

Thermodynamic Description of Translational Energy Relaxation in Binary Mixtures of Dilute Gases*

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An expression relating the phenomenological coefficient L to the relaxation time τ and temperatures is derived within the formalism of non-equilibrium thermodynamics. For the model of hard spheres the coefficient L is expressed by number densities of components, the molecular masses, the diameters of spheres, the correlation function and temperatures. The values of τ and L are calculated for binary mixtures of noble gases. It is shown that L (similarly to τ) is time dependent, because the temperatures of components change during the relaxation process. Such changes are smaller than 10 percent even for relatively large temperature differences.

Key words: energy relaxation, non-equilibrium thermodynamics, noble gases

The equilibration of energies between components of a gas can play an important role [1]. This process can be observed not only in some special phenomena: 1. such as (a) the mixing of hot and cold molecules at a shock or detonation front (b) the slow thermalization of massive molecules by a much lighter diluent, which appears in the transport process of electron swarms in gases [2–4], but also in 2. typical chemical reactions, in which the homogeneous production of species with energy distribution, different from those of the reactants, takes place [5,6]. Such different energies of reagents, arising from non-equilibrium kinetic effects, have been recently shown to have a large effect on the rate of chemical reaction [7]. The role of different temperatures of reagents have been also analyzed in [8–13]. It has been also shown that the equilibration of temperatures of reagents can have an additional effect on the rate of chemical reaction in gaseous systems [7, 11, 14].

In systems, in which two components have different temperatures, a process of equilibration of these temperatures may be regarded as an energy relaxation process. It is interesting to observe that such relaxation can be analyzed in terms of two main quantities: 1. the temperature difference, which can be treated as the cause of the process and 2. the change of each of the temperatures in time, which can be treated as its result. Therefore, the situation is similar to that in linear non-equilibrium

thermodynamics [15] in the case in which, in a system divided into two subsystems with different temperatures, the heat flux appears. A linear phenomenological equation is sufficient to describe such a process as a flux caused by a thermodynamic force. Such a description is simple and very clear. That is why we think that it is worthwhile to describe the process of temperature relaxation in the same way, *i.e.* to use the formalism of linear non-equilibrium thermodynamics for this purpose. As within this formalism the phenomenological coefficients can be usually expressed in terms of measurable quantities, we shall derive the relation between the phenomenological coefficient and the relaxation time. It is worthwhile to observe that Shizgal [16] criticized that in the formulas describing the rate of change of temperature of one component only some authors introduced the difference of temperatures of the components [17].

The aim of this paper is to use non-equilibrium thermodynamics to derive the phenomenological equation for the energy relaxation in gases and to relate the phenomenological coefficient to the relaxation time and other measurable quantities.

RESULTS

a) Phenomenological equations. Although very often in such processes as heat transfer, diffusion [18] and transport phenomena in electrolyte solutions [15, 19–21] the continuous systems are considered and the gradients of temperatures or concentrations appear, in some cases, such as *e.g.* membrane transport [22] the system can be divided into two subsystems and instead of the gradients mentioned the differences between the temperatures (concentrations) in both the subsystems can play an important role [22]. Looking for similarities between the process of energy relaxation with the processes mentioned above could seem to be difficult. However, taking into consideration such descriptions as in [1, 7, 14, 16, 23–25], we decide to make the following "artificial" assumption.

We treat a two component gas system as divided into two subsystems. Each of them is assumed to be in "thermodynamic local equilibrium". This corresponds to the assumption that each of subsystem A and B is characterized by the Maxwell-Boltzmann velocity distribution function

$$f_i = n_i \left(\frac{m_i}{2\pi kT_i} \right)^{3/2} \exp \left(- \frac{m_i c_i^2}{2kT_i} \right) \quad (i = A, B) \quad (1)$$

where n_i denotes the number densities, m_i – the molecular masses, c_i – velocities, T_i – the temperatures and k is the Boltzmann constant.

The average energy of each subsystem is

$$E_i = \int \frac{m_i c_i^2}{2} dc_i = \frac{3}{2} n_i k T_i \quad (i = A, B) \quad (2)$$

whereas the total average energy is

$$E = E_A + E_B \quad (3)$$

* Dedicated to Prof. B. Baranowski on the occasion of his 70th birthday.

We treat both subsystems as if they were separated in the same way as two discontinuous systems (see Chapter XV in [15]).

Therefore, we can write for the entropy production σ

$$\sigma = \frac{1}{T_A} \frac{dE_A}{dt} + \frac{1}{T_B} \frac{dE_B}{dt} \tag{4}$$

Since the total average energy must be conserved, from (3) and (4) we get

$$\sigma = \frac{dE_A}{dt} \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \tag{5}$$

We see that (5) can be written in the form

$$\sigma = JX \tag{6}$$

where $J = \frac{dE_A}{dt}$

and

$$X = \frac{1}{T_A} - \frac{1}{T_B} = \frac{T_B - T_A}{T_A T_B} \tag{8}$$

can be treated as the thermodynamic flux J and force X , respectively. Because of (6)–(8) an appropriate thermodynamic phenomenological equation is

$$J = LX \tag{9}$$

where L is the phenomenological coefficient.

This phenomenological coefficient can be related to the measurable quantities in the following way. From (7), (2), (9) and (8) it follows

$$\frac{dT_A}{dt} = \frac{2}{3n_A k} \frac{dE_A}{dt} = \frac{2}{3n_A k} LX = \frac{-2}{3n_A k} \frac{L}{T_A T_B} (T_A - T_B) \tag{10}$$

This equation has a form similar to that in which the relaxation time τ_T is introduced (see, e.g. [23])

$$\frac{dT_A}{dt} = -\frac{1}{\tau_T} (T_A - T_{eq}) = -\frac{1}{\tau_T} (T_A - T_B) \tag{11}$$

where T_{eq} is the equilibrium temperature. From (10) and (11) we get

$$L = \frac{3}{2} \frac{n_A k T_A T_B}{\tau_T} \tag{12}$$

Recently, generalization of the kinetic theory of the translational energy relaxation in dilute gases [23,24] gave the following expression for dense gases composed of hard spheres [25,26]

$$\tau_T = \frac{3}{16} \frac{(m_A + m_B)^2}{m_A m_B} \frac{1}{n_B d_{AB}^2 \chi_{AB}} \left[\frac{T_A}{m_A} + \frac{T_B}{m_B} \right]^{-1/2} \tag{13}$$

where d_{AB} is the average diameter of the spheres A and B, whereas χ_{AB} is the radial distribution function at the point of contact of colliding spheres. From (12) and (13) it follows that

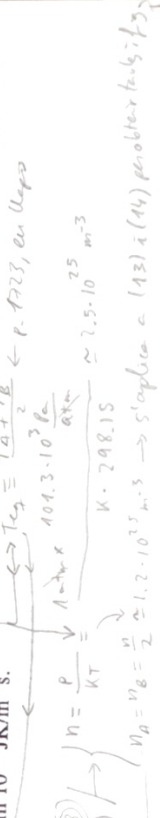
$$L = 8 \frac{n_A n_B m_A m_B d_{AB}^2 \chi_{AB} k T_A T_B}{(m_A + m_B)^2} \left[\frac{T_A}{m_A} + \frac{T_B}{m_B} \right]^{-1/2} \tag{14}$$

This is the fundamental equation we have been looking for.

b) Phenomenological coefficient L for noble gas mixtures. As discussed in [27] the model of hard spheres is convenient for the analysis of transport processes in noble gases (e.g. the average molecular diameters calculated for this model from the measurements of shear viscosity and diffusion coefficients have similar values within an accuracy of a few percent). That is why we will calculate the values of L for noble gases. It is worthwhile to observe that the computer simulations [28] for hard spheres systems (Monte Carlo Naabu-Babovsky and Bird algorithms for the dilute systems and the molecular dynamics simulations for the dense systems) have confirmed the validity of such expressions as (13) within an accuracy of a few percent.

Since the coefficient L depends on temperatures T_A and T_B , we present the results for two values of T_A and T_B , namely for $T_A - T_B$ equal to 50 K and 100 K. We analyze mixtures of noble gases, which in equilibrium would be described by standard temperature and pressure, i.e. (298.15 K and 1 atm), respectively. We present these results for equal molar fractions of the components. We introduce $\chi_{AB} = 1$ and the values of d_A and d_B calculated from the shear viscosity coefficient [27]. In Table 1 we present such results for the relaxation time τ_T , whereas in Table 2 the results for the phenomenological coefficient L . In both tables the results for $T_A - T_B = 100$ K are given in parentheses. It is worthwhile to observe that the quantities τ_T and L , given for the same gas, e.g. He-He, may seem to be useless quantities. However, they are presented here not only to show the very simple artificial systems but also because, as shown in [29], the number of collisions during such a relaxation time for "self-relaxation" of hard spheres is the same as the number of collisions during the relaxation time for energy equilibration of translational energy in perpendicular directions, which can take place in shock waves.

In Fig. 1 we show additionally the effect of the temperatures difference $T_A - T_B$ on τ_T and L for the systems characterized by a very large ratio of masses: I. Xe-He (with He atoms at the lower temperature), II. He-Xe (with Xe atoms at the lower temperature). The results in Fig. 1 for τ_T are presented in 10^{-10} s, whereas those for L in 10^{16} JK/m³.



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Table 1. The relaxation time τ_T for the mixtures of noble gases. The results of τ_T calculated from eq. (13) are presented in 10^{-10} s. For a given value in the table, the column indicates the component at higher temperature and the row shows that at the lower temperature. The temperatures are 273.15 K and 323.15 K (248.15 and 348.15 for the values inside parentheses).

	He	Ne	Ar	Kr	Xe
He	4.161 (4.161)	8.379 (8.640)	10.05 (10.25)	16.18 (16.89)	19.89 (20.80)
Ne	7.922 (7.720)	6.637 (6.637)	6.010 (6.097)	8.096 (8.324)	9.301 (9.621)
Ar	9.208 (8.926)	5.846 (5.769)	4.722 (4.722)	5.533 (5.620)	6.058 (6.205)
Kr	14.99 (14.49)	7.691 (7.510)	5.372 (5.296)	5.194 (5.194)	5.143 (5.192)
Xe	18.38 (17.74)	8.745 (8.502)	5.793 (5.673)	5.049 (5.003)	4.699 (4.699)

Table 2. The phenomenological coefficient L in 10^{16} JK/m³ s (calculated from eq. (12)). The columns and rows of the array are represented in the same way as in Table 1.

	He	Ne	Ar	Kr	Xe
He	5.901 (5.775)	2.930 (2.782)	2.444 (2.345)	1.517 (1.423)	1.234 (1.155)
Ne	3.100 (3.113)	3.700 (3.621)	4.086 (3.942)	3.033 (2.887)	2.640 (2.498)
Ar	2.667 (2.693)	4.200 (4.166)	5.200 (5.089)	4.437 (4.276)	4.053 (3.873)
Kr	1.638 (1.659)	3.193 (3.200)	4.571 (4.538)	4.728 (4.628)	4.775 (4.629)
Xe	1.336 (1.354)	2.808 (2.827)	4.239 (4.237)	4.864 (4.804)	5.226 (5.115)

DISCUSSION

It is interesting that the coefficient L , similarly as the relaxation time, depends on the temperature difference $T_A - T_B$ and because of (8) on the thermodynamic force X . Therefore, the energy relaxation in a nonlinear process as J in (9) additionally depends on X because $L = L(X)$. Only for small $T_A - T_B$ this process can be treated as approximately linear. As it can be seen from these tables, the values of τ_T and L calculated for $T_A - T_B$ equal to 50 K and 100 K differ less than 10 percent. From Fig. 1 it can be seen that, even for the largest atomic mass differences, i.e. for He, Xe mixtures, (for $T_A - T_B$ in the ranges of 10–100 K) τ_T and L also do not change much. It means, that the thermodynamic description presented here looks reasonable, because the phenomenological coefficient is nearly a constant quantity. Naturally, it would be the best if L could be a constant. However, such a situation of constant phenomenological coefficient cannot be expected in other non-equilibrium processes either (see [18,19,21]).

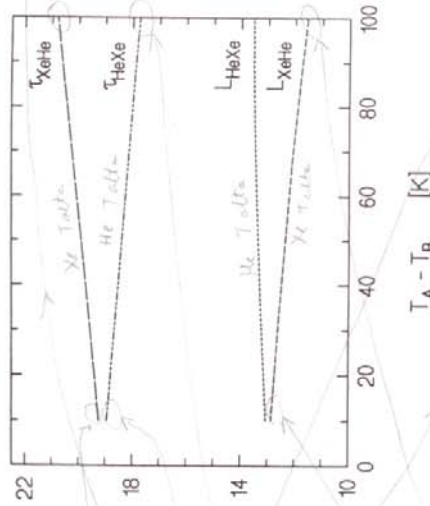


Figure 1. The relaxation time τ_T and the phenomenological coefficient L for the He-Xe system as a function of $T_A - T_B$. The units of τ_T are 10^{-10} s and those of L are 10^{16} JK/m³ s. The average temperature is 298.15 K.

We would like to emphasize that the assumptions necessary for the derivations are not trivial and that the description based on these assumptions is relatively simple. The results obtained in this paper can be helpful on the one hand for understanding of the energy relaxation process, namely to see what can be treated as thermodynamic flux and force. On the other hand, this elementary treatment can be helpful as the first step for construction more complicated descriptions such as can be met, e.g. in extended non-equilibrium thermodynamics [30–32].

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