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Ideal systems in classical thermodynamics

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Abstract. The term 'ideal' is currently employed for thermodynamic systems of different natures (gases, elastic systems, magnetic systems, etc). However, different meanings are usually given to this term. Joule's law, which establishes that the internal energy of a system depends exclusively on temperature, is considered here as a general criterion for an ideal system in classical thermodynamics. The conditions that a system should satisfy to obey Joule's law and the implications of these conditions on the equation of state are discussed. Some similarities and differences between ideal systems of different natures are also emphasized.

Resumen. El término 'ideal' se emplea en la actualidad para sistemas termodinámicos de naturaleza distinta (gases, sistemas elásticos, sistemas magnéticos, etc). Sin embargo, es habitual dar a este término distintos significados. La ley de Joule, que establece que la energía interna de un sistema depende sólo de la temperatura, se considera aquí como un criterio general para la condición de sistema ideal. Se discuten las condiciones que un sistema debe satisfacer para verificar la ley de Joule, así como las implicaciones de estas condiciones sobre la ecuación de estado. Se subrayan también las similitudes y diferencias entre sistemas ideales de distinta naturaleza.

1. Introduction

Many undergraduate textbooks on classical thermodynamics for physics, physical chemistry and chemical engineering courses consider ideal thermodynamic systems. Besides the classical ideal gas, the ideal paramagnetic substance [1–4] and the ideal rubber-like elastic material (or ideal elastomer) [5–15] are two widely used examples. The classical ideal gas is characterized by the fulfilment of two conditions, e.g. Joule's law and Boyle–Mariotte's law. (The sole use of Joule's law does not necessarily lead to the equation of state of the classical ideal gas.) For the rubber-like elastic material and the ideal paramagnetic substance, the attribute 'ideal' is often given to systems whose internal energy is a function exclusively of temperature [1, 2, 4, 10–15]; however, some authors do not mention this requirement explicitly [3]. Finally, there are other texts that use the attribute 'ideal' for systems which do not obey Joule's law [5–7, 9]. In this context, the question of what conditions a thermodynamic system should meet to be considered 'ideal' arises naturally.

The aim of this paper is to contribute some ideas to the question of the definition of an ideal system from the point of view of classical thermodynamics. We emphasize that statistical physics can provide a general criterion for a system to be ideal and consider Joule's law as this general criterion. The conditions that a system should satisfy to obey Joule's law as well as the implications of these conditions on the equation of state are then discussed. The similarities and differences between ideal systems of different nature are also emphasized. For pedagogical reasons, we consider only two thermodynamic systems: gases and elastomers (materials that consist of an isotropic network of long polymer chains), and clarify some potentially misleading assertions found in the literature, such as considering rubber as an ideal system [10–13, 15] or asserting that Joule's law is an exclusive characteristic of the ideal gas [16, 17].

2. Joule's law

The earliest attempts to determine the dependence of the internal energy of a gas on its volume were made by Gay-Lussac (1807) and Joule (1844). As the Gay-Lussac–Joule experiment was not capable of a precise measurement of the extremely small changes in temperature in a free expansion, Joule and Thomson (later Lord Kelvin) devised another experiment during the years 1852–62. As a conclusion of this experiment, it follows that the internal energy U of an ideal gas is a function of temperature T only (Joule's law). Thus,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0, \tag{1}$$

where V is the gas volume.

Mayer (1842) suggested that the difference between the thermal capacities of an ideal gas following a constant pressure process, C_p, and a constant volume process, C_V, is due to the work needed to expand the gas volume against the constant external pressure. Using data from previous experiments, Mayer came to the conclusion that

$$C_p - C_V = \left(\frac{\delta W}{\mathrm{d}T}\right)_p = nR, \tag{2}$$

which constitutes Mayer's law and is strictly valid for ideal gases. Here R is the universal gas constant and n is the number of moles in the gas system.

The laws of Joule and Mayer are usually considered as the most representative of classical ideal gas behaviour. However, the fulfilment of Boyle–Mariotte's law (1660) is also required in order to obtain the equation of state of the ideal gas

$$pV = nRT. \tag{3}$$

Indeed, the first and second principles of thermodynamics give [18]

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{4}$$

when applied to a p–V system, so that Joule's law requires only an equation of state of the form

$$pf(V) = T, \tag{5}$$

where $f(V)$ is an arbitrary function of V. On the other hand, Mayer's law requires

$$p\left(\frac{\partial V}{\partial T}\right)_p = nR. \tag{6}$$

It is now evident that the most general equation of state satisfying both equations (5) and (6) is

$$p(V - nb) = nRT \tag{7}$$

where b is a constant. Equation (7) is known as the equation of state of the gas of hard spheres [19] and describes the behaviour of real gases in the limit of high temperatures, where the attractive intermolecular forces can be neglected. This is the case, for example, of the hot dust gas [20] and the metallurgical gas [21]. Obviously, equation (7) does not verify Boyle–Mariotte's law.

3. The generalized definition of an 'ideal' thermodynamic system

In the previous section we have shown that Joule's law leads to the equation of state (5) for a p–V system and not necessarily to equation (3), which describes the classical ideal gas. However, we have also mentioned in the introduction that Joule's law is often considered as the criterion for defining an ideal system. We then have to decide to either change the criterion for ideality or admit other ideal systems in addition to the classical ideal gas.

In statistical thermodynamics, the ideal gas is defined as a system of free non-interacting particles in the classical regime [22]. (The term 'free' means that the system of particles is not under the influence of an external field.) As an extension to this definition, condensed systems are sometimes considered to be 'ideal systems' when studying those phenomena where the interaction between the constituent elements can be ignored. The absence of interactions leads to an average value of the internal energy depending only on temperature, which constitutes Joule's law.

What happens when there are interactions between the constituent elements of the system? In these cases Joule's law is not obeyed in general, *except* for those particular systems where all allowed microscopic configurations of the system have the same potential energy. For these systems, the average value of the internal energy depends exclusively on temperature, which is just what happens in the case of an absence of interactions. The hard-spheres system, for instance, satisfies this condition (and thus Joule's law) because the repulsive interaction between particles due to their finite size can be included in the boundary conditions for the system of particles if the concept of available volume (defined as the total volume minus the excluded volume) is introduced.

The case of systems of particles under the influence of magnetic, electrical or gravitational fields lies outside the scope of this contribution.

From the point of view of macroscopic thermodynamics, Joule's law can indeed be considered as representative of the ideal behaviour. We are now going to derive the formal equation of state of a system obeying this law by using the formalism of generalized thermodynamics [23]. Let A and a be the intensive and extensive parameters, respectively, of a given thermodynamic system, which are defined so that the generalized elementary work takes the form $\delta W = A\,\mathrm{d}a$. Equation (4) can then be put in the form [24]

$$\left(\frac{\partial U}{\partial a}\right)_T = T\left(\frac{\partial A}{\partial T}\right)_a - A, \tag{8}$$

and Joule's law

$$\left(\frac{\partial U}{\partial a}\right)_T = 0 \tag{9}$$

now requires that the equation of state takes the form

$$Af(a) = T, \tag{10}$$

where $f(a)$ is an arbitrary function of the extensive parameter. Therefore, a thermodynamic system verifies Joule's law if and only if the intensive parameter A is proportional to temperature when the extensive parameter a is constant.

Moreover, Mayer's law in generalized thermodynamics takes the form [25]

$$C_A - C_a = \left[\left(\frac{\partial U}{\partial a}\right)_T + A\right]\left(\frac{\partial a}{\partial T}\right)_A, \tag{11}$$

which reduces to

$$C_A - C_a = \left(\frac{\delta W}{\mathrm{d}T}\right)_A = A\left(\frac{\mathrm{d}a}{\mathrm{d}T}\right)_A \tag{12}$$

when Joule's law (equation (9)) is satisfied. There is an important difference, however, between equations (2) and (12), while equation (12) only indicates how to calculate $C_A - C_a$, equation (2) also gives the value of $C_p - C_V$. In particular, it can be easily seen from equation (10) that

$$C_A - C_a = \left[\frac{\mathrm{d}f(a)}{\mathrm{d}a}\right]^{-1} \tag{13}$$

is constant only when $f(a)$ is a linear function, as was the case in equation (7).

4. The ideal elastomer

Now let us consider a thermodynamic system composed of an elastomer band of length L. An external force τ is applied along the band axis. Taking into account that the volume remains approximately constant under deformation [26], the thermodynamic state of the band can be described in terms of variables τ, L and T. The equation of state of this system is often written in the form [26–30]

$$\tau = kT\left[\frac{L}{L_0} - \left(\frac{L_0}{L}\right)^2\right], \tag{14}$$

where L_0 is the length for $\tau = 0$ and k is a constant. (Strictly speaking, equation (14) is not a proper equation of state because it involves two different states of the system.)

For τ–L systems, the generalized parameters are $A = -\tau$ and $a = L$, so that equation (10) requires that L_0 is independent of temperature if Joule's law is to be obeyed. This fact is frequently ignored in the literature [5–7, 9], though some authors have noted it previously [8, 10, 15]. Note that if L_0 does not depend on T for an ideal elastomer, the linear expansion coefficient of an unstretched elastomer

$$\lambda_0 \equiv \frac{1}{L_0}\frac{\mathrm{d}L_0}{\mathrm{d}T} \tag{15}$$

must be zero. Either from equations (12) or (13), Mayer's relation for the ideal elastomer takes the form

$$C_\tau - C_L = kL_0\frac{[(L/L_0)^3 - 1]^2}{(L/L_0)^4 + 2L/L_0} \tag{16}$$

which is clearly dependent on the band length and not constant, in contrast to the case of an ideal gas.

5. Deviations from ideal behaviour

The deviation from the ideal behaviour of gases can be observed either in the variations of internal energy in processes at constant temperature or in the non-constant value of the difference $C_p - C_V$. For instance, if we consider a real gas whose behaviour can be described by the van der Waals equation of state

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) - nRT, \tag{17}$$

where a and b are two constants, it can easily be shown that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{n^2a}{V^2} \tag{18}$$

and

$$C_p - C_V = nR\frac{1}{1 - [2na(V - nb)^2/RTV^3]}. \tag{19}$$

It is worth noting that $(\partial U/\partial V)_T$ is obtained as the difference between two magnitudes, $T(\partial p/\partial T)_V$ and p, which tend to cancel each other. Thus, the deviation from ideality tends to zero as V increases, i.e. at high temperatures and/or low densities.

As a real elastomer, we consider the case of rubber. It is well known that rubber has a unique elastic behaviour: it has enormous extendibility (up to 400% compared with less than 1% for ordinary solids [31]). This behaviour follows from the configurational properties of its isotropic network of long polymer chains. For moderate deformations, the behaviour of rubber can be described by equation (14). However, rubber has a non-zero linear expansion coefficient when $\tau = 0$ and this implies that L_0 is a function of T when equation (14) is applied to rubber. In particular, $k = 4.86 \times 10^{-3}$ N K^{-1} [32] and $\lambda_0 = 2.2 \times 10^{-4}$ K^{-1} at 25 °C [33]. It can now be shown that

$$\left(\frac{\partial U}{\partial L}\right)_T = \tau - T\left(\frac{\partial \tau}{\partial T}\right)_L = kT^2\lambda_0\left[\frac{L}{L_0} + 2\left(\frac{L_0}{L}\right)^2\right] \tag{20}$$

and

$$C_\tau - C_L = kL_0\frac{\{(L/L_0)^3 - 1 - T\lambda_0[(L/L_0)^2 + 2]\}^2}{(L/L_0)^4 + 2L/L_0}. \tag{21}$$

Figure 1 gives $(\partial U/\partial L)_T$ from equation (20) for a moderately large deformation range. In order to emphasize the small values attained by $(\partial U/\partial L)_{T'}$ we have also shown the two terms in the right-hand side of equation (20). In figure 2 we have shown $(C_\tau - C_L)/L_0$ against L/L_0 for the cases of an ideal elastomer and rubber with the above values for k and λ_0. Since $C_\tau - C_L$ is not constant for an ideal elastomer, the deviation from the ideal behaviour is more easily observed in figure 1 (non-zero value of $(\partial U/\partial L)_T$) than in figure 2. Therefore, we conclude that $(\partial U/\partial L)_T$ not only rules the criterion for ideality but also provides a good measure of the deviations from ideality.

6. Similarities between ideal systems

The first and second principles of thermodynamics lead to the equation

$$\mathrm{d}F = -S\,\mathrm{d}T - A\,\mathrm{d}a, \tag{22}$$

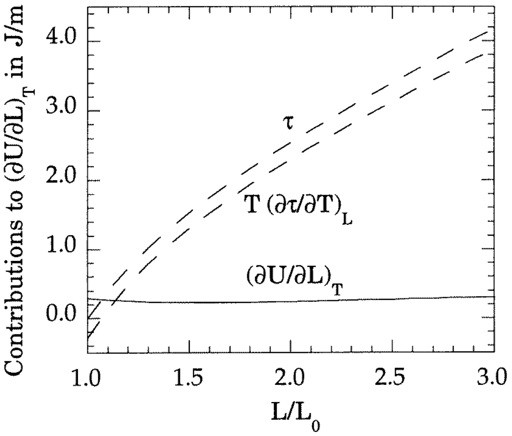

Figure 1. The derivative $(\partial U/\partial L)_T$ and the two terms τ and $T(\partial\tau/\partial T)_L)$ in equation (20).

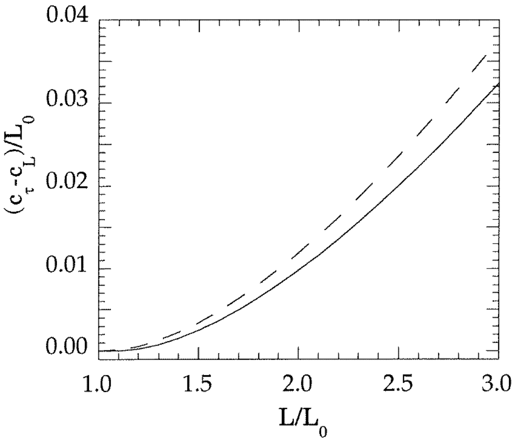

Figure 2. Rubber (full curve) and ideal elastomer (broken curve) values of $(C_\tau - C_L)/L_0$ against L/L_0.

where F and S are the Helmholtz function and the entropy of an A–a system, respectively. Since $F \equiv U - TS$, we have

$$A = -\left(\frac{\partial F}{\partial a}\right)_T = -\left(\frac{\partial U}{\partial a}\right)_T + T\left(\frac{\partial S}{\partial a}\right)_T. \qquad (23)$$

For an ideal elastomer Joule's law is verified and therefore

$$\tau = -T\left(\frac{\partial S}{\partial L}\right)_T. \qquad (24)$$

Thus, the force τ depends on how S varies with L at constant T. An ideal gas behaves in a similar way, i.e.

$$p = T\left(\frac{\partial S}{\partial V}\right)_T. \qquad (25)$$

This entropic origin of both p and τ constitutes the main similarity between ideal systems if we use Joule's law to define them.

The pressure of the ideal gas is an entropic effect which derives from the translational kinetic energy of its molecules [12]. Similarly, in an ideal elastomer the elasticity is considered to be an entropic effect which derives from the rotational kinetic energy rather than from the intermolecular potential energy of the carbon atoms about each C–C bond [31]. The latter remains constant when an ideal elastomer is extended, which is not surprising for a condensed phase of constant volume [12].

The real elastomers (rubber, for example) deviate from ideality due to the existence of intermolecular forces between constituents causing restrictions to the internal rotation. In real gases, intermolecular forces are also responsible for the non-ideal behaviour. In both cases, the result of the forces is that not all allowed microscopic configurations of the system have the same potential energy and then the statistical average value of the internal energy does not depend exclusively on temperature.

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