Phys 7230

Final Exam

May 5

1 Classical particle in a strange potential

A particle of mass m can move in one direction in the potential $U(x)$ (x is the displacement of this particle) such that $U(x) = \infty$ for $x < 0$ and $U(x) = \alpha\, x^{25}$ when $x > 0$ where α is some constant. Calculate the heat capacity of this particle. The particle is completely classical (so that one could use the Bohr-Sommerfeld approximation for its partition function).

Solution

This problem centers on the application of the equipartition theorem (or in fact, of the methods used to derive the equipartition theorem).

The partition function is given by

$$Z = \int \frac{dxdp}{2\pi\hbar} e^{-\frac{p^2}{2mT} - \frac{U(x)}{T}} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp\, e^{-\frac{p^2}{2mT}} \int_0^\infty dx\, e^{-\frac{\alpha x^{25}}{T}}. \tag{1.1}$$

Change variables according to $p = \sqrt{T} s$, $x = T^{\frac{1}{25}} u$, to find

$$Z = T^{\frac{27}{50}} \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} ds\, e^{-\frac{s^2}{2m}} \int_0^\infty du\, e^{-\alpha u^{25}} = T^{\frac{27}{50}} C, \tag{1.2}$$

where C is a temperature independent constant whose precise value is not relevant.

The Helmholtz free energy is

$$F = -T \ln Z = -\frac{27}{50} T \ln T - T \ln C. \tag{1.3}$$

The entropy is

$$S = -\frac{\partial F}{\partial T} = \frac{27}{50} \ln T + \frac{27}{50} + \ln C. \tag{1.4}$$

The heat capacity is

$$C = T \frac{\partial S}{\partial T} = \frac{27}{50}. \tag{1.5}$$

2 Degenerate Fermi gas in a gravitational potential

A degenerate $T = 0$ Fermi gas of spin-1/2 electrons sits in a rectangular box, of infinite height and with the area of its bottom surface A, in the presence of the gravitational force mg acting on each electron. (In practice, the gravitational field is very weak and almost never needs to be taken into account in problems involving such small particles as electrons, but for the purpose of this problem let's assume that it is not weak, or that some other force mimics a strong gravitational field acting on the electrons).

Calculate the total number N of electrons in this gas if its Fermi energy is ϵ_F. Use the Bohr-Sommerfeld approximation in the calculation of the partition function.

Solution

The Fermi-Dirac distribution, when applied to this problem, states that

$$N = 2 \int \frac{d^3p \; dxdydz}{(2\pi\hbar)^3} \frac{1}{e^{\frac{p^2}{2mT} + \frac{mgz}{T} - \frac{\mu}{T}} + 1}. \tag{2.1}$$

Here 2 in front is the number of spin polarizations. For definiteness, let us say z is the distance from the bottom of the box in the upward direction.

The degenerate Fermi gas limit is achieved as $T \to 0$, or

$$N = 2 \int dxdydz \int \frac{d^3p}{(2\pi\hbar)^3} \, \theta \left(\epsilon_F - \frac{p^2}{2m} - mgz \right). \tag{2.2}$$

Here θ is the Heaviside's step function, which is zero if its argument is negative, and 1 if it is positive. ϵ_F is the Fermi energy, which is nothing but the chemical potential μ at $T = 0$.

It is easiest to do the integral over p first. This gives the volume of the sphere of radius $r = \sqrt{2m}\sqrt{\epsilon_F - mgz}$. Thus

$$N(z) \equiv 2 \int \frac{d^3p}{(2\pi\hbar)^3} \, \theta \left(\epsilon_F - \frac{p^2}{2m} - mgz \right) = \frac{2}{(2\pi\hbar)^3} \frac{4}{3} \pi \left[(\epsilon_F - mgz) 2m \right]^{\frac{3}{2}}. \tag{2.3}$$

Now $N(z)$ turns to zero if $z > \epsilon_F/(mg)$. So the integral becomes

$$N = \int dxdydz \, N(z) = A \int_0^{\epsilon_F/(mg)} dz \, N(z) = \frac{4\sqrt{2}A}{15} \frac{\sqrt{m\epsilon_F^5}}{g\pi^2\hbar^3}. \tag{2.4}$$

3 Our favorite - absorbing sites!

An absorbing surface consists of 2 sites, A and B. Site A can absorb no more than one atom, while site B can absorb an arbitrary number of atoms. It does not cost any energy to absorb an atom in either of the sites.

The two sites are in equilibrium with a gas of atoms at temperature T. The pressure of this gas is chosen in such a way that the total number of atoms absorbed, on the average, on two sites is N. What is the average number of atoms N_B absorbed in site B?

What is the fluctuation $\left\langle (\delta N_B)^2 \right\rangle$ of the atoms absorbed in this site?

<u>Solution</u>

The site which can absorb only one atom is described by a Fermi-Dirac distribution, while the site which can absorb an infinite number of atoms is described by a Bose-Einstein distribution. All energies are zero, thus we find

$$\frac{1}{e^{-\frac{\mu}{T}}-1}+\frac{1}{e^{-\frac{\mu}{T}}+1}=N. \tag{3.1}$$

This is an equation for μ, in fact a quadratic equation. Its solution reads

$$e^{-\frac{\mu}{T}}=\frac{1+\sqrt{N^2+1}}{N} \tag{3.2}$$

(the second solution is negative and thus unphysical). It follows from here that

$$N_B=\frac{1}{e^{-\frac{\mu}{T}}-1}=\frac{N}{\sqrt{1+N^2}-N+1}. \tag{3.3}$$

The fluctuations are given by

$$\left\langle (\Delta N_B)^2 \right\rangle = T\frac{\partial N_B}{\partial \mu}=\frac{e^{-\frac{\mu}{T}}}{\left(e^{-\frac{\mu}{T}}-1\right)^2}=N\frac{1+\sqrt{1+N^2}}{\left(1-N+\sqrt{1+N^2}\right)^2} \tag{3.4}$$

Useful formulae

Thermodynamic potentials

- Energy $E(S,V,N)$: $dE = TdS - PdV + \mu dN$.
- Enthalpy $H(S,P,N)$: $H = E + PV$, $dH = TdS + VdP + \mu dN$.
- Helmholtz free energy $F(T,V,N)$: $F = E - TS$, $dF = -SdT - PdV + \mu dN$.
- Gibbs free energy $G(T,P,N)$: $G = E - TS + PV$, $dG = -SdT + VdP + \mu dN$. $G = N\mu$.
- Grant canonical potential $\Omega(T,V,\mu)$: $\Omega = E - TS - \mu N$, $d\Omega = -SdT - pdV - Nd\mu$. $\Omega = -PV$.

Canonical ensemble.

- Partition function $Z = \sum_n e^{-\frac{E_n}{T}}$, where E_n are the energy levels of the system.
- Free energy $F = -T\ln Z$. Energy of the system $E = F + TS$. $dF = -SdT - PdV + \mu dN$, $dE = TdS - PdV + \mu dN$.
- Probability that the system's energy is equal to E_n is $p_n = \frac{1}{Z}e^{-\frac{E_n}{T}}$.

Grand canonical ensemble.

- Partition function $Z = \sum_{N,n} e^{-\frac{E_{N,n}}{T} + \frac{\mu N}{T}}$, where $E_{N,n}$ are the energy levels of the system on the assumption that the system has exactly N particles.
- Grand canonical free energy $\Omega = -T\log Z$. $d\Omega = -SdT - PdV - Nd\mu$. $\Omega = F - \mu N$. $\Omega = -PV$.
- Probability that the system's energy is equal to $E_{N,n}$ if it has N particles (where n labels different energy levels of the system on a condition that it has N particles) is $p_{N,n} = \frac{1}{Z}e^{-\frac{E_{N,n}}{T} + \frac{\mu N}{T}}$.

Thermodynamic Fluctuations

- Probability of a fluctuation is proportional to $\sim \exp\left[(\Delta P \Delta V - \Delta T \Delta S)/(2T)\right]$.
- $\langle (\Delta T)^2 \rangle = \frac{T^2}{C_V}$, $\langle (\Delta V)^2 \rangle = -T\left(\frac{\partial V}{\partial P}\right)_T$, $\langle \Delta T \Delta V \rangle = 0$.
- $\langle (\Delta S)^2 \rangle = C_P$, $\langle (\Delta P)^2 \rangle = -T\left(\frac{\partial P}{\partial V}\right)_S$, $\langle \Delta P \Delta S \rangle = 0$.
- $\langle (\Delta N)^2 \rangle = T\left(\frac{\partial N}{\partial \mu}\right)_{T,V}$.

Other formulae

- Heat capacity is the amount of heat pumped into the system to increase its temperature by dT. At fixed volume it is given by $c_v = T\left(\frac{\partial S}{\partial T}\right)_V$. At fixed pressure it is given by $c_p = T\left(\frac{\partial S}{\partial T}\right)_P$. Specific heat is the heat capacity per particle.

- Maxwell relations are relations between derivatives which follow from the fact that partial second derivatives of thermodynamic potentials do not depend on the order of differentiation. For example,

$$dE = TdS - PdV \to \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V.$$

- Quasiclassical approximation to the partition function of a particle

$$Z = \int \frac{d^3x d^3p}{(2\pi\hbar)^3}\, e^{-\frac{p^2}{2mT} - \frac{U(x)}{T}}$$

- Equipartition theorem: specific heat of a quasiclassical system is equal to 1/2 per degree of freedom which enters its energy quadratically.

- Fermi-Dirac and Bose-Einstein grand canonical free energy $\Omega = -Tsg\sum_n \ln\left(1 + s\, e^{-\frac{\epsilon_n}{T} + \frac{\mu}{T}}\right)$, where $s = 1$ for Fermi-Dirac and $s = -1$ for Bose-Einstein distributions and ϵ_n are energy levels of one particle. g is a degeneracy of each single particle level (due to spin, for example).

- Bose-Einstein distribution $N = N_0 + \int \frac{d^3p\ d^3x}{(2\pi\hbar)^3} \frac{1}{e^{\frac{p^2}{2mT} - \frac{\mu}{T}} - 1}$, where N is the total number of particles, and N_0 are the particles in the condensate. $N_0 = 0$ at $T > T_c$, while $\mu = 0$ at $T < T_c$. It is assumed here that $g = 1$.

- Fermi-Dirac distribution

$$N = g \int \frac{d^3p\ d^3x}{(2\pi\hbar)^3} \frac{1}{e^{\frac{p^2}{2mT} - \frac{\mu}{T}} + 1}.$$