Ideal Gas

Computational Biology 2018

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1 Conclusions [1]

1.1 Question 4

From our simulation experiment, it follows that the partition function has the form:

$$q = \sum_{\mathbf{n}} \exp[-\beta E_{\mathbf{n}}] = \sum_{\mathbf{n}} \exp\left[-\frac{\beta h^2 (n_x^2 + n_y^2 + n_z^2)}{8mL^2}\right] = \left(\sum_{n}^{\infty} \exp\left[-\frac{\beta h^2 n^2}{8mL^2}\right]\right)^3 \tag{1}$$

where the power of 3 is due to the fact the the summations over the three quantum numbers n_x, n_y, n_z are independent of each other. For the average energy energy of one particle we find:

$$\langle E \rangle = \frac{1}{q} \sum_{\mathbf{n}} E_{\mathbf{n}} \exp[-\beta E_{\mathbf{n}}] = \frac{3}{q^{1/3}} \sum_{n=1}^{\infty} \frac{h^2 n^2}{8mL^2} \exp\left[-\frac{\beta h^2 n^2}{8mL^2}\right] \tag{2}$$

In the lectures we derived an aproximation for q via the semiclassical approximation. We will take a similar route.

For all practical circumstances, *i.e.* realistic size and temperature, many terms will contribute to the summations of eqs. (1) and (2), thus they can be treated as continuous variables. Indeed for $\alpha << 1$ we can employ:

$$\sum_{n=1}^{\infty} \exp[-\alpha n^2] \approx \int_0^{\infty} dn \exp[-\alpha n^2] = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \tag{3}$$

and

$$\sum_{n=1}^{\infty} n^2 \exp[-\alpha n^2] \approx \int_0^{\infty} dn n^2 \exp[-\alpha n^2] = \frac{1}{4\alpha}\sqrt{\frac{\pi}{\alpha}} \tag{4}$$

Employing these approximations for eqs. (1) and (2), we get:

$$q = \left(\frac{\pi}{4\alpha}\right)^{3/2} = \left(\frac{L}{\Lambda}\right)^3 = \frac{V}{\Lambda^3} \tag{5}$$

with

$$\Lambda \equiv \frac{h}{\sqrt{2\pi m k_B T}} = \frac{h}{\sqrt{2\pi m/\beta}} \tag{6}$$

if often called the thermal wavelength. For $\langle E \rangle$ we get

$$\langle E \rangle = \frac{3}{2\beta} = \frac{3}{2} k_B T \tag{7}$$

Try to derive the relations by yourself!!!

References

[1] Thijs J.H. Vlugt, Jan P.J.M. van der Eerden, Marjolein Dijkstra, Berend Smit, and Daan Frenkel. *Introduction to Molecular Simulation and Statistical Thermodynamics.* Delft, The Netherlands, 2008.