

Stat Mech Summer 2014

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1. Consider a system of N non-interacting diatomic molecules at temperature T inside a volume V . Let the Hamiltonian function of a single molecule be given by

$$H(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}_1, \mathbf{r}_2) = \frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2m} + \alpha \frac{|\mathbf{r}_1 - \mathbf{r}_2|^2}{2}$$

- (a) Derive the expression for the classical canonical partition function, and show that it is of the form $Z(T, V, N) = c_N V^N (kT)^{9N/2}$ where c_N is a function of N .
(b) Derive an equation of state of the form $f(p, T, V, N) = 0$.
(c) Find the heat capacity at constant volume $C_v(T, V, N)$

- (a) For the classical continuous partition function, we must integrate over the phase space density. Since the particles are non-interacting, we have the factorization

$$Z = (Z_1)^N.$$

In addition, the momentum and spatial dependence in the hamiltonian factorizes (when used in the Boltzmann factor $e^{-\beta H}$, so

$$Z_1 = \frac{1}{h^6} \iiint_{-\infty}^{\infty} d^3 p_1 d^3 p_2 e^{-\beta \left(\frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2m} \right)} \iiint_{-L/2}^{L/2} d^3 q_1 d^3 q_2 e^{-\beta \alpha \left(\frac{|\mathbf{r}_1 - \mathbf{r}_2|^2}{2} \right)}$$

For the purpose of this problem, the quantization of the momentum eigenvalues $k = \frac{2\pi}{L}n$ subject to boundary conditions $\psi(x) = \psi(x + L)$ has been done in a box centered at the origin. This way our position integral runs over even bounds, which allow us to evaluate the Gaussian at infinity.

For the momentum portion, we need only evaluate a single instance of

$$\iiint_{-\infty}^{\infty} d^3 p e^{-\frac{\beta}{2m} \mathbf{p}^2} = \left(\frac{2m\pi}{\beta} \right)^{3/2}.$$

Now, for the spring potential, the Gaussian at finite limits gives us a error function (not useful). The only realistic way of getting a sensible answer here is to take $L \rightarrow \infty$

$$\lim_{L \rightarrow \infty} \iiint_{-L/2}^{L/2} d^3 q_1 d^3 q_2 e^{-\beta \alpha \left(\frac{|\mathbf{r}_1 - \mathbf{r}_2|^2}{2} \right)}$$

The only relevant integral here is

$$\iint_{-\infty}^{\infty} dq_1 dq_2 e^{-\frac{\beta \alpha}{2} (q_1 - q_2)^2} = \sqrt{\frac{2\pi}{\beta \alpha}}$$

Even when you are integrating over another variable (such as q_2), the result will never depend on q_2 . You would think it would have to if you break up the Gaussian as

$$e^{-\frac{\beta\alpha}{2}(x_1^2-2x_1x_2)}e^{-\frac{\beta\alpha}{2}x_2^2}$$

yet the result comes out exactly the same. I guess the point is the integral will always be $\sqrt{\frac{2\pi}{\beta\alpha}}$ irrespective of any possible q_2 value. Anyway, the position integrals are now

$$\lim_{L \rightarrow \infty} \iiint_{-L/2}^{L/2} d^3q_1 d^3q_2 e^{-\beta\alpha\left(\frac{|\mathbf{r}_1-\mathbf{r}_2|^2}{2}\right)} = \left(\frac{2\pi}{\beta\alpha}\right)^{3/2} V$$

The single particle partition function is then

$$Z_1 = \frac{1}{h^6} V \left(\frac{2m\pi}{\beta}\right)^3 \left(\frac{2\pi}{\beta\alpha}\right)^{3/2} = \frac{V}{h^6} \left(\frac{(2\pi)^3 m^2}{\alpha}\right)^{3/2} \left(\frac{1}{\beta}\right)^{9/2}$$

I am not sure on this, but it is my belief that we should divide by $2!$. The reasoning is that we should not be able to distinguish between a diatomic molecule that has been rotated by π about the difference vector $|\mathbf{r}_1 - \mathbf{r}_2|$. With Z_1 in hand, we raise it to the N power for N molecules and also divide by $N!$ since the diatomic molecule are indistinguishable. Hence we finally arrive at

$$Z = \frac{1}{h^{6N} 2^N N!} \left(\frac{(2\pi)^3 m^2}{\alpha}\right)^{3N/2} V^N (kT)^{9N/2}.$$

(b) We use the thermodynamic connection

$$F = -kT \ln Z.$$

From this, we should be able to find pressure as a function of T, V, N

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

Let's denote

$$\gamma^{3N/2} = \left(\frac{(2\pi)^3 m^2}{2^{2/3} h^4 \alpha}\right)^{3N/2}$$

then

$$Z = \frac{\gamma^{3N/2}}{N!} V^N (kT)^{9N/2}$$

$$-kT \ln Z = -kT \left[\frac{3N}{2} \ln \gamma - N \ln N + N + N \ln V + \frac{9N}{2} \ln(kT) \right]$$

$$p = \frac{NkT}{V}.$$

or

$$f(p, T, V, N) = p - \frac{NkT}{V} = 0.$$

(c) We may find the internal energy by

$$U = -\frac{\partial}{\partial \beta} \ln Z.$$

$$U = -\frac{\partial}{\partial \beta} \left(-\frac{9N}{2} \ln \beta \right) = \frac{9N}{2} kT$$

then

$$C_V = \frac{9N}{2} k.$$

2. Find the probability distribution $P(\omega_1, \omega_2, \omega_3)$ for the angular velocities ω_i , $i = 1, 2, 3$ in 3D rotation of polyatomic molecules in a classical ideal gas at the temperature T . The respective principal moments of inertia of this molecule are I_1, I_2, I_3 . From the distribution P , determine the mean squares of angular velocity $\langle \omega^2 \rangle$ and angular momentum $\langle \mathbf{L}^2 \rangle$ of a molecule.

The probability distribution of a single particle, in this classical case, is just

$$\frac{e^{-\beta H}}{Z}$$

used in the form

$$\langle A \rangle = \frac{1}{h^3} \iiint d^3p d^3q \frac{e^{-\beta H(p,q)}}{Z} A(p, q).$$

The hamiltonian is that due to the kinetic energy of rotation

$$H = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}.$$

In 3D we have an inertia tensor with principle moments of inertia (all lying orthogonal to each other) and we can thus formulate the hamiltonian as

$$H = \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3}.$$

I would think we should be able to transform from a phase space in p, q to L, q so that

$$\begin{aligned} Z &= \frac{1}{h^3} \iiint_{-\infty}^{\infty} dL_1 dL_2 dL_3 \int d\Omega e^{-\beta H} \\ &= \frac{4\pi}{h^3} \prod_{i=1}^3 \int_{-\infty}^{\infty} dL_i e^{-\beta \frac{L_i^2}{2I_i}} \\ &= \frac{4\pi}{h^3} \prod_{i=1}^3 \sqrt{\frac{2\pi I_i}{\beta}} \\ &= \frac{4\pi}{h^3} \left(\frac{2\pi}{\beta} \right)^{3/2} \sqrt{I_1 I_2 I_3}. \end{aligned}$$

To find the mean square of angular velocity, we note

$$\omega^2 = \sum_i \left(\frac{L_i}{I_i} \right)^2.$$

Compute the following

$$\langle \omega_1^2 \rangle = \frac{1}{h^3} \iiint dL_1 dL_2 dL_3 \frac{e^{-\beta H}}{Z} \left(\frac{L_1}{I_1} \right)^2$$

$$= \frac{4\pi}{h^3} \left(\frac{2\pi}{\beta} \right) \sqrt{I_2 I_3} \frac{1}{Z I_1^2} \int_{-\infty}^{\infty} dL_1 e^{-\beta \left(\frac{L_1^2}{2I_1} \right)} L_1^2$$

I won't evaluate the rest, but the calculation is clear.

3. Consider an ideal Fermi gas of particles with two interconverting species 1 and 2, such as two hyperfine states in an atom. Suppose it is possible to effect the conversion in such a way that an atom picks up an added energy $\Delta\epsilon$ when it moves from species 1 to species 2, and loses energy $\Delta\epsilon$ in the reverse transition. This could happen, say, if an off-resonant microwave field is transferring atoms between the species. Write the total density of the gas 2ρ , and denote the densities of the individual species by $\rho_{1,2} = \rho \mp \frac{1}{2}\Delta\rho$.

- (a) Given the global temperature and pressure, and the energy difference, the equilibrium condition for the two species is $\mu_1 + \Delta\epsilon = \mu_2$. Why?
- (b) Show that for a small energy difference $\Delta\epsilon$ and at zero temperature, the density difference equals

$$\Delta\rho = \frac{3\rho}{\epsilon_F} \Delta\epsilon$$

where ϵ_F is the Fermi energy of a single species at the density ρ .

- (a) Ultimately, this comes down to just arguing that the change in free energy as we move from one species to another must increase by $\Delta\epsilon$. Typically we try to make an equilibrium argument as

$$dG(p, T)_{eq} = 0$$

$$dN_1 = -dN_2 \equiv dN$$

$$dG = dG_1 + dG_2 = dN(\mu_1 - \mu_2) = 0.$$

As we go from species $1 \rightarrow 2$ the change in Gibbs energy is

$$\Delta G_{1 \rightarrow 2} = -\mu_1 + \mu_2 + \Delta\epsilon$$

and as we go from $2 \rightarrow 1$

$$\Delta G_{2 \rightarrow 1} = \mu_1 - \mu_2 - \Delta\epsilon$$

and if $\Delta G = 0$ for both cases it must be that

$$\mu_1 = \mu_2 + \Delta\epsilon.$$

- (b) From the last equation we are looking for $\rho_2 - \rho_1$. The density in each case may be found by integrating up to the fully occupied fermi energy ϵ_F

$$\rho_1 = \frac{g}{6\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon_F^{3/2}$$

$$\rho_2 = \frac{g}{6\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} (\epsilon_F + \Delta\epsilon)^{3/2}$$

The fermi energy for species two has the additional energy term. Now we simply take the difference for $\Delta\epsilon$ small and denote $\rho_1 \approx \rho$. We expand the small energy term using the binomial expansion. We end up with

$$\Delta\rho = \frac{3\rho}{2\epsilon_F} \Delta\epsilon$$

4. Collective elementary excitations called *spin waves* or *magnons* determine the low-T specific heat of a spin system that has undergone the ferromagnetic phase transition. For a small wave vector \mathbf{k} the dispersion relation of magnons is $\omega(k) \propto k^2$. What is the temperature dependence of the heat capacity of magnons at low temperatures?

Hint: As usual in three dimensions, at least at low energies the density of states as a function of the wave number $k = |\mathbf{k}|$ is proportional to k^2 .

It seems that excitations of a particular field are mediated by *massless* bosons. This means that these bosonic excitations probably do not conserve particle number and hence we set the chemical potential to zero. In this event, the occupations are

$$\langle n_{\mathbf{k}} \rangle = \frac{1}{e^{\beta \epsilon_k} - 1}$$

Let's define the dispersion relation as $\epsilon(k) = \alpha k^2$ then we can find the energy as

$$U = \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle \epsilon(k) \rightarrow 4\pi\alpha \left(\frac{L}{2\pi} \right)^3 \int_0^\infty dk \frac{k^4}{e^{\alpha\beta k^2} - 1}$$

In the low temperature approximation, $\beta \rightarrow \infty$ and so it seems justified that we should be able to integrate over the full range of wavevectors. We need to convert this to a dimensionless integral to determine the T dependence

$$U = \gamma/2 \left(\frac{1}{\alpha\beta} \right)^{5/2} \int_0^\infty d(\alpha\beta k^2) \frac{\alpha\beta k^2 \sqrt{\alpha\beta k^2}}{e^{\alpha\beta k^2} - 1}$$

and so we have

$$U \propto T^{5/2}$$

and

$$C_V \propto T^{3/2}.$$