Free expansion of an ideal gas by kinetic
gas theory

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Abstract

We consider the adiabatic free expansion of an ideal gas. According to classical thermodynamics, the internal energy of the gas is not affected by the expansion, but kinetic gas theory predicts an average energy difference between escaping and remaining gas. This difference is transient if the gas escapes into a finite volume, consistent with the equilibrium prediction of classical thermodynamics. For escape into an infinite volume, classical thermodynamics is not applicable. Numerical calculations of the magnitude of the predicted effect are provided.

Keywords: ideal gas, free expansion, kinetic gas theory, thermodynamics

1. Introduction

The connection between deterministic, time-reversible (classical) mechanics and irreversible thermodynamics is one of philosophical inquiry, with the Zermelo and Loschmidt paradoxes constituting the nexus [1]. These paradoxes resolve if the underlying mechanics is assumed not completely deterministic, e.g. the molecular chaos assumption of Maxwell [2]. Quantum mechanics, with its inherent indeterminacy, ultimately offers an epistemic rationale for this kind of assumption. Even so, to recover classical thermodynamics one must appeal to the limiting notion of an infinite system, the so-called ‘thermodynamic limit’ [3]. In this short paper, we offer a pedagogical discussion of the adiabatic free expansion of an ideal gas. This is a
system for which the kinetic theory of gases (that is, statistical mechanics) and classical thermodynamics do not agree, regardless of any molecular chaos assumption, and consequently offers an interesting discussion.

The conceptual argument, devoid of any mathematical details, on which the paper rests is very simple and proceeds as follows. Imagine that we have a heat-insulated container of an ideal gas that is not completely sealed in an otherwise empty Universe (this is our ‘thermodynamic system’ which is not closed to the ‘surroundings’). Since there is a distribution of molecular velocities in the gas, the faster molecules will escape at a higher rate than the slower ones out from the container into the ‘infinite void’. Therefore, the average kinetic energy per molecule of the remaining gas molecules will decrease with time. From energy conservation, it is clear that the escaping gas will have a correspondingly higher average kinetic energy. It is therefore not entirely proper to speak of a ‘cooling’ of the gas, since the gas does not have a unique temperature in the process but it does not necessarily follow that an observer measuring the average kinetic energy of the escaping gas will speak of a ‘warming’ of the gas, since the escaping gas has a net center-of-mass translational motion away from the container that needs to be subtracted to give the internal energy.

Classical thermodynamics prescribes no change of the average internal energy in the adiabatic expansion above. However, classical thermodynamics is a theory of equilibrium states [4]. If the gas expands into a finite volume, rather than into an infinite void as we have assumed, the reverse flow of gas that grows gradually more important as time progresses will ensure both that (1) the fast ‘hot’ molecules in the emission return to the original vessel at a higher rate than the slow ‘cold’ ones, so that the temperature eventually equilibrates at one and the same starting value in both volumes, and that (2) there is no net center-of-mass translation for the escaping gas after it is reflected in the opposing wall. There is hence no contradiction with equilibrium thermodynamics in this case, provided sufficient time to allow the escaping gas to sample the entire volume. For an expansion into an infinite void, the equilibrium state does not exist and classical thermodynamics is not applicable.

In the remaining part of this paper, we will calculate the magnitude of this ‘non-classical’ effect under different simplifying assumptions. The mathematical treatment is at the level of a physics undergraduate. As for the physical content, it is assumed that the reader is familiar with the Boltzmann distribution, equipartition and the kinetic theory of gases. We stay within the safe confines of the ideal gas: the complications offered by the free expansion of a real gas (that may either cool down or warm up, depending on the conditions) are pedagogically discussed in the paper by Goussard and Roulet [5], albeit within the confines of equilibrium statistical mechanics: in their treatment the energy of the ideal gas is unaffected by a free expansion. Last, before we proceed to the problem, we draw the reader’s attention to the discussion of a related but different one in reference [6]. In that reference, the gas expands into a finite, but rapidly enlarging, volume and the system boundary lies not between escaping and remaining gas, but between expanding gas and surroundings.

2. Explicit calculations

Consider a rectangular box containing $N_0$ molecules of an ideal gas and a Cartesian coordinate system aligned with the sides of the box with the origin at one of its corners. This particular alignment of the coordinate system simplifies the mathematical treatment to be presented. At time $t = 0$, two small holes are made on opposite sides of the box along the $x$-axis sharing identical $y$- and $z$-coordinates, letting the confined gas escape out into an infinite void. Each hole covers an area $a/2$, whereas each side itself has an area $A$. Letting the gas escape from two
opposite orifices means that the reference frame of the box coincides exactly with the inertial center-of-mass reference frame of the combined system of remaining gas, escaping gas and container. In this reference frame, the vessel is then stationary and the gas can perform no work on it. With only a single opening, the gas would lose also some energy through the work of accelerating the container, increasing the magnitude of the calculated cooling effect in that case.

We also make the simplifying assumption that either the heat capacity of the container is negligible (because it has no internal degrees of freedom that are not heavily quantized) or that the rate of heat transfer between the container and the gas is (because the atomic mass of the gas is much smaller than that of the container). Without this assumption the gas recuperates some of the energy lost by heat transfer from the container. With this said, we now proceed to calculate the magnitude of the energy loss per unit time in two extreme cases: one where the energy redistribution is infinitely slow among the molecules, and one where it is instantaneous.

2.1. Case without energy redistribution

We will only explicitly consider the translation of the ideal gas molecules along the $x$-direction. These will oscillate between the walls of the container with a period of $2L/v_x$, $L$ being the length of the box and $v_x$ the speed along the $x$-direction which is invariant in time for any one gas molecule if we assume the walls to be perfectly smooth and the collisions to be perfectly elastic (the molecules being point particles, there are no collisions among them). There is then no redistribution of energy among any degrees of freedom.

Let $\rho_x(t; v_x)dv_x$ be the number of gas molecules at time $t$ traveling at a speed between $v_x$ and $v_x + dv_x$ along the $x$-direction. The number of molecules escaping per unit time is the product of the frequency of collision with both walls, $v_x/L$, the probability of hitting each hole, $a/(2A)$, and the number of molecules in the box. We hence have the following differential equation for $\rho_x(t; v_x)$,

$$ \frac{d\rho_x(t; v_x)}{dt} = -\frac{av_x}{2AL}\rho_x(t; v_x) $$

whose solution is well-known,

$$ \rho_x(t; v_x) = \rho_x(0; v_x) \exp\left(-\frac{av_x t}{2AL}\right). $$

Since the situation for $t \leq 0$ is one of equilibrium, we have the Boltzmann distribution ($k$ is Boltzmann’s constant)

$$ \rho_x(0; v_x) = N_0 \sqrt{\frac{2m}{\pi kT_0}} \exp\left(-\frac{mv_x^2}{2kT_0}\right) $$

so that the function $\rho_x(t; v_x)$ is completely determined by the initial temperature, $T_0$, number of molecules, $N_0$, and their individual mass, $m$.

The average kinetic energy of the remaining gas molecules is the sum of the average kinetic energy along all of the Cartesian directions. Since the motion along the $y$- and $z$-directions does not contribute to the escape of molecules along the $x$-direction, there is no preponderance of any particular kinetic energy along these directions for the escaping molecules. Therefore, the average kinetic energy along these directions is independent of time, leading to a total average
kinetic energy per molecule of

\[
\langle E_k(t) \rangle = kT_0 + \int_0^\infty \int_0^\infty \rho_x(t; v_x) \frac{1}{2} m v_x^2 \, dv_x \, \rho_y(t; v_y) \, dv_y \, \rho_z(t; v_z) \, dv_z
\]

\[
= kT_0 + \frac{kT_0}{8} \left( 4 + a^2 \frac{kT_0}{2} \frac{1}{A^2 L^2 m} \exp \left( -\frac{a^2 kT_0}{8 m \sqrt{8} \pi m} \right) \right) \tag{4}
\]

which decreases monotonically in time from the maximum value of \(3kT_0/2\), approaching the limiting value of \(kT_0\) asymptotically. The rate of energy loss with no energy redistribution constitutes a lower limit to the actual value.

2.2. Case with immediate energy redistribution

If we instead assume that the kinetic energy is redistributed so that the entropy is maximized, then there will be a diffusive flux among the distributions of each Cartesian dimension: \(\rho_x(t; v_x)\), \(\rho_y(t; v_y)\), and \(\rho_z(t; v_z)\). Consequently, the average energy will decrease to the lower limit of zero (instead of \(kT_0\)) and at a higher average rate, although the maximum rate will be the same. The maximum rate of cooling is the initial rate which is proportional to the same initial distribution in both cases considered.

In the extreme case, the energy is redistributed instantaneously so that \(\rho_x(t; v_x) = \rho_y(t; v_y) = \rho_z(t; v_z)\) at all times and the energy distribution of the system is always that of equilibrium. The derivative of equation (4) for \(t = 0\) furnishes the rate of energy decrease close to equilibrium,

\[
\left. \frac{d\langle E_k(t) \rangle}{dr} \right|_{r=0} = -\frac{a(kT_0)^2}{AL\sqrt{8\pi m}}. \tag{5}
\]

Since the gas is assumed to pass through a continuous succession of equilibrium states, we may replace \(T_0\) by \(T(t)\) and write the differential equation,

\[
\frac{dT(t)}{dt} = -\frac{2a(kT(t))^2}{3AL\sqrt{8\pi m}} \tag{6}
\]

after substituting the equipartition theorem, \(3kT(t)/2 = \langle E_k(t) \rangle\). The solution is

\[
T(t) = 4T_0 \left( 2 + \frac{2a \sqrt{kT_0}}{3AL\sqrt{8\pi m}} \right)^{-2}. \tag{7}
\]

As already noted, under these assumptions, the temperature drops asymptotically to absolute zero instead of \(2T_0/3\) as in the previous case. The unphysical assumption of instantaneous redistribution of the energy among all the degrees of freedom means that the prediction of equation (7) constitutes an upper limit for the rate of temperature decrease.

3. Final remarks

Finally, we compute the magnitude of this effect by way of numerical example. From equation (5) and \(T_0 = 300\) K, \(a = 1\) \(\text{mm}^2\), \(A = 1\) \(\text{m}^2\), \(L = 1\) \(\text{m}\) and \(m = 3.32 \times 10^{-27}\) kg
Figure 1. Predicted energy per molecule by kinetic gas theory as a function of time for an ideal gas that undergoes an adiabatic free expansion into an infinite void, under the assumption of instantaneous energy equipartition among all molecules and directions (solid curve) or no equipartition at all (dashed curve). The ordinate is given in units of kelvin, using the scale-factor of the three-dimensional equipartition theorem $\langle E_k \rangle = 3kT/2$ in both cases merely for commensurability. See text for parameter values.

(the mass of a hydrogen molecule), we have (at time $t = 0$, it makes no difference to the rate whether the energy redistributes or not)

$$\frac{d\langle E_k(t) \rangle}{dt} \bigg|_{t=0} = -\frac{a(kT_0)^\frac{3}{2}}{AL\sqrt{8\pi m}} \approx -9.23 \times 10^{-25} \text{ J s}^{-1}$$

(8)

corresponding to a temperature decrease of about $-0.04 \text{ K s}^{-1}$. While this might seem small, it is actually quite high as it should be compared to that of the loss of gas substance, obtained from equation (1) as,

$$\frac{dN}{dt} \bigg|_{t=0} = -\frac{N_0 a}{2AL} \sqrt{\frac{2m}{\pi kT_0}} \int_0^\infty v_x \exp\left(-\frac{mv_x^2}{2kT_0}\right) dv_x$$

$$= -\frac{N_0 a}{2AL} \frac{2kT_0}{\pi m} \approx -4.5N_0 \times 10^{-4} \text{ s}^{-1}.$$  

(9)

In general, the ratio of these two initial rates, when normalized by their respective initial function values, is

$$\frac{d\langle E_k(t) \rangle/dt|_{t=0}/\langle E_k(0) \rangle}{dN/dt|_{t=0}/N_0} = \frac{1}{3}.$$  

(10)
Under the assumption of instantaneous equilibration, this ratio is constant in time; otherwise it tends to zero and thereby to agreement with classical thermodynamics.

The predicted temperature curves over the time span of roughly one hour predicted under our two sets of assumptions are given in figure 1 (needless to say, the gas will be extremely rarefied after such a long time). The rate of cooling exhibited by equation (10) in particular is quite substantial if prolonged in time, and this proves that the assumption of instantaneous equilibration is untenable in light of experimental evidence. In fact, the time scale of the equilibration should be of the order of the average time between molecular collisions. As a real gas becomes ideal only in the limit of vanishing density, for which the mean free path tends to infinity, the slower heat loss predicted by equation (4) becomes asymptotically correct for any real gas that is rarefied, assuming either that the container walls are perfectly flat or the thermodynamic limit (so that collisions with the walls can be neglected). In fact, in the thermodynamic limit, $AL \to \infty$ and both equations (4) and (7) predict no energy loss then. This, however, is merely the trivial consequence of neglecting all boundary effects of which the energy loss considered is but one.

Arguably, the most fundamental difference between our treatment and those of references [5, 6] is that we have considered an open system in which matter is lost to the surroundings, whereas they consider closed systems. Like Zimba’s [6] exposition, our Gedanken experiment is difficult to carry out in practice, and thus purely of philosophical or pedagogical interest, whereas the results of Goussard and Roulet [5] are of clear practical significance. They explain qualitatively the anomalously low inversion temperature of helium gas, and students may be amused to learn that gases that heat up in the adiabatic free expansion were once jokingly called ‘plus-que-parfaits’ in the early 20th century.

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