PHYS 427 - Thermal and Statistical Physics - Discussion 13

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1. **Diffusion in three dimensions**: A drop of red dye is deposited into the center of a large tub of still water. The dye particles are jostled around randomly by collisions with thermally agitated water molecules. Over time, the dye particles *diffuse* through the water, i.e. the drop of dye spreads out.

   Let $n(\boldsymbol{r}, t)$ denote the number density of dye particles, where $\boldsymbol{r} = x\hat{\boldsymbol{x}} + y\hat{\boldsymbol{y}} + z\hat{\boldsymbol{z}}$ is the position vector.

   (a) The total number of particles contained within an arbitrary subvolume V is

   $$N(t) = \int_V n(\boldsymbol{r}, t) d^3 r. \tag{1}$$

   The only way for $N(t)$ to change is if particles enter or leave V. Mathematically, this is expressed as

   $$\frac{dN}{dt} = -\int_{\partial V} \boldsymbol{J} \cdot d\boldsymbol{A}, \tag{2}$$

   where $\int_{\partial V}$ denotes a surface integral over the boundary ∂V of the subvolume. We have introduced $\boldsymbol{J}$, the *particle current density*, such that $\boldsymbol{J} \cdot d\boldsymbol{A}$ is the number of particles per second going *out* of the surface element $d\boldsymbol{A}$.

   Using the divergence theorem of multivariate calculus, show that (2) is equivalent to the *continuity equation*

   $$\frac{\partial n}{\partial t} + \boldsymbol{\nabla} \cdot \boldsymbol{J} = 0. \tag{3}$$

   (b) Under certain approximations, in the lecture you will derive Fick's law,

   $$\boldsymbol{J} = -D\boldsymbol{\nabla} n, \tag{4}$$

   where $D > 0$ is a constant called the *diffusion coefficient*. For now, just notice that this is the simplest, most intuive law one could have—it says that particles flow toward less dense regions, which tends to smooth out variations in density. When Fick's law is inserted into the continuity equation, we get the *diffusion equation*

   $$\frac{\partial n}{\partial t} - D\nabla^2 n = 0. \tag{5}$$

(c) Show that

$$n(\boldsymbol{r}, t) = \frac{N_0}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt} \tag{6}$$

is a solution of the diffusion equation, where $r = \sqrt{x^2 + y^2 + z^2}$ and N_0 is a constant. *Hint: recall* $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.

(d) Sketch (6) as a function of r at various times. Is this what you expect a drop of dye to do?

(e) Show that

$$\int_{\text{all space}} n(\boldsymbol{r}, t) d^3 r = N_0 \tag{7}$$

is the total number of dye particles[1]. *Hint:* $\int_{-\infty}^{\infty} e^{-\alpha x} dx = \sqrt{\pi/\alpha}$.

(f) Show that

$$\langle r^2 \rangle \equiv \frac{\int_{\text{all space}} d^3 r \; r^2 n(\boldsymbol{r}, t)}{\int_{\text{all space}} d^3 r \; n(\boldsymbol{r}, t)} = 6Dt. \tag{8}$$

Hint: first observe that $\int d^3 r \; r^2 e^{-\alpha r^2} / \int d^3 r \; e^{-\alpha r^2} = -\frac{d}{d\alpha} \ln \left(\int d^3 r \; e^{-\alpha r^2} \right)$.

You have shown that

$$r_{rms} \equiv \sqrt{\langle r^2 \rangle} = \sqrt{6Dt}. \tag{9}$$

That is, the root-mean-square position of a dye particle, which is some measure of the "average" displacement of a dye particle from the origin, increases as $t^{1/2}$ over time. This is the characteristic time-dependence of diffusive processes. If the diffusion constant D is bigger, then the dye particle will move more quickly on average, but still as $t^{1/2}$. This $t^{1/2}$ behavior occurs for diffusion in any number of dimensions, not just three.

(g) Suppose it takes the dye about five minutes to diffuse appreciably throughout a cup of water. Estimate the value of D. *Answer:* $D \approx 10^{-4}$ m^2 s^{-1}.

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2. **Paramagnet (review)**: A simple model for a paramagnet consists of a lattice with N sites, each of which can be in either a "spin up" or "spin down" state. The spins do not interact with each other, but each spin interacts with the external magnetic field. If a spin is "up", it contributes an energy μB. If it is "down", it contributes an energy $-\mu B$.

(a) Consider the paramagnet as a closed system with fixed energy U, compute the entropy.

(b) Plot the entropy as a function of U. For what values of U is the temperature negative?

(c) Suppose the paramagnet is prepared with a negative temperature. If it is put into thermal contact with a "normal" system, i.e. one which can only have a positive temperature, which way will energy spontaneously flow?

[1]Note that this doesn't change over time. This is a consequence of the assumption of particle number conservation that went into the derivation of the continuity equation in part (a).

3. **Rotational partition function (review)**: Consider a diatomic molecule whose moment of inertia is I. The center of mass of the molecule is at rest, but it is allowed to rotate. In quantum mechanics, one finds that the energy eigenstates are labelled by two integers $\ell = 0, 1, 2, \ldots$ and $m = -\ell, -\ell+1, \ldots, \ell$ with corresponding energies

$$E_{\ell m} = \frac{\hbar^2}{2I}\ell(\ell+1). \tag{10}$$

Note that the energy does not depend on m.

(a) Suppose the molecule is in contact with a thermal reservoir. Express its canonical partition function as a sum over ℓ only.

(b) Keeping the two smallest terms, write down an approximate form for Z which is valid at very low temperature. What does "very low temperature" mean quantitatively? (use the symbol $\gg$ in your answer)

(c) Show that the average rotational energy at low temperatures is

$$U_{\text{rot}} \approx E_{00}\left(1 + 3e^{-E_{00}/k_BT}\right) \tag{11}$$

(d) At very high temperature, the sum in Z can be approximated by an integral. Justify this statement and evaluate the integral to obtain an approximate expression for Z. *Answer:* $Z \approx k_BT/E_{00}$.

(e) Compute the average rotational energy at high temperatures.

(f) Use your answers to (c) and (e) to make a rough sketch of the graph of $U_{\text{rot}}(T)$ over all temperatures. Roughly indicate where $T = E_{00}/k_B$ is located on this sketch.

(g) Calculate the heat capacity of the molecule at high temperatures. Does your result agree with the equipartition theorem?

4. **2d magnon gas (review)**: Magnons are quantized spin-waves; they are <u>bosonic</u> collective excitations that emerge in the low-temperature description of certain models of magnetism. Magnons are analogous to phonons, which are quantized sound waves that emerge when analyzing the vibrations of a crystal lattice using quantum mechanics.

   Consider a system of N spins on a 2d square lattice, and assume the low-energy description of the system is a non-interacting gas of magnons with energies $\varepsilon_{\vec{k}} = \hbar\omega_{\vec{k}}$, where

   $$\omega_{\vec{k}} = \frac{Ja^2}{2}|\vec{k}|^2. \tag{12}$$

   In this dispersion relation, "J" represents the coupling between neighbouring spins and "a" is the lattice spacing. Because of the discrete structure of the lattice, the wavevectors are quantized according to $\vec{k} = \pi\vec{n}/L$ where $n_x = 1, 2, \ldots, N_x$ and $n_y = 1, 2, \ldots, N_y$ with $L = N_x a = N_y a$ and $N = N_x N_y$.

   Furthermore, although the original degrees of freedoms are spins, there is only one "type" of magnon (i.e. there is no spin degeneracy as one might guess).

   (a) Compute the magnon density of states $\mathcal{D}(\omega)$ and the Debye frequency ω_D.

   That is, show for $N \gg 1$ (the thermodynamic limit) that we can replace certain sums over wavevectors by an integral over frequency, namely

   $$\sum_{\vec{k}} F(\omega_{\vec{k}}) \approx \int_0^{\omega_D} d\omega\, \mathcal{D}(\omega) F(\omega), \tag{13}$$

   where $F(\omega)$ is an arbitrary function.

   (b) Compute the energy of the system as a function of temperature. *Note: your final answer can be left in terms of a dimensionless integral.*

   (c) Show that the heat capacity goes like T at low temperatures and approaches a constant at high temperatures. Compute the value of the constant.