

which has three translational quadratic terms per molecule and two rotational quadratic terms per molecule. The energy given by the equipartition theorem is then

$$U = \frac{5}{2}NkT. \quad (64)$$

Recall also that for point particles (no rotational degrees of freedom) the energy is

$$U = \frac{3}{2}NkT, \quad (65)$$

which is just what the equipartition theorem gives if only the translational quadratic terms are present in the Hamiltonian.

HW Problem. Schroeder problem 6.32, pp. 240–241.

Reading assignment. Schroeder, sections 6.5 and 6.6.

0.1.3 The Maxwell velocity distribution

Now that we have the formalism of Boltzmann statistics available in a form applicable to classical systems, it is very straightforward to apply it to the problem of the distribution of velocities in an ideal gas. We'll concentrate mainly on the probability distribution, but we'll see later how to obtain from that other interesting distributions, such as the number of particles per unit volume having velocities in any given range. The probability distribution $\mathcal{P}(\mathbf{v})$ for the velocity of a single particle is defined via its product with a suitable volume element in velocity space:

$$\mathcal{P}(\mathbf{v}) d^3v = \left\{ \begin{array}{l} \text{Probability that the particle's ve-} \\ \text{locity lies within the volume ele-} \\ \text{ment } d^3v \text{ about the value } \mathbf{v} \end{array} \right\}. \quad (66)$$

To derive an explicit expression for $\mathcal{P}(\mathbf{v})$, we'll assume that the gas is monatomic and there are no external forces acting on it that would impart a position dependence to the Hamiltonian. Later, we'll show how those assumptions can be relaxed.

Recall from our discussion of the equipartition theorem that the probability distribution for the generalized coordinates and momenta of a classical system is

$$\mathcal{P}(q, p) = \frac{e^{-\beta\mathcal{H}(q, p)}}{\mathcal{I}}, \quad (67)$$

where \mathcal{H} is its Hamiltonian. For our particle, the Hamiltonian is very simple:

$$\mathcal{H}(q, p) \rightarrow \mathcal{H}(\mathbf{p}) = \frac{p^2}{2m} = \frac{1}{2}mv^2, \quad (68)$$

which depends explicitly only on the magnitude of the velocity. Thus, we can immediately write down the probability distribution for the velocity of the particle:

$$\mathcal{P}(\mathbf{v}) = Ce^{-\beta mv^2/2} = Ce^{-mv^2/2kT}, \quad (69)$$

where the normalization constant is just the inverse of the normalization integral \mathcal{I} .

The normalization integral is just the cube of a familiar Gaussian integral:

$$\begin{aligned}
\mathcal{I} &= \int e^{-mv^2/2kT} d^3v \\
&= \prod_{i=1}^3 \int_{-\infty}^{\infty} e^{-mv_i^2/2kT} dv_i \\
&= \left(\int_{-\infty}^{\infty} e^{-\alpha x^2} dx \right)^3 \\
&= \left(\frac{\pi}{\alpha} \right)^{3/2},
\end{aligned} \tag{70}$$

where

$$\alpha = \frac{m}{2kT}. \tag{71}$$

Thus, the normalization constant is

$$C = \left(\frac{m}{2\pi kT} \right)^{3/2}, \tag{72}$$

and the probability density is

$$\mathcal{P}(\mathbf{v}) = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT}. \tag{73}$$

Now this can easily be generalized to include the possibility of other internal coordinates, such as rotational coordinates and/or momenta, as well as external potentials, such as a gravitational field, if those features all appear in terms of the Hamiltonian that are separate from the center-of-mass momentum (velocity) term:

$$\mathcal{H}(q, p) = \frac{p_{\text{cm}}^2}{2m} + B(X), \tag{74}$$

where X subsumes all coordinates and momenta other than the three components of the center-of-mass momentum. Then the probability distribution for the particle velocity can be obtained by integrating over all coordinates and momenta in X , the number of which we denote by M :

$$\begin{aligned}
\mathcal{P}(\mathbf{v}) &= \frac{\int e^{-[\frac{mv^2}{2} + B(X)]/kT} d^M X}{\int e^{-[\frac{mv^2}{2} + B(X)]/kT} d^3v d^M X} \\
&= \frac{e^{-mv^2/2kT}}{\int e^{-mv^2/2kT} d^3v} \times \underbrace{\frac{\int e^{-B(X)/kT} d^M X}{\int e^{-B(X)/kT} d^M X}}_1,
\end{aligned} \tag{75}$$

which is the same as the result for a point particle with no external force acting on it.

The probability density can be used to obtain other useful densities. For example, in a gas of uniform number density n , the product of that density with the probability distribution gives the useful distribution:

$$f(\mathbf{v}) d^3v = n\mathcal{P}(\mathbf{v}) d^3v = \left\{ \begin{array}{l} \text{Number of particles per unit volume} \\ \text{that have velocity lying within } d^3v \\ \text{about } \mathbf{v} \end{array} \right\}. \quad (76)$$

0.1.4 The Maxwell speed distribution

You may have noticed that the Maxwell velocity distribution, derived in the previous section, actually doesn't depend on the direction of the velocity vector. This means all velocities with the same magnitude have the same probability density. Because of this it is useful, as well as customary, to integrate out the directional dependence, which appears only in the volume element, to obtain the probability density for the speed:

$$\begin{aligned} \mathcal{P}(v) dv &= \left\{ \begin{array}{l} \text{Probability that the particle's speed} \\ \text{lies within the differential element } dv \\ \text{about the value } v \end{array} \right\} \\ &= \int_{|\mathbf{v}|=v} \mathcal{P}(\mathbf{v}) d^3v \\ &= \int_0^{2\pi} \int_0^\pi \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} v^2 \sin\theta d\theta d\phi dv \quad (77) \\ &= \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} \underbrace{\int_0^{2\pi} \int_0^\pi \sin\theta d\theta d\phi}_{4\pi} dv \\ &= 4\pi v^2 \mathcal{P}(\mathbf{v}) dv, \end{aligned}$$

where θ and ϕ denote the polar and azimuthal angles of the velocity vector.

Thus, the Maxwell speed distribution is

$$\mathcal{P}(v) = \left(\frac{m}{2\pi kT} \right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}. \quad (78)$$

It's useful to notice that the mathematical distinction between the Maxwell velocity distribution and the Maxwell speed distribution lies in the definitions of the corresponding probabilities. The probability corresponding to the velocity distribution uses a three-dimensional volume element in velocity space, whereas the probability corresponding to the speed distribution uses a one-dimensional differential element in velocity space. Thus, the distributions have different dimensions, though the associated probabilities are dimensionless.

HW Problem. Schroeder problem 6.37, p. 246.

HW Problem. Schroeder problem 6.39, p. 246.

0.1.5 Connecting Boltzmann statistics to thermodynamics

The formalism of Boltzmann statistics provides us with a statistical tool for calculating the probabilities of the states of a system in thermal contact with a reservoir that sets the temperature. This is analogous to, and we showed it to follow from, our earlier formalism in which the probabilities of macrostates of an isolated system are given by the ratios of their multiplicities to the total multiplicity of the system. The partition function

$$Z = \sum_n e^{-\beta E_n} \quad (79)$$

in the new formalism, being the normalization constant that turns Boltzmann factors into probabilities:

$$\mathcal{P}_n = \frac{e^{-\beta E_n}}{Z}, \quad (80)$$

is analogous to the total multiplicity, which turns macrostate multiplicities into probabilities in the original formalism:

$$\mathcal{P}_{\text{macrostate}} = \frac{\Omega_{\text{macrostate}}}{\Omega_{\text{tot}}}. \quad (81)$$

Just as the Boltzmann definition of the entropy

$$S = k \ln \Omega \quad (82)$$

relates multiplicity to the thermodynamic entropy, there is a thermodynamic analog of the logarithm of the partition function. But in this case, the analogy follows directly from the earlier Boltzmann definition of the entropy, with no need to introduce a new definition.

[EOC, Wed. 3/29/2006, #31]
