb) - Nb) = Nt\frac{8a}{27b}$$

$$\left(\frac{a}{b^2}\frac{p}{27} + \frac{a}{b^2}\frac{1}{9v^2}\right)(Nb)(3v - 1) = \frac{a}{b}\frac{8Nt}{27}$$

$$\frac{Na}{27b}\left(p + \frac{3}{v^2}\right)(3v - 1) = \frac{aN}{27b}(8t)$$

$$\left(p + \frac{3}{v^2}\right)(3v - 1) = 8t$$

▷ **2.**

Consider a system which can be in one of six states: there is one ground state, two states with energy 0.01 eV, and three states with energy 0.03 eV (as shown). Call the ground state G and one of the highest-energy microstates H.
(a) Find the partition function as a function of $\beta = 1/kT$.
(b) Use the partition function to calculate the system's average energy.
Assume the reservoir is at room temperature $\beta = 40 /eV$ for the rest of the problem.
(c) How much more likely is the ground state compared to the microstate H?
(d) What is the probability of the ground state?
(e) What is the probability that the system has energy 0.01 eV?

0.03eV ⎯⎯ ⎯⎯ H ⎯⎯

0.01eV ⎯⎯ ⎯⎯

0eV   G ⎯⎯

Answer:——————————————————————

(a) The partition function is the sum of Boltzmann factors, and there are six of them here.
$$Z = 1 + 2e^{-\beta(0.01\,\text{eV})} + 3e^{-\beta(0.03\,\text{eV})}$$

(b) The system average energy is given by
$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$
$$= -\frac{-2(0.01\,\text{eV})e^{-\beta(0.01\,\text{eV})} - 3(0.03\,\text{eV})e^{-\beta(0.03\,\text{eV})}}{1 + 2e^{-\beta(0.01\,\text{eV})} + 3e^{-\beta(0.03\,\text{eV})}}$$
$$= \frac{0.02e^{-(0.01\,\text{eV})\beta} + 0.09e^{-(0.03\,\text{eV})\beta}}{1 + 2e^{-\beta(0.01\,\text{eV})} + 3e^{-\beta(0.03\,\text{eV})}}\,\text{eV}$$

For the next three problems, it's easiest just to calculate the three different Boltzmann factors at once:

$$0\,\text{eV} : e^{-\beta(0\,\text{eV})} = 1$$

$$0.01\,\text{eV} : e^{-\beta(0.01\,\text{eV})} = e^{-(40\,/\text{eV})(0.01\,\text{eV})} = 0.670$$

$$0.03\,\text{eV} : e^{-\beta(0.03\,\text{eV})} = e^{-(40\,/\text{eV})(0.03\,\text{eV})} = 0.301$$

(c) The probability of a given microstate is the ratio of its Boltzmann factor to the partition function, and so
$$\frac{P(G)}{P(H)} = \frac{1/Z}{0.301/Z}$$
$$= \frac{1}{0.301} = \boxed{3.3}$$

(d) To find the probability of the ground state, we need the partition function:

$$Z = 1(1) + 2(0.670) + 3(0.301) = 3.243$$

and so

$$P(G) = \frac{1}{3.243} = \boxed{31\%}$$

(e) The probability that the system is in one of the $0.01\,\text{eV}$ microstates is

$$P(0.01\,\text{eV microstate}) = \frac{0.670}{3.243} = 20.7\%$$

There are three different microstates however, and so the probability that the system is in any of them is

$$P(0.01\,\text{eV}) = 3 \times 20.7\% = \boxed{62\%}$$

which makes this twice as likely as finding the system in the ground state.

▷ **3.**

This problem concerns a collection of N identical harmonic oscillators (perhaps an Einstein solid or the internal vibrations of gas molecules) at temperature T. The allowed energies of each oscillator are 0, hf, $2hf$, and so on. We will use the infinite series

$$1 + x + x^2 + x^3 + \cdots = \frac{1}{1-x} \quad , 0 < x < 1$$

(a) Evaluate the partition function for a single harmonic oscillator.
(b) Find an expression for the average energy of a single oscillator at temperature T.
(c) What is the total energy of the system of N oscillators at temperature T?
(d) Compute the heat capacity $C = \frac{dU}{dT}$, and find the limit of C at $T \to 0$: prove that it satisfies the third law of thermodynamics.

Answer:———————————————————————————

(a) Taking the ground state energy to be zero, Z is the sum of the Boltzmann factors

$$Z = e^0 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \cdots = \boxed{\frac{1}{1 - e^{-\beta\epsilon}}}$$

where $\epsilon = hf$.

(b) The average energy of the oscillator is

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= -(1 - e^{-\beta\epsilon})\frac{\partial}{\partial \beta}(1 - e^{-\beta\epsilon})^{-1}$$

$$= -(1 - e^{-\beta\epsilon})\left[-(1 - e^{-\beta\epsilon})^{-2}(-e^{-\beta\epsilon})(-\epsilon)\right]$$

$$= \frac{\epsilon e^{-\beta\epsilon}}{1 - e^{-\beta\epsilon}} = \boxed{\frac{\epsilon}{e^{\beta\epsilon} - 1}}$$

(c) Because the oscillators are independent, the total energy is

$$U = N\bar{E} = \boxed{\dfrac{N\epsilon}{e^{\beta\epsilon} - 1}}$$

(d) The heat capacity is

$$C = \frac{\partial U}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial U}{\partial \beta}$$

$$= -\frac{1}{kT^2}\frac{-N\epsilon}{(e^{\beta\epsilon} - 1)^2}(\epsilon e^{\beta\epsilon})$$

$$= \boxed{\frac{N\epsilon^2}{kT^2}\frac{e^{\beta\epsilon}}{(e^{\beta\epsilon} - 1)^2}}$$

When T is small, β is large and $e^{\beta\epsilon}$ is also large, so $e^{\beta\epsilon} - 1 \approx e^{\beta\epsilon}$. Then

$$C \approx \frac{N\epsilon^2}{kT^2}\frac{e^{\beta\epsilon}}{e^{2\beta\epsilon}} = \boxed{\frac{N\epsilon^2}{k}\frac{e^{-\epsilon/kT}}{T^2}}$$

Now both numerator and denominator go to zero as $T \to 0$, but the exponential goes to zero much faster than any polynomial; it wins, and so $C = 0$ at zero temperature, which is what we'd want to see. (This result goes to zero too quickly however, as we will see in Chapter 7 and the phonon gas correction.)