temperature of a system with respect to a given thermometer The value of the thermometric parameter of the thermometer when the latter is placed in thermal contact with the system and allowed to come to equilibrium with it.

mean free path The average distance which a molecule travels in a gas before it collides with another molecule.

Suggestions for Supplementary Reading

F. J. Dyson, "What is Heat?", *Sci. American* **191**, 58 (Sept. 1954).

R. Furth, "The Limits of Measurement," *Sci. American* **183**, 48. (July 1950). A discussion of Brownian motion and other fluctuation phenomena.

B. J. Alder and T. E. Wainwright, "Molecular Motions," *Sci. American* **201**, 113 (Oct. 1959). This article discusses the application of modem high-speed computers to the study of molecular motions in various macroscopic systems.

Problems

1.1 Fluctuations in a spin system

Consider an ideal system of 5 spins in the absence of an external magnetic field. Suppose that one took a movie of this spin system in equilibrium. What fraction of the movie frames would show n spins pointing up? Consider all the possibilities $n = 0, 1, 2, 3, 4$, and 5.

1.2 Diffusion of a liquid

Suppose that a drop of a dye (having the same density as water) is introduced into a glass of water. The whole system is kept at a constant temperature and is left mechanically undisturbed. Suppose that one took a movie of the process occurring after the drop of dye had been put into die water. What would one see on a screen on which the movie is projected? What would one see if the movie is run backward through the projector? Is the process reversible or irreversible? Describe the process in terms of the motion of the dye molecules.

1.3 Microscopic explanation of friction

A wooden block, which has originally been given a push, is sliding on the floor and gradually comes to rest. Is this process reversible or irreversible? Describe the process as it would appear on a movie played backward. Discuss what happens during this process on the microscopic scale of atoms and molecules.

1.4 The approach to thermal equilibrium

Consider two gases A and A' in separate containers. Initially the average energy of a molecule of gas A is quite different from the average energy of a molecule of gas A'. The two containers are then placed in contact with each other so that energy in the form of heat can be transferred from gas A to the molecules of the container walls and thence to gas A'. Is the ensuing process reversible or irreversible? Describe in microscopic detail the process that would appear if one filmed, die situation and ran this film backward through a projector.

1.5 *Variation of gas pressure with volume*

A container is divided into two parts by a partition. One of these parts has a volume V_i and is filled with a dilute gas; the other part is empty. Remove the partition and wait until the final equilibrium condition is attained where the molecules of the gas are uniformly distributed throughout the entire container of volume V_f

(*a*) Has the total energy of the gas been changed? Use this result to compare the average energy per molecule and the average speed of a molecule in the equilibrium situations before and after the removal of the partition.

(*b*) What is the ratio of the pressure exerted by the gas in the final situation to that of the pressure exerted by it in the initial situation?

1.6 *Number of gas molecules incident on an area*

Consider nitrogen (N_2) gas at room temperature and atmospheric pressure. Using the numerical values given in the text, find the average number of N_2 molecules striking a $1-m^2$ area of the container walls per second.

1.7 *Leak rate*

A 1-liter glass bulb contains N_2 gas at room temperature and atmospheric pressure. The glass bulb, which is to be used in conjunction with some other experiment, is itself enclosed in a large evacuated chamber. Unfortunately the glass bulb has, unbeknown to the experimenter, a small pinhole about 10^{-7} m in radius. To assess the importance of this hole, estimate the time required for 1 percent of the N_2 molecules to escape from the bulb into the surrounding vacuum.

1.8 *Average time between molecular collisions*

Consider nitrogen gas at room temperature and atmospheric pressure. Using the numerical values given in the text, find the average time a N_2 molecule travels before colliding with another molecule.

1.9 *Equilibrium between atoms of different masses

Consider a collision between two different atoms having masses m_1 and m_2. Denote the velocities of these atoms before the collision by $\mathbf{v}_1$ and $\mathbf{v}_2$, respectively; denote their velocities after the collision by $\mathbf{v}_1'$ and $\mathbf{v}_2'$, respectively. It is of interest to investigate the energy transferred from one atom to the other as a result of the collision.

(*a*) Introduce the relative velocity $\mathbf{V} \equiv \mathbf{v}_1 - \mathbf{v}_2$ and the center-of-mass velocity $\mathbf{c} \equiv (m_1\mathbf{v}_1 + m_2\mathbf{v}_2)/(m_1 + m_2)$. The relative velocity after the collision is then $\mathbf{V}' \equiv \mathbf{v}_1' - \mathbf{v}_2'$. In a collision $\mathbf{c}$ remains unchanged by virtue of conservation of momentum, while $|\mathbf{V}'| = |\mathbf{V}|$ by virtue of conservation of energy. Show that the energy gain $\Delta\epsilon_1$ of atom 1 in a collision is given by

$$\Delta\epsilon_1 = \frac{1}{2}m_1\left(v_1'^2 - v_1^2\right) = m_1 m_2 (m_1 + m_2)^{-1}\mathbf{c}\cdot(\mathbf{V}' - \mathbf{V}). \qquad \text{(i)}$$

(*b*) Denote by θ the angle between $\mathbf{V}'$ and $\mathbf{V}$, by φ the angle between the plane containing $\mathbf{V}'$ and $\mathbf{V}$ and the plane containing $\mathbf{c}$ and $\mathbf{V}$, and by ψ the angle between $\mathbf{c}$ and $\mathbf{V}$. Show that (i) then becomes

$$\Delta\epsilon_1 = m_1 m_2 (m_1 + m_2)^{-1} cV\left[(\cos\theta - 1)\cos\psi + \sin\theta\sin\psi\cos\varphi\right] \qquad \text{(ii)}$$

where $cV\cos\psi = \mathbf{c}\cdot\mathbf{V} = (m_1+m_2)^{-1}[m_1v_1^2 + (m_2-m_1)\mathbf{v}_1\cdot\mathbf{v}_2 - m_2v_2^2]$.

(*c*) Consider two atoms of this kind in a gas where many collisions occur. On the average, the azimuthal angle φ is then as often positive as negative so that $\overline{\cos\varphi} = 0$; also, since $\mathbf{v}_1$ and $\mathbf{v}_2$ have random directions, the cosine of the angle between them is as often positive as negative so that $\overline{\mathbf{v}_1\cdot\mathbf{v}_2} = 0$. Show that (ii) therefore becomes, on the average,

$$\overline{\Delta\epsilon_1} = \frac{2m_1m_2}{(m_1+m_2)^2}(\overline{1\cos\theta})(\bar{\epsilon}_2 - \bar{\epsilon}_1) \qquad \text{(iii)}$$

where $\epsilon_1 = \frac{1}{2}m_1v_1^2$ and $\epsilon_2 = \frac{1}{2}m_2v_2^2$..

In the equilibrium situation in particular the energy of an atom must, on the average, remain unchanged so that $\overline{\Delta\epsilon_1} = 0$. Show that (iii) then implies that in equilibrium,

$$\bar{\epsilon}_2 = \bar{\epsilon}_1. \qquad \text{(iv)}$$

Thus the average energies of interacting atoms in equilibrium are equal even if the masses of the atoms are different.

1.10 *Comparison of molecular speeds in a gas mixture*

Consider a gas mixture enclosed in some container and consisting of monatomic molecules of two different masses m_1 and m_2.

(*a*) Suppose that this gas mixture is in equilibrium. Use the result of the preceding problem to find the approximate ratio of the average speed $\bar{v}_1$ of a molecule of mass m_1 to the average speed $\bar{v}_2$ of a molecule of mass m_2.

(*b*) Suppose that the two kinds of molecules are He (helium) and Ar (argon) which have atomic weights equal to 4 and 40, respectively. What is the ratio of the average speed of a He atom to that of an Ar atom?

1.11 *Pressure of a gas mixture*

Consider an ideal gas which consists of two kinds of atoms. To be specific, suppose that there are, per unit volume, n_1 atoms of mass m_1 and n_2 atoms of mass m_2. The gas is assumed to he in equilibrium so that the average energy $\bar{\epsilon}$ per atom is the same for both kinds of atoms. Find an approximate relation for the average pressure $\bar{p}$ exerted by the gas mixture. Express your result in terms of $\bar{\epsilon}$.

1.12 *Mixing of two gases*

Consider a container divided into two equal parts by a partition. One of these parts contains 1 mole of helium (He) gas, the other 1 mole of argon (Ar) gas. Energy in the form of heat can pass through the partition from one gas to the other. After a sufficiently long time, the two gases will, therefore, come to equilibrium with each other. The average pressure of the helium gas is then pi, that of the argon gas is $\bar{p}_2$.

(*a*) Compare the pressures $\bar{p}_1$ and $\bar{p}_2$ of the two gases.

(*b*) What happens when the partition is removed? Describe the process as it would appear on a movie played backward. Is it reversible or irreversible?

(*c*) What is the average pressure exerted by the gas in the final equilibrium situation?

1.13 *Effect of a semipermeable partition ("osmosis")*

A glass bulb contains argon (Ar) gas at room temperature and at a pressure of 1 atmosphere. It is placed in a large chamber containing helium (He) gas also at room temperature and at a pressure of 1 atmosphere. The bulb is made of a glass which is permeable to the small He atoms, but is impermeable to the larger Ar atoms.

(*a*) Describe the process which ensues.

(*b*) What is the most random distribution of the molecules which is attained in the ultimate equilibrium situation?

(*c*) What is the average pressure of the gas inside the bulb when this ultimate equilibrium situation has been attained?

1.14 *Thermal vibrations of the atoms in a solid*

Consider nitrogen (N_2) gas in equilibrium within a box at room temperature. In accordance with the result of Prob. 1.9, it is then reasonable to assume that the average kinetic energy of a gas molecule is roughly equal to the average kinetic energy of an atom in the solid wall of the container. Each atom in such a solid is localized near a fixed site. It is, however, free to oscillate about this site and should, to good approximation, perform simple harmonic motion about this position. Its potential energy is then, on the average, equal to its kinetic energy.

Suppose that the walls consist of copper which has a density of 8.9 gm/cm^3 and an atomic weight of 63.5.

(*a*) Estimate the average speed with which a copper atom vibrates about its equilibrium position.

(*b*) Estimate roughly the mean spacing between the copper atoms in the solid. (You may assume them to be located at the corners of a regular cubic lattice.)

(*c*) When a force F is applied to a copper bar of cross-sectional area A and length L, the increase in length ΔL of the bar is given by the relation

$$\frac{F}{A} = Y\frac{\Delta L}{L}$$

where the proportionality constant Y is called *Young's modulus*. Its measured value for copper is $Y = 1.28 \times 10^{11}$ N/m^2. Use this information to estimate the restoring force acting on a copper atom when it is displaced by some small amount x from its equilibrium position in the solid.

(*d*) What is the potential energy of an atom when it is displaced by an amount x from its equilibrium position? Use this result to estimate the average magnitude $|x|$ of the amplitude of vibration of a copper atom about its equilibrium position. Compare $|x|$ with the separation between the copper atoms in the solid.