Problems for the course FYS4130

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Chapter 4

Basic principles of statistical mechanics

4.6. The partition function for a system of some kind of particles is

$$Z_N = \left[(V - Nb)/\lambda^3\right]^N \exp(\beta a N^2/V)\,,$$

where

$$\lambda = \sqrt{2\pi\hbar^2/mk_BT}$$

and a and b are constants, V is the volume and N is the number of particles; all other symbols have their usual meaning.

(a) Find the internal energy $E(N,T,V)$.

(b) Find the pressure $P(N,T,V)$.

(c) Find the entropy $S(N,T,V)$.

(d) Is this expression for S a valid fundamental relation, except perhaps at $T = O$? If not, what is wrong, and how can Z_N be appropriately corrected?
Hint: Recall Gibbs paradox.

Solution 4.6

(a) Since $E = -\partial \ln Z/\partial\beta$ with $\beta \equiv (k_BT)^{-1}$ we rewrite the partition function as

$$\ln Z_N = N\ln(V - Nb) - 3N\ln\lambda + \beta a N^2/V$$

with $\lambda = \sqrt{\beta\hbar/m}$. Having in mind that $\partial\lambda/\partial\beta = 1/2\beta = k_BT/2$ we get:

$$E = (3/2)Nk_BT - aN^2/V\,.$$

(b) Let us define the Helmholtz free energy

$$F = -k_B T \ln Z_N = -k_B T \left[N \ln(V - Nb) - 3N \ln \lambda + \beta a N^2/V \right] .$$

We have

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{N k_B T}{V - Nb} + \frac{aN^2}{V^2} .$$

(c)

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} \\ &= N k_B \left[\frac{3}{2} + \ln \frac{V - Nb}{\lambda^3} \right] . \end{aligned}$$

(d) Entropy is not an additive quantity. The states created by permutation of the particles are actually the same, so the partition function Z_N should be divided by $N!$. In the main approximation it will result in the expression

$$S = N k_B \left[\frac{3}{2} + \ln \frac{v - b}{\lambda^3} \right] , \quad v \equiv V/N .$$

Another point is that the entropy does not vanish as $T \to 0$. One cannot correct this property within classical statistics.

4.8. Calculate the partition function and the free energy for an ideal classical gas consisting of N molecules at temperature T contained in a vessel and subjected to a centrifugal force $-M\omega^2 z^2/2$, where z is the distance of the particle from the axis of rotation and ω is the angular velocity of rotation of the centrifuge.

Solution 4.8: When the external field is present, the integrand in the partition function contains an extra factor $e^{-\beta U}$ where $U \equiv -M\omega^2 z^2/2$. Then one has to replace volume in the usual expression for the partition function by $\int d^3 r\, e^{-\beta U}$. This procedure yields an extra factor

$$\begin{aligned} \frac{1}{V} \int d^3 r\, e^{-\beta U} &= \frac{2\pi L}{\pi R^2 L} \int_0^R z\, dz\, e^{\beta M \omega^2 z^2/2} \\ &= \frac{2}{\beta M \omega^2 R^2} \int_0^{\beta M \omega^2 R^2/2} d\eta\, e^{\eta} = \frac{2}{\beta M \omega^2 R^2} \left(e^{\beta M \omega^2 R^2/2} - 1 \right) . \end{aligned}$$

Thus,

$$Z = \frac{2 Z_0}{\beta M \omega^2 R^2} \left(e^{\beta M \omega^2 R^2/2} - 1 \right) , \quad F = F_0 - N k_B T \ln \frac{2 k_B T}{M \omega^2 R^2} \left(e^{M \omega^2 R^2/2 k_B T} - 1 \right) .$$

4.9. Consider an ideal monoatomic gas of N molecules in the presence of an external magnetic field H, where each molecule behaves as an Ising spin. Calculate the free energy, energy, and entropy and interpret the result physically. Find the limit of S at $T \to 0$.

Solution 4.9: The energy of the Ising spin Sin magnetic field can be written as $U = -\mu S_H H$ where S_H acquires the values $\pm S$. Consequently, the partition function can be written as

$$Z_1 = Z_0 \cdot \sum_{\pm} e^{\mp\beta\mu SH} = 2\cosh(\beta\mu SH)\,.$$

Here Z_0 allows for non-magnetic degrees of freedom. Consequently,

$$\begin{aligned}
Z &= Z_1^N/N! = (Z_0^N/N!)\,[2\cosh(\beta\mu SH)]\,, \\
F - F_0 &= -(N/\beta)\ln[2e\cosh(\beta\mu SH)]\,, \\
E - E_0 &= -\partial Z/\partial\beta = -N\mu SH\tanh(\beta\mu SH)\,, \\
(S - S_0)/k_B &= \beta(E-F) = N\ln[2e\cosh(\beta\mu SH)] - \beta N\mu SH\tanh(\beta\mu SH)\,.
\end{aligned}$$

4.12. Evaluate the contribution of a one-dimensional *anharmonic* oscillator having a potential $V(x) = cx^2 - gx^3 - fx^4$ to the heat capacity. Discuss the the dependence of the mean value of the position x of the oscillator on the temperature T. Here c, g, f are positive constants. Usually, $g \ll c^{3/2}(k_BT)^{-1/2}$ and $f \ll c^2/k_BT$.

Solution 4.12. Since g and f are small let us try to apply perturbation theory. Since the typical value of the displacement $\bar{x} = (k_BT/c)^{1/2}$ we obtain

$$g\bar{x}^3/k_BT = (k_BT)^{1/2}c^{-3/2} \ll 1\,, \quad f\bar{x}^4/k_BT = fk_BT/c^2 \ll 1\,.$$

Thus one can expand the exponential to obtain

$$e^{-\beta V(x)} \approx e^{-\beta cx^2}\left(1 - \beta gx^3 - \beta fx^4\right)\,.$$

As a result,

$$Z = Z_0\int_{-\infty}^{\infty} dx\, e^{-\beta V(x)} \approx \sqrt{\frac{\pi}{\beta c}}\left(1 + \frac{3f}{4\beta c^2}\right)\,.$$

Here Z_0 is the contribution of kinetic energy. Consequently,

$$\begin{aligned}
\ln Z &= \ln Z_0 + (1/2)\ln(\pi/c) - (1/2)\ln\beta + \ln(1 + 3f/4\beta c^2) \\
&= \ln Z_0 + (1/2)\ln(\pi/c) - (1/2)\ln\beta + 3f/4\beta c^2\,, \\
E &= -\partial\ln Z_0/\partial\beta - \partial\ln Z/\partial\beta \\
&= 1/2\beta + 1/2\beta + 3f/4\beta^2c^2 \\
&= k_BT + 3f(k_BT)^2/4c^2\,, \\
C &= k_B\left(1 + 3fk_BT/2c^2\right)\,.
\end{aligned}$$

To estimate $\langle x\rangle$ we calculate

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} dx\, x e^{-\beta V(x)}}{\int_{-\infty}^{\infty} dx\, e^{-\beta V(x)}} \approx -\beta g\frac{\int_0^{\infty} x^4\, dx\, e^{-\beta cx^2}}{\int_0^{\infty} dx\, e^{-\beta cx^2}} = \frac{3}{4}\frac{g}{\beta c^2} = -\frac{3}{4}\frac{g\bar{x}}{\beta^{1/2}c^{3/2}} \ll \bar{x}\,.$$

We have $\langle x \rangle \propto T$.

4.13. The energy of *anharmonic* oscillator is given by

$$H = p^2/2m + bx^{2n}$$

where n is a positive integer and $n > 1$. Consider a thermodynamic system consisting of a large number of these identical noninteracting oscillators.

(a) Derive the single oscillator partition function.

(b) Calculate an average kinetic energy of an oscillator.

(c) Calculate an average potential energy of an oscillator.

(d) Show that the heat capacity is

$$C = (Nk_B/2)(1 + 1/n).$$

Solution 4.13.

(a)

$$\begin{aligned} Z_1 &= \int \frac{dp}{2\pi\hbar} e^{-\beta p^2/2m} \int dx\, e^{-\beta b x^{2n}} \equiv Z_k \cdot Z_p, \\ Z_k &= \frac{m^{1/2}}{\hbar(2\pi\beta)^{1/2}}, \\ Z_p &= \frac{\Gamma(1/2n)}{n(\beta b)^{1/2n}}. \end{aligned}$$

where $\Gamma(t) = \int_0^\infty dx x^{t-1} e^{-x}$.

(b)

$$E_k = -\partial \ln Z_k / \partial\beta = k_B T/2.$$

(c)

$$E_p = -\partial \ln Z_p / \partial\beta = k_B T/2n.$$

(d) Straightforward.