Question #61148, Physics / Molecular Physics | Thermodynamics

Write an expression for the partition function for an ideal gas made up of N indistinguishable particles. Using this expression, obtain Sackur-Tetrode equation.

Solution

Let us consider first the ideal gas in microcanonical ensemble. In the microcanonical ensemble for *N* non-interacting point particles of mass *M* confined in the volume *V* with total energy in δE at *E* we must calculate

$$\Delta\Gamma = \int dq_1 ... dq_{3N} \int dp_1 ... dp_{3N} = V^N \int dp_1 ... dp_{3N} \quad (6.1)$$

where the momentum space integral is to evaluated subject to the constraint that

$$E - \delta E \le \frac{1}{2M} \sum_{i=1}^{3N} p_i^2 \le E \quad (6.2)$$

by the construction of the ensemble. The accessible volume in momentum space is that of a shell of thickness $(\delta E)(M/2E)^{1/2}$ on a hypersphere of radius $(2ME)^{1/2}$. If the result were sensitive to the value of δE employed, we would have difficulty in deciding on a value δE.

Fortunately we can prove that for a system of large numbers of particles the value of $\ln \Delta\Gamma$ is not sensitive to the value of δE, we may even replace δE by entire range from *0* to *E.*

The proof now follows. We write

$$V(R) = CR^{\nu} \quad (6.3)$$

for the volume of a ν-dimensional sphere of radius *R*. The volume of a shell of thickness *s* at the surface of this *hypersphere* is

$$V_s = V(R) - V(R-s) = C[R^{\nu} - (R-s)^{\nu}] = CR^{\nu}\left[1 - \left(1 - \frac{s}{R}\right)^{\nu}\right] \quad (6.4)$$

or, by the definition of the exponential function ,

$$V_s \cong CR^{\nu}\left[1 - e^{-s\nu/R}\right] \quad (6.5)$$

Therefore if ν is large enough so that s^{ν}>>R, V_s is practically the volume $V(R)$ of the whole sphere. If ν~10^{23} as for a macroscopic system, the requirement $s>>R/10^{23}$ may be satisfied without any practical imprecision in the specification of the energy of the microcanonical ensemble.

We can replace now the constraint (6.2) by the relaxed condition

$$0 \le \frac{1}{2M}\sum_{i=1}^{3N} p_i^2 \le E \qquad (6.6)$$

because for any reasonable (not too thin) shell the *volume of the shell* is essentially *equal* to the *volume of the entire hypersphere*. In other words, we want to evaluate the volume of the *3*ν*-dimensional sphere of radius* $R=(2ME)^{1/2}$. We can evaluate the volume V_ν of the hypersphere by the following argument: Consider the integral

$$\mathrm{G} = \int_{-\infty}^{\infty} e^{-(x_1^2+x_2^2+\ldots+x_\nu^2)} dx_1 dx_2 \ldots. dx_\nu = \left\{\int_{-\infty}^{\infty} e^{-x^2} dx\right\}^{\nu} = \pi^{\nu/2} \qquad (6.7)$$

We may also write

$$\mathrm{G} = \int_0^{\infty} e^{-r^2} r^{\nu-1} S_\nu dr = \frac{1}{2} S_\nu \int_0^{\infty} e^{-t} t^{(\nu-2)/2} dt = \frac{1}{2} S_\nu \left(\frac{\nu}{2}-1\right)! \qquad (6.8)$$

where $R^{\nu-1}S_\nu$ denotes the surface area of the ν*-dimensional sphere*. On comparison of the two results (6.7) and (6.8) we find

$$S_\nu = \frac{2\pi^{\nu/2}}{\left(\frac{\nu}{2}-1\right)!} \qquad (6.7)$$

$$\mathrm{G} = \pi^{\nu/2} \qquad (6.8)$$

$$\mathrm{G} = \frac{1}{2} S_\nu \left(\frac{\nu}{2}-1\right)! \qquad (6.9)$$

so that the volume of the sphere is

$$V_\nu = \int_0^R S_\nu R^{\nu-1} dR = \frac{\pi^{\nu/2}}{(\nu/2)!} R^\nu \qquad (6.10)$$

In the 3-dimensional case, $V_3=4\pi R^3/3$ and surface *are* $a_3=4\pi R^2$. In the two-dimensional case, we obtain $V_2=\pi R^2$ and *surface are* $a_2=2\pi R$ and in the one-dimensional case $V_1=2R$ and *surface are* $a_1=2$.

$$\Delta\Gamma = V^N V_\nu \qquad (6.11)$$

and using the Stirling approximation to evaluate factorial

$$\sigma = \ln \Delta\Gamma = N \ln[V\pi^{3/2}(2ME)^{3/2}] - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2} \qquad (6.12)$$

where in the expression for V_ν we have to put $\nu=3N$ and $R=(2ME)^{1/2}$

It turns out that if the *N* particles are identical we must not count as different conditions, which differ only by interchange of identical particles in phase space. We have to overestimate the volume of phase space by a factor which is *N!* under classical conditions. Taking this factor into account *e* as the base of natural logarithms

$$\sigma = \ln(\Delta\Gamma / N!) = N \ln[(V/N)(4\pi M/3)^{3/2}(E/N)^{3/2} e] + \frac{3N}{2} \qquad (6.13)$$

To complete the expression for the entropy of ideal gas we need to introduce the unit of volume in phase space $\hbar^{3N}$, so that

$$\sigma = \ln(\Delta\Gamma / N!\hbar^{3N}) = N \ln\left[\frac{(2M)^{3/2}\pi^{3/2} e (V/N)(E/N)^{3/2}}{\left(\frac{3}{2}\right)^{3/2}\hbar^3}\right] + \frac{3}{2}N \qquad (6.14)$$

From (3.13) we have

$$1/\theta = \left(\frac{\partial\sigma}{\partial E}\right)_{V,N} = \frac{\partial}{\partial E}(3N/2)\ln E = 3N/2E \qquad (6.15)$$

so that

$$E = 3N\theta / 2 = 3NkT / 2 \quad (6.16)$$

in agreement with the elementary result for the internal energy of a perfect monatomic gas. We can consider (6.16) as establishing the connection between θ and T. Further

$$p / \theta = (\partial\sigma / \partial V)_{N,V} = \frac{\partial}{\partial V} N \ln V = N / V \quad (6.17)$$

whence

$$pV = N\theta = NkT \quad (6.18)$$

Using (6.16) and $S=k\sigma$, we have the famous *Sackur-Tetrode formula* for the entropy of an ideal gas:

$$S = Nk\ln[(V/N)e(2\pi MkT/ \hbar^2)^{3/2}] + 3Nk/2$$