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## Free expansion for real gases

Jacques-Olivier Goussard; Bernard Roulet



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reason for Bose–Einstein condensation: If the particle density exceeds a critical value, the additional particles must be provided by the ground state (second) term in Eq. (17) or by the rest  $R$ . The ground state term becomes extensive if

$$1-z = O(V^{-1}), \quad (19)$$

which we assume from now on. Note that in the thermodynamic limit  $N/V$  is constant, but not necessarily  $z$ . We now show that the terms in  $R$  in Eq. (18) are small as a consequence of Eq. (19). The double integral can be integrated in planar polar coordinates

$$\int_0^\infty \int_0^\infty \frac{dx_2 dx_3}{z^{-1} \exp[x_2^2 + x_3^2] - 1} = -\frac{\pi}{4} \log(1-z).$$

Hence the corresponding term is  $O[L^2 \log(1-z)] = O(L^2 \log L) \ll O(L^3)$ . The term is small compared with the ground state term for all values of  $z \leq 1$ . The one-dimensional integral in Eq. (18) can be simply estimated after splitting it up:

$$\begin{aligned} \int_1^\infty dx_1 \frac{z \exp[-x_1^2]}{1-z \exp[-x_1^2]} &\leq \frac{1}{2} \int_1^\infty dx_1 \frac{2x_1 z \exp[-x_1^2]}{1-z \exp[-x_1^2]} \\ &= -\frac{1}{2} \log(1-ze^{-1}) = O(1), \end{aligned}$$

$$\begin{aligned} z \int_0^1 \frac{dx_1}{\exp[x_1^2] - z} &\leq z \int_0^1 \frac{dx_1}{1+x_1^2 - z} \\ &= \frac{z}{\sqrt{1-z}} \arctan \frac{1}{\sqrt{1-z}} = O(L^{3/2}). \end{aligned}$$

The corresponding term is  $O(L^{5/2}) \ll O(L^3)$ .

Finally, in the last two terms of Eq. (18) the nature of the one-particle energy spectrum is important:

$$\begin{aligned} \frac{1}{z^{-1} \exp\left[\left(\frac{\lambda_T}{L}\right)^2\right] - 1} &\leq \frac{z}{1 + \left(\frac{\lambda_T}{L}\right)^2 - z} \\ &= \frac{z}{\left(\frac{\lambda_T}{L}\right)^2 + O(V^{-1})} = O(L^2) \ll O(L^3). \end{aligned}$$

Summing up, all terms of the rest  $R$  in Eq. (17) are small compared with the ground state term in the thermodynamic limit. This is the common belief.

<sup>1</sup>F. London, *Superfluids*, Vol. II (Dover, New York, 1954), p. 45.

<sup>2</sup>R. Becker, *Theorie der Wärme* (Springer-Verlag, Berlin, Heidelberg, New York, 1961), p. 176.

<sup>3</sup>K. Huang, *Statistical Mechanics*, 2nd ed. (Wiley, New York, 1987), pp. 288–289.

## Free expansion for real gases

Jacques-Olivier Goussard

*Magistère de Physique, Université Denis Diderot Paris 7, France*

Bernard Roulet

*Groupe de Physique des Solides, associé au CNRS, URA 17, Université Paris 7 et Paris 6, Tour 23, 2, Place Jussieu, 75251-Paris Cedex 05, France*

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It is sometimes “proved” by simple physical arguments that real gases get cooler when experiencing a free expansion. These arguments are in some way incorrect since the result is in contradiction with experiment, at least for some gases. We show how these arguments can be corrected and find that there is an “inversion temperature” for all real gases. Values of the inversion temperature can be easily estimated and are compared with experiments.

### I. INTRODUCTION

In general, textbooks on thermodynamics give the free (or Joule) expansion and the throttling process (or Joule–Kelvin expansion) of gases as first examples of irreversible processes. Most of them study in detail the temperature change of real gases in the case of a throttling process (which is used for liquefaction) and consider free expansion only for perfect gases.

In some textbooks, however, temperature variation of real gases during a Joule expansion is considered. One then finds two different methods for dealing with the matter: either authors use a phenomenological equation of state<sup>1–3</sup>

and the physical meaning of the phenomenon is hidden in the temperature dependence of the coefficients of the equation, or they use a very appealing physical argument<sup>4–6</sup> which shows that a real gas always gets cooler during a free expansion. Now it is known that a Joule expansion can result in an increasing temperature for some gases such as helium and hydrogen. So this qualitative physical argument must be in some way incorrect.

In the present paper, we first review briefly the process of Joule expansion (Sec. II), we then examine the physical argument proposed as quite general by some textbooks (Sec. III). In Sec. IV, we show how this argument can be corrected and find that there is an inversion temperature

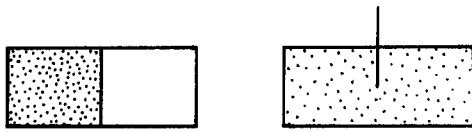


Fig. 1. A Joule expansion.

for all real gases undergoing a free expansion. This is compared with the well-known inversion temperature observed in throttling processes.<sup>1-5,7,8</sup> At last, in Sec. 5, we try to give estimates of the inversion temperature and compare them with the experimental values obtained by using the second virial coefficient.

## II. THE JOULE EXPANSION

A Joule expansion is one in which the gas exchanges no work and no heat with its surroundings. Such is the case, for example, when the gas, initially confined in a thermally isolated vessel, expands into a vacuum (Fig. 1). Thus, according to the first law of thermodynamics, a Joule expansion causes no change in the internal energy  $E$  of the gas.

For a perfect gas, the internal energy  $E$  is a function of the temperature  $T$  only and thus an expansion which keeps the energy constant is also isothermal. For real gases, however, the internal energy depends on  $T$  and on the volume  $V$ . This is due to the interaction between molecules which is a function of their relative distances. The temperature change during a free expansion can be calculated if one knows the so-called Joule coefficient

$$J = \left( \frac{\partial T}{\partial V} \right)_E = - \left( \frac{\partial T}{\partial E} \right)_V \left( \frac{\partial E}{\partial V} \right)_T = - \frac{1}{C_V} \left( \frac{\partial E}{\partial V} \right)_T \quad (1)$$

Since the heat capacity at constant volume  $C_V$  is always positive, the sign of the temperature variation is given by the sign of  $(\partial E/\partial V)_T$ .

The Joule coefficient can also be calculated knowing  $C_V$  and the equation of state of the gas since<sup>4</sup>

$$\left( \frac{\partial T}{\partial V} \right)_E = \frac{1}{C_V} \left[ p - T \left( \frac{\partial p}{\partial T} \right)_V \right] \quad (2)$$

## III. A (TOO) SIMPLE QUALITATIVE ARGUMENT

The following argument is commonly made to explain the temperature change that occurs in a free expansion.

The internal energy of a gas is the sum of the kinetic energy  $E_{\text{kin}}$  of its  $N$  molecules and of the potential energy  $U$  resulting from the molecular interactions

$$E = E_{\text{kin}} + U \quad (3)$$

The kinetic energy depends only on the temperature  $T$  and is always an increasing function of  $T$ .<sup>9</sup> Since in a gas the density is low, the potential energy can be considered as the sum of the potential energies of all pairs of molecules. The interaction energy  $u(r)$  between two molecules as a function of their relative separation  $r$  is shown in Fig. 2. At large distances ( $r > r_0$ ) there are weak attractive forces and  $u(r)$  increases slowly with  $r$ . At small separation ( $r < r_0$ ) the forces become strongly repulsive and  $u(r)$  decreases very rapidly with  $r$ . Real gases always have an average

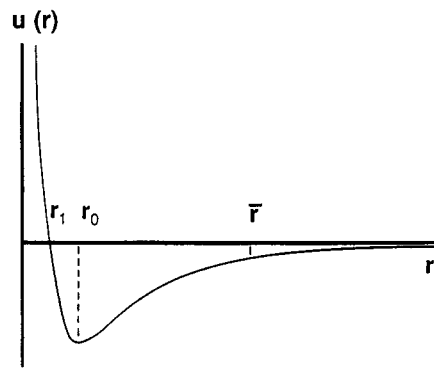


Fig. 2. The potential energy of two molecules as a function of their separation  $r$ .

intermolecular separation  $\bar{r}$  greater than  $r_0$  which corresponds to the density of the liquid, so that  $U$  must increase with the separation of molecules.

In a free expansion, since  $V$  increases, it is clear that  $\bar{r}$  increases and so must  $U$ . Now  $E$  is constant in such an expansion, so  $E_{\text{kin}}$  must decrease: this can be done only if  $T$  decreases. The conclusion is then that a real gas always cools during a Joule expansion.

This effect is very weak and can hardly be experimentally verified. However, for some gases, experiments lead to the inverse observation. For instance, helium at usual temperature (and pressure) is warmer after a free expansion. The above explanation, although very simple and appealing, must be wrong in some way.

## IV. A CORRECT QUALITATIVE ARGUMENT

The reason for this discrepancy is in fact quite clear: what we must consider is not the potential energy taken at the average intermolecular separation  $\bar{r}$  but instead the average potential energy itself. This is given by

$$U = \frac{N(N-1)}{2} \frac{\iiint_V u(r) e^{-u/kT} d\mathbf{r}}{\iiint_V e^{-u/kT} d\mathbf{r}} \quad (4)$$

The range over which  $u(r)$  is not negligible is at most a few nanometers and is very much smaller than the size (of order  $V^{1/3}$ ) of the container. The integral in the numerator is then practically independent of  $V$  and the denominator is

$$\iiint_V e^{-u/kT} d\mathbf{r} \approx V, \quad (5)$$

so that

$$J = - \frac{1}{C_V} \left( \frac{\partial E}{\partial V} \right)_T = - \frac{1}{C_V} \left( \frac{\partial U}{\partial V} \right)_T \approx + \frac{N^2}{2V^2 C_V} \iiint_V u(r) e^{-u/kT} d\mathbf{r} \quad (6)$$

The heating or cooling of the gas during a free expansion then depends on the sign of the integral in Eq. (6). Since

$$\frac{d}{dT} \left[ u \exp \left( - \frac{u}{kT} \right) \right] = \frac{u^2}{kT^2} \exp \left( - \frac{u}{kT} \right) > 0 \quad \text{for all } u(r) \neq 0, \quad (7)$$

the integrand increases monotonically at every value of  $r$  as the temperature increases, and so does  $J$ . Let us write

$$I(T) = A_1(T) + A_2(T) = \iiint_{r < r_1} dr ue^{-u/kT} + \iiint_{r > r_1} dr ue^{-u/kT}, \quad (8)$$

where  $r_1$  is the intermolecular distance for which  $u(r_1) = 0$ .

Due to the mutual "impenetrability" of the atoms,  $u(r)$  becomes very large at small  $r$ .  $A_1(T)$  is then always positive, increasing monotonically from zero to infinity as the temperature increases; more exactly, we show in the Appendix below that this is true if  $u(r)$  diverges at small  $r$  at least like  $r^{-3}$  which is the case for all practical models (the Lennard-Jones model takes  $u(r) \sim r^{-12}$  for  $r \rightarrow 0$ ).  $A_2(T)$  is always negative and increasing with  $T$ .  $I(T)$  is then a monotonically increasing function, negative for  $T = 0$  and positive for  $T \rightarrow \infty$ .

So  $I(T)$  must change its sign for a unique "inversion temperature"  $T_I$ . If  $T < T_I$ ,  $I$  and  $J$  are negative, the gas is cooler after a free expansion; if  $T > T_I$ ,  $J > 0$  and the gas is warmer.

The physical reason for that phenomenon can be easily elucidated: if the temperature is high, the molecules have enough kinetic energy to come very close to each other, to distances smaller than  $r_0$  thus making the average forces repulsive; although the mean intermolecular distance is much greater than  $r_0$ , the interacting potential becomes so high for  $r < r_0$  that the repulsive part can overcome the attractive one.

Such an inversion temperature exists for all real gases, the value of which depends on the characteristics of the intermolecular interaction potential.

Let us remark that the existence of an inversion temperature comes directly from the fact that there is a high but not infinite repulsive part in  $u(r)$ . For a hard sphere repulsive part [ $u(r) = +\infty$  for  $r < r_0$ ],  $(\partial U/\partial V)_T$  is always positive and the gas always cools in a Joule expansion; that is the case for a van der Waals gas<sup>2,3</sup> since the parameter  $b$ , which takes into account the "finite size" of the molecules, is supposed temperature independent.<sup>9</sup>

Let us remark also that one finds by the above argument, an inversion temperature  $T_I$  which is pressure independent. This is because the analysis is restricted to dilute gases (for which the average intermolecular distance  $\bar{r}$  is much larger than  $r_0$ ). Indeed, it is only in this limit that relation (4) is valid (or equivalently the third virial coefficient negligible). Clearly, one would expect  $T_I$  to decrease if the gas becomes less dilute, that is, if the pressure increases. The same kind of phenomena is observed for the Joule-Kelvin inversion temperature (throttling process): as it is well known, this latter is pressure dependent,<sup>1,2,4,7</sup> but one finds a pressure independent result<sup>8</sup> if one takes for  $U$  the sum of the potential energies of all pairs of molecules [relation (4)].

## V. ESTIMATES OF THE INVERSION TEMPERATURE

To make an estimate of the value of  $T_I$  we take for  $u(r)$  the Lennard-Jones potential

$$u_{LJ}(r) = u_0 \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right] = u_0 f \left( \frac{r}{r_0} \right). \quad (9)$$

From the preceding analysis we may expect that the smaller  $u_0$ , the smaller  $T_I$ . So it is not surprising that helium which has a very small  $u_0$  (that is why helium is so hard to liquefy) gets hotter in a free expansion undertaken at usual temperature.

Plugging  $u_{LJ}(r)$  into Eq. (6) one finds, since  $(\partial U/\partial V)_{T=0}$  for  $T = T_I$ , the following equation for  $T_I$ :

$$\int_0^{+\infty} dx x^2 f(x) e^{-u_0 f(x)/kT_I} = 0. \quad (10)$$

In this model,  $T_I$  is then proportional to  $u_0$ . A numerical resolution gives

$$T_I \approx 25 \frac{u_0}{k}. \quad (11)$$

For example, for helium, the literature gives<sup>10</sup>  $u_0 \approx 7 \times 10^{-4}$  eV so that

$$T_I(\text{He}) \approx 200 \text{ K.}$$

For hydrogen one gets<sup>10</sup>  $u_0 \approx 28 \times 10^{-4}$  eV, so that

$$T_I(\text{H}_2) \approx 800 \text{ K.}$$

For most of the gases,  $u_0$  is at least of the order of  $10^{-2}$  eV, and then  $T_I \geq 2500$  K.

To compare these results with experiments, the best is to link the calculation of the Joule coefficient (2) to the second virial coefficient  $B(T)$ . Indeed, the first correction to the perfect gas equation of state is

$$\frac{p}{kT} = \frac{N}{V} + B(T) \left( \frac{N}{V} \right)^2 + \dots, \quad (12)$$

which gives, when using Eq. (2),

$$J = \left( \frac{\partial T}{\partial V} \right)_E = -k \frac{N^2 T^2}{C_V V^2} \frac{dB}{dT}. \quad (13)$$

The sign of the Joule coefficient relies on the sign of  $dB/dT$ , and the inversion temperature corresponds to the maximum of  $B(T)$ . The experimental variations of  $B$  measured by Hollborn and Otto are given in Callen's Book.<sup>7</sup> One can see that the estimation given above is excellent for helium, but twice too big for hydrogen. This might be due to the fact that an interaction potential like Eq. (9) is too simple to describe the interaction between two molecules which are not monoatomic.

Finally, let us remark that our result (6) can be obtained exactly when we replace in Eq. (13)  $B(T)$  by its theoretical expression obtained by statistical mechanics<sup>8,9</sup>

$$B(T) = \frac{1}{2} \iiint dr [1 - e^{-u(r)/kT}]. \quad (14)$$

But this result requires a much more elaborate theory than the simple argument used above.

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## APPENDIX

We want to prove that, if  $u(r)$  diverges at small  $r$  at least like  $r^{-3}$ ,

$$A_1(T) = \iiint_{r < r_1} dr u(r) e^{-u(r)/kT}$$

$$= \int_0^{r_1} 4\pi r^2 u(r) e^{-u/kT} dr$$

has the two following properties:

- (i)  $A_1(0) = 0$ ,
- (ii)  $A_1(+\infty) = +\infty$ .

Since  $ue^{-u/kT}$  is maximum for  $u = kT$ , and since  $u(r) > 0$  for  $r < r_1$ , we can write

$$0 < A_1(T) < \frac{kT}{e} \iiint_{r < r_1} dr,$$

which clearly leads to point (i).

On the other hand, the integrand in  $A_1(T)$  is always positive and then

$$A_1(T) \geq \int_{r_2(T)}^{r_1} 4\pi r^2 u(r) e^{-u/kT} dr > 0,$$

where  $r_2(T)$  is the intermolecular distance for which  $u(r) = kT$ . For  $r < r_1$ ,  $u(r)$  decreases monotonically from  $+\infty$  to 0, so  $r_2(T)$  is a well-defined function of  $T$ , decreasing from  $r_1$  to 0 as  $T$  goes from 0 to  $+\infty$ .

For  $r_2(T) < r < r_1$ ,

$$e^{-u/kT} > \frac{1}{e}$$

leads to

$$A_1(T) > \frac{4\pi}{e} \int_{r_2(T)}^{r_1} r^2 u(r) dr$$

and

$$\lim_{T \rightarrow \infty} A_1(T) > \frac{4\pi}{e} \int_0^{r_1} r^2 u(r) dr.$$

The integral in the right-hand side is infinite if  $u(r)$  diverges at  $r=0$  more rapidly than (or at least like)  $r^{-3}$ . If it is the case  $A_1(+\infty) = +\infty$ .

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<sup>8</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed., Part 1 (Pergamon, London, 1980).

<sup>9</sup>See, for example, B. Diu, C. Guthmann, D. Lederer, and B. Roulet, *Éléments de Physique Statistique* (Hermann, Paris, 1989).

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## Frame grabbing techniques in undergraduate physics education

W. Benenson and W. Bauer

*Lyman Briggs School, and Department of Physics and Astronomy and National Superconducting Cyclotron Laboratory, Michigan State University, East Lansing, Michigan 48824-1321*

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The availability of video and frame grabbing technology for desktop computers permits a new form of visualization and measurement in mechanics experiments. Simple systems such as bouncing balls can be studied in detail and with enough precision to determine important aspects of the motion. For example, the system can be used for introductory students to measure the acceleration of gravity,  $g$ , and it also can be coupled with advanced mathematical techniques to find the drag coefficient and elasticity of the bounce. Conventional spreadsheet programs can be used to carry out all but the most mathematical treatments of the data. Examples of analyses which were carried out by high school students through senior physics majors at college are given.

### I. INTRODUCTION

Mechanics experiments and demonstrations in undergraduate physics often are carried out over a period of only a few seconds or less. As a consequence, stroboscopic pictures or elaborate encoding systems are used for quantitative

studies of the motion. These methods require either large supply budgets, such as in the case of Polaroid pictures, or commercial interface systems. Modern video cameras of the ordinary domestic type, however, have the ability to take high shutter speed images at a very well known and precise rate and can therefore be used as a tool for the