

PHYS7721 Homework 3

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Exercise 1. Show that for a system in the canonical ensemble

$$\langle (\Delta E)^3 \rangle = k^2 \left\{ T^4 \left(\frac{\partial C_V}{\partial T} \right)_V + 2T^3 C_V \right\},$$

Verify that for an ideal gas

$$\left\langle \left(\frac{\Delta E}{U} \right)^2 \right\rangle = \frac{2}{3N} \text{ and } \left\langle \left(\frac{\Delta E}{U} \right)^3 \right\rangle = \frac{8}{9N^2}$$

Solution. Starting with the intuition that

$$\frac{\partial U}{\partial \beta} = -\langle E^2 \rangle + \langle E \rangle^2$$

we take the second partial derivative with respect to β ,

$$\frac{\partial^2 U}{\partial \beta^2} = \langle E^3 \rangle - E^2 \langle E \rangle + 2\langle E \rangle \frac{\partial U}{\partial \beta}$$

and substituting the first derivative gives us the desired result,

$$\frac{\partial^2 U}{\partial \beta^2} = \langle E^3 \rangle - 3\langle E^2 \rangle U + 2U^3 \langle (\Delta E)^3 \rangle$$

Now that we know that we are just calculating the second partial of U with respect to β , we just take the derivative,

$$\langle (\Delta E)^3 \rangle = \left(\frac{\partial^2 U}{\partial \beta^2} \right)_{E_r} = -kT^2 \left[\frac{\partial}{\partial T} (-kT^2 C_v) \right]_V$$

which is equivalent to the desired quantity. Now for an ideal gas, substitute

$$U = \frac{3}{2} NkT \text{ and } C_v = \frac{3}{2} Nk$$

$$\left\langle \left(\frac{\Delta E}{U} \right)^2 \right\rangle = \frac{kT^2 C_V}{U^2} = \frac{kT^2 (\frac{3}{2} Nk)}{(\frac{3}{2} NkT)^2} = \frac{2}{3N}$$

$$\left\langle \left(\frac{\Delta E}{U} \right)^3 \right\rangle = \frac{1}{U^3} k^2 T^2 \left[2T \left(\frac{3}{2} Nk \right) + T^2 \left(\frac{\partial (\frac{3}{2} Nk)}{\partial T} \right)_V \right] = \frac{k^2 T^2}{\frac{27 N^3 k^3 T^3}{8}} [3TNk] = \frac{8}{9N^2}$$

□

Exercise 2. Show that, for a statistical system in which the interparticle potential energy $u(\vec{r})$ is a homogenous function (of degree n) of the particle coordinates, the *virial* V is given by

$$V = -3PV - nU$$

and, hence, the *mean kinetic energy* K by

$$K = -\frac{1}{2}V = \frac{1}{2}(3PV + nU) = \frac{1}{(n+2)}(3PV + nE);$$

here, U denotes the *mean potential energy* of the system while $E = K + U$. Note that this result holds not only for a classical system but for a quantum-mechanical one as well.

Solution. We apply the *virial equation of state* to identify the contribution to the virial of interactions between particles which becomes,

$$-\sum_{i < j} \frac{\partial u * r_{ij}}{\partial r_{ij}} r_{ij} = -\sum r \frac{\partial u}{\partial r} = -nU$$

where U is the average potential of the system. Considering the contribution of the virial of a noninteracting system (3.7.12) $-3PV$, we get

$$V = -3PV - nU$$

From (3.7.14) we have the relation $V = -2K$ which implies $K = -\frac{V}{2}$ and

$$K = -\frac{3PV - nU}{2}$$

and the rest of the result is done in the problem. \square

Exercise 3. (a) When a system of N oscillators with total energy E is in thermal equilibrium, what is the probability p_n that a particular oscillator among them is in the quantum state n . [Hint: Use expression (3.8.25).]

Show that, for $N \gg 1$ and $R \gg n$, $p_n \approx (\bar{n})^n / (\bar{n} + 1)^{n+1}$, where $\bar{n} = R/N$.

(b) When an ideal gas of N monatomic molecules with total energy E is in thermal equilibrium, show that the probability of a particular molecule having an energy in the neighborhood of ϵ is proportional to $e^{-\beta\epsilon}$, where $\beta = 3N/2E$. [Hint: Use expression (3.5.16) and assume that $N \gg 1$ and $E \gg \epsilon$.]

Solution.

(a) The hint refers us to expression (3.8.25) which gives the number of permutations that can be realized by shuffling R objects with $(N-1)$ partitioning lines along a row,

$$\frac{(R+N-1)!}{R!(N-1)!}$$

We want to find the number of microstates corresponding to this system. We have $N \rightarrow N-1$, $E \rightarrow E - (n + \frac{1}{2})\hbar\omega$, $R \rightarrow R - n$, so

$$\frac{(R+N-1)!}{R!(N-1)!} \rightarrow \frac{(R-n+N-2)!}{(R-n)!(N-2)!}$$

and we divide by the total number of microstates to get the probability of this state arising,

$$P_n = \frac{(R-n+N-2)!}{(R-n)!(N-2)!} / \frac{(R+N-1)!}{R!(N-1)!}$$

To find P_n in the limit requested, consider

$$\frac{P_{n+1}}{P_n} = \frac{R-n}{R-n+N-2} \approx \frac{R}{R+N} \frac{\bar{n}}{\bar{n}+1}$$

So we can construct a formula by induction on a base element P_0 ,

$$P_n = P_0 \left(\frac{\bar{n}}{\bar{n} + 1} \right)^n$$

But then,

$$P_0 = \frac{N - 1}{R + N - 1} \approx \frac{-1}{\bar{n} + 1}$$

and substituting,

$$P_n = \left(\frac{\bar{n}^n}{(\bar{n} + 1)^{n+1}} \right)$$

(b) We are told to start with (3.5.16),

$$g(E) \approx \frac{1}{N!} \left(\frac{V}{h^3} \right)^N \frac{(2\pi m)^{3N/2}}{((3N/2) - 1)!} E^{(3N/2) - 1}$$

Our probability is proportional to the density of states, so the probability is proportional to

$$(E - \epsilon)^{\frac{3}{2}(N-1) - 1}$$

which in the limit of $1 \ll N$ is $(1 - \frac{\epsilon}{E})^{\frac{3}{2}N}$. In the limit of $\epsilon \ll -E$, we further reduce the proportionality to $e^{\frac{-3N\epsilon}{2E}}$.

□

Exercise 4. The energy levels of a quantum-mechanical, one-dimensional, anharmonic oscillator may be approximated as

$$\epsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega - x \left(n + \frac{1}{2} \right)^2 \hbar\omega; \quad n \in \mathbb{Z}^+$$

The parameter x , usually $\ll 1$, represents the degree of anharmonicity. Show that, to the first order in x and the fourth order in $u (= \hbar\omega/kT)$, the specific heat of a system of N such oscillators is given by

$$C = Nk \left[\left(1 - \frac{1}{12}u^2 + \frac{1}{240}u^4 \right) + 4x \left(\frac{1}{u} + \frac{1}{80}u^3 \right) \right].$$

Note that the correction term here increases with temperature.

Solution. To find C , we must first find Q . For a single oscillator of this type, we have

$$Q(\beta) = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega + \beta x(n+\frac{1}{2})^2 \hbar\omega}$$

which in the limit of $x \ll 1$ becomes,

$$Q(\beta) = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} \left(1 + \beta x(n + \frac{1}{2})^2 \hbar\omega + \dots \right)$$

Now we consider the power series expansion of $e^{-\beta(n+\frac{1}{2})\hbar\omega}$ with each of the terms of the other exponential power series expansion. Let $u = \beta\hbar\omega$. By expanding as exponentials we find an equivalence with the exponential identity of the sinh function (using Mathematica),

$$\sum_{n=0}^{\infty} e^{-u(n+\frac{1}{2})} = \frac{1}{2 \sinh(\frac{1}{2}u)}$$

The second order term,

$$\sum_{n=0}^{\infty} e^{-u(n+\frac{1}{2})} \left(n + \frac{1}{2} \right)^2 = \left(4 \sinh(\frac{1}{2}u) \right)^{-1} \left(\coth^2(\frac{1}{2}u) - \frac{1}{2} \right)$$

Taking the natural log

$$\ln Q \approx -\ln\left(2\sinh\left(\frac{1}{2}u\right)\right) + \frac{1}{2}xu\left(\coth^2\left(\frac{1}{2}u\right) - \frac{1}{2}\right)$$

Taking the power series expansion of the first part and finding the contribution to the internal energy then the contribution to the specific heat we get

$$C = Nk\left(1 - \frac{1}{12}u^2 + \frac{1}{240}u^4\right)$$

Now for the second part (not done in 3.8.20/21) we take the power series in u ,

$$x\left[\frac{2}{u} + \frac{u}{12} + \frac{u^3}{120} + \dots\right]$$

which contributes to the internal energy per oscillator,

$$x\hbar\omega\left[\frac{2}{u^2} - \frac{1}{12} - \frac{u^2}{40} - \dots\right]$$

which contributes to the specific heat.

$$xk\left[\frac{4}{u} + \frac{u^2}{20} + \dots\right]$$

and summing these specific heat contributions we get the desired result. \square

Exercise 5. (a) Consider a gaseous system of N noninteracting, diatomic molecules, each having an electric dipole moment μ , placed in an external electric field of strength E . The energy of such a molecule will be given by the kinetic energy of rotation as well as translation plus the potential energy of orientation in the applied field:

$$\epsilon = \frac{p^2}{2m} + \left\{ \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} \right\} - \mu E \cos \theta$$

where I is the moment of inertia of the molecule. Study the thermodynamics of this system, including the electric polarization and the dielectric constant. Assume that (i) the system is a classical one and (ii) $|\mu E| \ll kT$.

(b) The molecule H_2O has an electric dipole moment of 1.85×10^{-18} e.s.u. Calculate, on the basis of the preceding theory, the dielectric constant of steam at 100 C and at atmospheric pressure.

Solution.

(a) We begin by finding the partition function,

$$Q_N = \frac{1}{N!} Q_1^N$$

where $Q_1 = \frac{V}{\lambda^3} Z$ and Z is the rotational component.

$$\begin{aligned} Z &= \int e^{-\beta\left(\frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} - \mu E \cos \theta\right)} \frac{dp_\theta dp_\phi d\theta d\phi}{h^2} = \int_0^\pi \left(\frac{2\pi I}{\beta}\right)^{\frac{1}{2}} \left(\frac{2\pi I \sin^2 \theta}{\beta}\right)^{\frac{1}{2}} e^{-\beta\mu E \cos \theta} \frac{2\pi d\theta}{h^2} \\ &= \frac{2 \sinh(\beta E)}{\beta \mu E} \frac{I}{\beta \hbar^2} \end{aligned}$$

To find the polarization we find first the net dipole moment,

$$M_z = N \langle \mu \cos \theta \rangle = \frac{N}{\beta} \frac{\partial \ln Z}{\partial E} = N \mu \left(\coth(\beta \mu E) - \frac{1}{\beta \mu E} \right)$$

In the limit $\mu E \ll kT$,

$$M_z \approx \frac{1}{3} N \mu^2 \beta E$$

and

$$P \approx \frac{n \mu^2 E}{3kT}$$

with the dielectric constant finally given by

$$\epsilon = \frac{E + e\pi P}{E} \approx 1 + \frac{4\pi n \mu^2}{3kT}$$

(b) Plugging in values we get that the dielectric constant is,

$$\epsilon \approx 1 + \frac{4\pi n \mu^2}{3kT} = 1 + \frac{4\pi(31.1)(1.85 * 10^{-18})^2}{3(8.62 * 10^{-5}) * 373.15} = 1.00$$

to find n we take $P = nkT \implies n = \frac{P}{kT} = \frac{1}{8.62 * 10^{-5} * 373.15} = 31.1$.

□