Kinetic Theory and Thermodynamics

Handout 2:

In Lectures 2 and 3 we use the ideas of statistics and probability which we developed in the first lecture to derive some important results about kinetic theory. The first task in Lecture 2 is to find a statistical definition of temperature. To a certain extent this is anticipating some of the results which will be covered in more detail in subsequent lectures and the Statistical Physics course next term. Specifically we find that the temperature T is given by

$$\frac{1}{k_{\mathrm{B}}T} = \frac{d\ln\Omega}{dE},$$

where k_{B} is the Boltzmann constant, E is the energy, and Ω is a degeneracy, the number of ways of arranging the quanta of energy in the system. (Note that it is customary to define the variable $\beta \equiv 1/k_{\mathrm{B}}T$.)

In the specific case of a small system connected to a large heat reservoir, so that the system can exchange energy with the reservoir, we will find that the probability that the system has energy $\mathcal{E}$ is given by

$$p(\mathcal{E}) \propto e^{-\beta\mathcal{E}}.$$

This situation is known as the canonical ensemble and the probability distribution is often called the Boltzmann distribution. The factor $e^{-\beta\mathcal{E}}$ is known as a Boltzmann factor. Its use will be illustrated in the lectures for a number of physical situations.

A physical situation which is very important in kinetic theory is the translational motion of atoms or molecules in a gas. Neglecting any rotational or vibrational energy contributions, the energy of a molecule is given by

$$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{1}{2}mv^2,$$

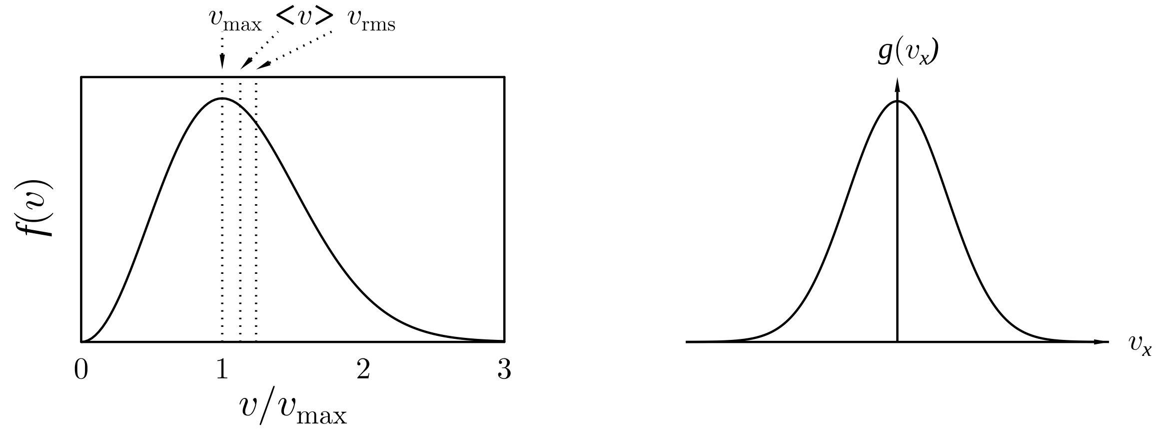
where $\mathbf{v} = (v_x, v_y, v_z)$ is the molecular velocity, and $v = |\mathbf{v}|$ is the molecular speed. Thus the probability distribution for a given component of velocity is given by

$$g(v_x) \propto e^{-mv_x^2/2k_{\mathrm{B}}T}.$$

In the lectures we show that the corresponding expression for the probability distribution of the molecular speed is given by

$$\boxed{f(v) \propto v^2 e^{-mv^2/2k_{\mathrm{B}}T}}$$

This is known as a Maxwell-Boltzmann distribution, or sometimes as a Maxwellian distribution. These two distributions are illustrated in the figures overleaf.

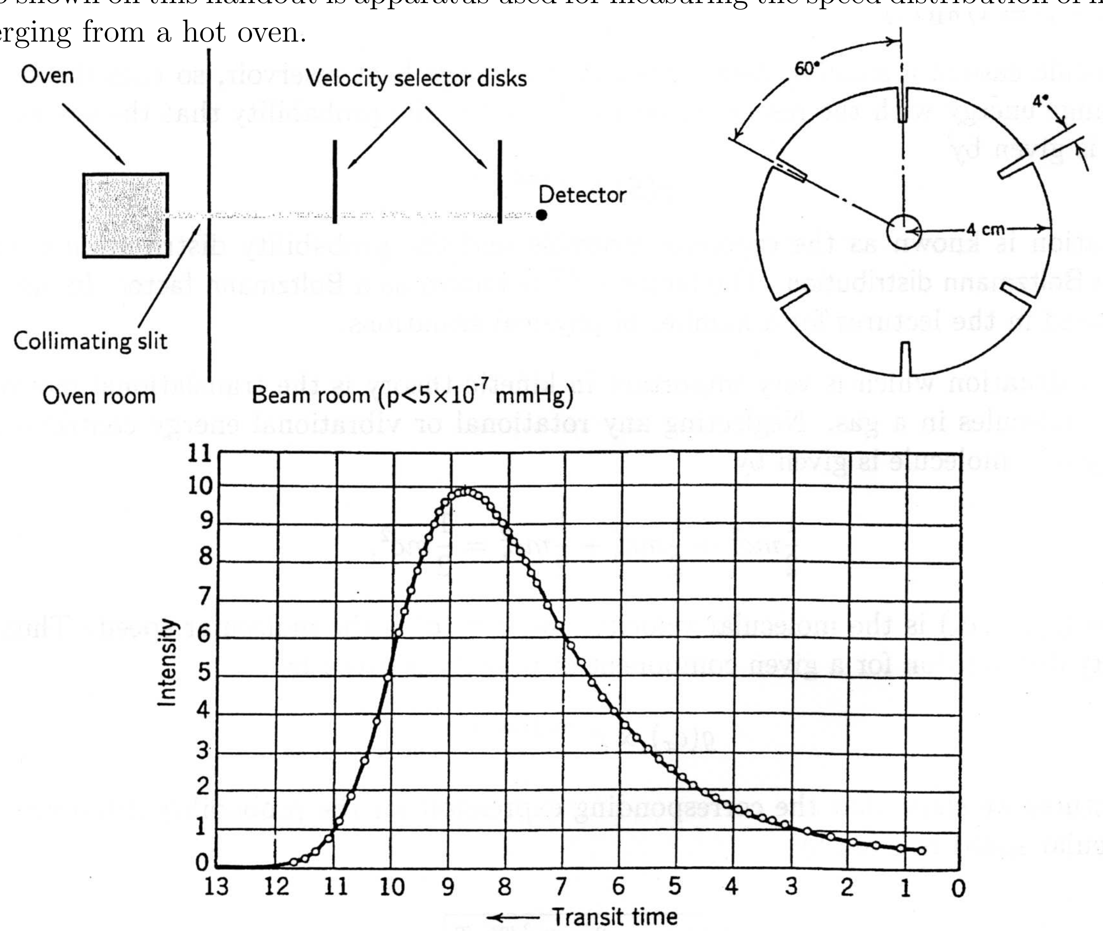


Left: $f(v)$, the distribution function for molecular speeds (Maxwell-Boltzmann distribution). **Right:** $g(v_x)$, the distribution function for a particular component of molecular velocity (a Gaussian distribution).

Two important moments of the Maxwell-Boltzmann distribution are

$$\langle v \rangle = \sqrt{\frac{8k_{\rm B}T}{\pi m}}, \qquad \langle v^2 \rangle = \frac{3k_{\rm B}T}{m}.$$

Also shown on this handout is apparatus used for measuring the speed distribution of molecules emerging from a hot oven.



Measured transmission points and calculated Maxwell transmission curve for K atoms exiting from an oven at 157°C. The experimental apparatus is shown in the top right. The oven, velocity selector, and detector arrangement are mounted on an optical bench. The velocity selector disks are turned at 8000 rpm and a phase shifter varies the phase of the voltage fed to one motor relative to the other. A light beam is used to determine when the velocity selector is set for zero transit time. This beam is produced by a small light source near one disk. The beam then passes through the velocity selector and is detected by a photocell near the other disk.

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