PHYS7721 Homework 1

Ryan Carelli

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Exercise 1. (a) Show that, for two large systems in thermal contact, the number $\Omega^{(0)}(E^{(0)}, E_1)$ of Section 1.2 can be expressed as a Gaussian in the variable E_1. Determine the root-mean-square deviation of E_1 from the mean value $\overline{E_1}$ in terms of other quantities pertaining to the problem.

(b) Make an explicit evaluation of the root-mean-square deviation of E_1 in the special case when the systems A_1 and A_2 are ideal classical gases.

Solution.

(a) Consider that $\Omega^0(E) = \Omega_1(E_1)\Omega_2(E - E_1)$. Expand $\ln \Omega^0(E_1)$ to quadratic order (we want a squared term in an exponential) in E_1 about $\overline{E_1}$.

$$\ln \Omega^{(0)}(E_1) = \ln \Omega_1(E_1) + \ln \Omega_2(E_2)$$

$$\approx \ln \Omega_1(\overline{E_1}) + \ln \Omega_2(\overline{E_2}) + \Big(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} + \frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\frac{\partial E_2}{\partial E_1}\Big)(E_1 - \overline{E_1}$$

$$+\frac{1}{2}\Big(\frac{\partial^2 \ln \Omega_1(E_1)}{\partial E_1^2} + \frac{\partial^2 \ln \Omega_2(E_2)}{\partial E_2^2}\Big(\frac{\partial E_2}{\partial E_1}\Big)^2\Big)(E_1 - \overline{E_1})^2$$

Now since we are expanding about equilibrium, apply the condition that $\beta_1 = \beta_2$ where $\beta_i = \Big(\frac{\partial ln\Omega_i(N_i, V_i, E_i}{\partial E_i}\Big)$. Then the linear term in the expansion vanishes because $\frac{\partial E_2}{\partial E_1} = -1$. So,

$$\ln \Omega^{(0)}(E_1) \approx \ln \Omega_1(\overline{E_1}) + \ln \Omega_2(\overline{E_2}) + \frac{1}{2}\Big(\frac{\partial \beta_1}{\partial E_1} + \frac{\partial \beta_2}{\partial E_2}\Big)(E_1 - \overline{E_1})^2$$

$$= \ln \Omega_1(\overline{E_1}) + \ln \Omega_2(\overline{E_2}) + \frac{1}{2}\Big(\frac{\partial \frac{1}{kT_1}}{\partial E_1} + \frac{\partial \frac{1}{kT_2}}{\partial E_2}\Big)(E_1 - \overline{E_1})^2$$

$$= \ln \Omega_1(\overline{E_1}) + \ln \Omega_2(\overline{E_2}) - \frac{1}{2}\Big(\frac{1}{kT_1^2(C_V)_1} + \frac{1}{kT_2^2(C_V)_2}\Big)(E_1 - \overline{E_1})^2$$

Now we can write,

$$\Omega^{(0)}(E_1) \approx \Omega_1(\overline{E_1})\Omega_2(\overline{E_2})e^{-\frac{1}{2}\Big(\frac{1}{kT_1^2(C_V)_1} + \frac{1}{kT_2^2(C_V)_2}\Big)(E_1 - \overline{E_1})^2}$$

The Gaussian distribution is of the form

$$g(x) = Ae^{\frac{-(x-a)^2}{2\sigma^2}}$$

where a is the mean and σ is the standard deviation. We can therefore identify $\Omega^0(E_1)$ with a Gaussian where

$$\sigma^2 = \frac{1}{\frac{1}{kT_1^2(C_V)_1} + \frac{1}{kT_2^2(C_V)_2}} \text{ and } a = \overline{E_1}$$

Consider that root-mean-square deviation is a theoretical variance and we can call $RMSE = \sigma^2$.

(b) Now consider systems of ideal classical gases A_1 and A_2. Just plug in the values that we derived in class for an ideal gas. $(C_V)_1 = \frac{3}{2}N_1 k$, $(C_V)_2 = \frac{3}{2}N_2 k$ and we can rewrite the variance,

$$\sigma^2 = RMSE = \frac{3}{2}k^2T^2\frac{N_1N_2}{N_1+N_2}$$

□

Exercise 2. In the classical gas of hard spheres (of diameter D), the spatial distribution of the particles is no longer uncorrelated. Roughly speaking, the presence of n particles in the system leaves only a volume of $(V - nv_0)$ available for the $(n+1)$th particle; clearly, v_0 would be proportional to D^3. Assuming that $Nv_0 << V$, determine the dependence of $\Omega(N, V, E)$ on V (compare to equation (1.4.1)) and show that, as a result of this, V in the ideal-gas law (1.4.3) gets replaced by $(V-b)$, where b is four times the actual volume occupied by the particles.

Solution. We have that

$$\Omega(N,E,V) \propto \prod_{n=0}^{N}(V - nv_0)$$

Apply the trick of taking the natural log to generate a sum,

$$\ln\Omega(N,E,V) \propto \ln(V) + \ln(V - v_0) + \ln(V - 2v_0) + \ln(V - 3v_0) + ...$$

And establish equality by including a constant k,

$$\ln\Omega(N,E,V) = k + \ln(V) + \ln(V - v_0) + \ln(V - 2v_0) + \ln(V - 3v_0) + ...$$

On Wikipedia, I found the logarithm identity $\ln(a - c) = \ln(a) + \ln(1 - \frac{c}{a})$. From this we can write a more compact expression,

$$\ln\Omega(N,E,V) = k + \ln(V) + \ln(V) + \ln\left(1 - \frac{v_0}{V}\right) + \ln(V) + \ln\left(1 - \frac{2v_0}{V}\right) + ...$$

$$\ln\Omega(N,E,V) = k + \ln(V^N) + \sum_{n=1}^{N-1}\ln\left(1 - \frac{nv_0}{V}\right)$$

Now apply the Taylor series expansion $\ln(1+x) = \sum_{n=1}^{\infty}(-1)^{n-1}\frac{x^n}{n}$,

$$\ln\Omega(N,E,V) \approx k + \ln(V^N) + \sum_{n=1}^{N-1}\left(\frac{-nv_0}{V}\right) \approx k + \ln(V^N) - \frac{N^2v_0}{2V}$$

Now apply (1.4.2) $\frac{P}{T} = k\Big(\frac{\partial\ln\Omega(N,E,V)}{\partial V}\Big)$,

$$\frac{P}{T} = k\Big(\frac{N}{V} + \frac{N^2v_0}{2V^2}\Big)$$

So that we can expand using $Nv_0 << V$, rearrange,

$$\frac{P}{T} = \frac{kN}{V}\Big(1 + \frac{Nv_0}{2V}\Big) \implies PV\Big(1 + \frac{Nv_0}{2V}\Big)^{-1} = NkT \implies PV\Big(1 - \frac{Nv_0}{2V}\Big) = NkT$$

Now we have that $b = \frac{Nv_0}{2}$. It remains to show that this is four times the actual volume occupied by the particles. Assuming that the particles are truly spheres, $v_0 = \frac{4}{3}\pi\Big(\frac{D}{2}\Big)^3$. Substituting,

$$b = 4\Big(N\frac{4\pi}{3}\Big(\frac{1}{2}D\Big)^3\Big)$$

which is four times the volume as desired. □

Exercise 3. Consider a system of quasiparticles whose energy eigenvalues are given by

$$\epsilon(n) = nhv; \ n = 0, 1, 2, ...$$

Obtain an asymptotic expression for the number Ω of this system for a given number N of the quasi-particles and a given total energy E. Determine the temperature T of the system as a function of E/N and hv, and examine the situation for which $E/(Nhv) >> 1$.

Solution. The total energy is the sum of the energies of discrete particles,

$$E = \sum_i n_i hv$$

where $\{n_i\}$ represents the states of each particle i. This system is isomorphic to the Einstein solid because of the discreteness of energies and their distribution. The expression for the multiplicity for q units of energy distributed among N oscillators is given by,

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!}.$$

In this case, we can drop the -1 because we are looking for an asymptotic expression for the number Ω. Let E' be the number of quanta of energy. Write,

$$\Omega(N, E') = \binom{E' + N}{E'} = \frac{(E' + N)!}{N!E'!}.$$

We need a partial derivative of entropy to find temperature. This requires that we compute $\ln \Omega$. Apply the Stirling approximation,

$$\ln \Omega = \ln((E'+N)!) - \ln(N!) - \ln(E'!) \approx (E'+N)\ln(E'+N) - (E'+N) - E'\ln(E') + E' - N\ln(N) + N$$

$$= N \ln\left(\frac{E' + N}{N}\right) + P \ln\left(\frac{P + N}{P}\right)$$

We want to restore E to the expression. Substitute $E' = \frac{E}{hv}$ into $S = k \ln \Omega$,

$$S = kN \ln\left(\frac{E}{Nhv} + 1\right) + \frac{kE}{hv} \ln\left(1 + \frac{Nhv}{E}\right)$$

Now $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N$.

$$\frac{1}{T} = \frac{kN}{E + Nhv} - \frac{kN}{E + Nhv} + \frac{k}{hv} \ln\left(1 + \frac{Nhv}{E}\right) \implies T = \frac{hv}{k \ln(1 + \frac{Nhv}{E})}$$

Now examining the limit,

$$\ln\left(1 + \frac{Nhv}{E}\right) \approx \frac{Nhv}{E} \implies T \approx \frac{E}{kN}.$$

$\square$

Exercise 4. Establish thermodynamically the formulae

$$V\left(\frac{\partial P}{\partial T}\right)_\mu = S \text{ and } V\left(\frac{\partial P}{\partial \mu}\right)_T = N.$$

Express the pressure P of an ideal classical gas in terms of the variables μ and T, and verify the above formulae.

Solution. This is a simple application of the fundamental thermodynamic relationship.

$$E = TS - PV + N\mu \implies dE = SdT + TdS - VdP - PdV + \mu dN + Nd\mu$$

But we know,

$$dE = TdS - PdV + \mu dN$$

so by comparison $SdT - VdP + Nd\mu = 0$. Now

$$SdT = VdP - Nd\mu$$

and if we fix μ,

$$S = V\left(\frac{\partial P}{\partial T}\right)_\mu.$$

Similarly.

$$VdP = SdT + Nd\mu$$

and if we fix T,

$$N = V\left(\frac{\partial P}{\partial \mu}\right)_T$$

□