



Microscopic expression of entransy in ideal gas system for diatomic molecules

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ABSTRACT

Cheng et al. gave the microscopic expression of entransy in the ideal gas system for monatomic molecules in an approximate non-interaction particle system. Diatomic molecular gas or polyatomic molecular gas is more widely used than monatomic molecules gas in industry. So this paper deduces the microscopic expression of entransy in the ideal gas system for diatomic molecules by using the approximate calculation of partition function.

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1. Introduction

Thermodynamics is a subject of studying thermal phenomena, the law of thermal motion and mutual transformation between thermal motion and other forms of motion [1]. It has been two and a half centuries after its fitful and erroneous development [2]. In 1850, Clausius expressed the second law of thermodynamics as “heat never flows spontaneously from a cooler to a hotter body without causing other changes.” In 1851, Kelvin put forward another expression “it is impossible to take heat from a single heat source, making it completely useful but without any other changes [3]”. The essence is the same though the two expressions are different, that is all the actual macroscopic processes associated with the thermal phenomena are irreversible.

Clausius proposed the entropy in 1865. Entropy is a state parameter closely related to the second law of thermodynamics, which provides a criterion for judging the direction of the practical process, whether the practical process can be achieved, reversible or irreversible. Then the entropy increase principle reveals the irreversibility of natural process, and the asymmetry of the natural process for the time direction. Reducing the total entropy of an isolated system is impossible, the ideal reversible process can only keep the total entropy unchanged. All the practical process is irreversible, so the practical thermodynamic process always in the direction of increasing total entropy of the isolated system [4].

Thermodynamics is a subject with wide universality and high reliability, which elaborates macroscopic theory of thermal phenomena based on experiments and involves macroscopic physical quantities. However, it does not study the microstructure of the material and the motion state of microscopic particles. Boltzmann committed himself to exploring the atomic mechanism of thermodynamics at micro level, demonstrating the proportional relation between entropy and the logarithm of microstate numbers. The inscription on Boltzmann's gravestone in the central cemetery of Vienna is the essence of this work, by means of which Max Planck summarized Boltzmann's somewhat obscure statements and summed it up as this simple equation [5].

$$S = k \ln \Omega \quad (1)$$

where k is the Boltzmann constant and Ω is microstate number.

Heat transfer is an irreversible process from a thermodynamic perspective, and entropy is the measure of this irreversible process. However, as far as the irreversibility of heat transfer is concerned, a question may be raised in that is it only entropy that describes the irreversibility of the process? In 2007, based on the analogy between heat transfer and electricity, Guo et al. proposed a new physical quantity—entransy, which is defined as half of the product of internal energy and temperature [6].

$$G = \frac{1}{2} UT \quad (2)$$

where U is internal energy and T is temperature.

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Nomenclature

e	the base of natural logarithm
$g_{e,0}$	degeneracy
G	entransy
h	Planck constant
I	rotational inertia
k	Boltzmann constant
m	molecular mass
n	amount of substance
N_A	Avogadro's constant
S	entropy
T	temperature
U	internal energy
\bar{U}	mean internal energy per mole
V	volume
Z	partition function

Z_e	electronic partition function
Z_n	nuclear partition function
Z_r	rotational partition function
Z_t	translational partition function
Z_v	vibrational partition function

Greek symbols

α	coefficient
β	coefficient
κ	coefficient
σ	symmetric number
Ω	microstate number
Θ_r	characteristic rotational temperature
Θ_v	characteristic vibrational temperature

Entransy has the “energy” property corresponding to the electric energy in the capacitor, which represents the total capacity of the object to transmit heat to the environment of zero temperature in K [6]. There always is an entransy dissipation in any heat transfer process, that is, when heat (thermal energy) transfers from a body of higher temperature to a one of lower temperature, the transferred heat itself is conserved while the total entransy of the system, i.e., the capacity of transferring heat to the 0 K environment, is reduced [7]. Therefore, entransy is another important physical quantity to indicate the irreversibility of the heat transfer process. The extremum principle of entransy [6,8], and the thermal resistance based on the entransy, have been widely used in heat transfer process optimization [9], thermodynamic processes optimization [10], heat exchanger parameter optimization [11–15], etc.

In terms of microcosmic research, inspired by the micro-expression of entropy, Cheng et al. proposed the microscopic expression of entransy in ideal gas system of monatomic molecules in 2010 [3],

$$G = \kappa \Omega^{4/(3N)} \quad (3)$$

where κ is a coefficient related to the particle number, particle mass and volume.

They showed that for an ideal gas system of monatomic molecules, entransy is a single-valued function of temperature when the particle population, particle mass and volume are given. Based on the relationship between entransy and microstate number, they further discussed the variations of the available transport entransy, the unavailable transport entransy, the available conversion entransy and the unavailable conversion entransy with the microstate number [16].

This paper aims at revealing the relationship between entransy of an ideal gas system of diatomic molecules and microstate number.

2. The microscopic expression of entransy of diatomic molecules system

Suppose there is an ideal gas system of diatomic molecules which keeps dynamic balance (Fig. 1), and the volume V , the internal energy U and the internal particles number N of the system are given.

The gas molecules can move freely in gas system, so that the ideal gas system is regarded as a non-distinguishable particle

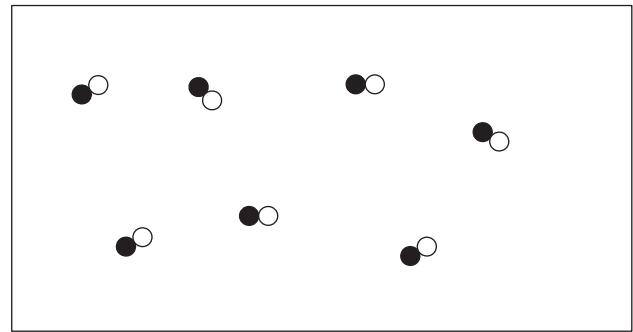


Fig. 1. The ideal gas system of diatomic molecules diagram. The symbol $\bullet\circ$ is the diatomic molecules.

system, then the microstate number of the system Ω can be expressed as

$$\Omega = (Z^N / N!) \exp(U/(kT)) \quad (4)$$

where Z is partition function of the system of diatomic molecules, T is temperature; k is Boltzmann constant [2]. The Stirling approximation can be used because the internal population of system N is very large,

$$\ln N! \approx N(\ln N - 1) \quad (5)$$

Then Eq. (4) can be simplified as

$$\Omega = (Ze/N)^N \exp(U/(kT)) \quad (6)$$

where e is the base of natural logarithm.

The internal energy U of an ideal gas system is

$$dU = nc_v dT \quad (7a)$$

where n is amount of substance of ideal gas system, $n = N/N_A$, N_A is Avogadro's constant. c_v is molar specific heat at constant volume. For the ideal gas, c_v is a function of temperature T . But it can be treated as constant specific heat when gases near room temperature [17]. Then Eq. (7a) will be

$$U = nc_v T \quad (7b)$$

The mean internal energy per mole of gas is simply [18]

$$\bar{U} = \frac{5}{2} NkT \quad (8)$$

The specific heat at constant volume of gas is then

$$c_v = \left(\frac{\partial \bar{U}}{\partial T} \right)_v = \frac{5}{2} Nk \tag{9}$$

Substituting Eqs. (7b) and (9) into Eq. (6), yielding the expression of the microstate number

$$\Omega = (Z/N)^N \exp(5nN/2) \exp(N) \tag{10}$$

The macroscopic definition of entransy is

$$G = \frac{1}{2} UT = \frac{1}{2} nc_v T^2 \tag{11}$$

It can be seen from Eq. (11) that for the ideal gas system of diatomic molecule, $G \sim f(T)$, so in order to reveal its micro expression of entransy for a diatomic molecular ideal gas system, the relation between system temperature and microstate number should be determined. In this paper, partition function will be used to derive this relationship [3].

Multiplying together the molecular partition functions of various forms of motions, then there is the total molecular partition function of a molecule. This is the factorial characteristics [19].

$$Z = z_t z_r z_v z_e z_n \tag{12}$$

where z_t, z_r, z_v, z_e, z_n are the translational, rotational, vibrational, electronic, and nuclear partition functions of molecules, respectively.

2.1. The electronic partition function

At normal temperature (less than thousands of degrees Celsius), the contribution of the electronic excitation level to the electronic partition function can be neglected [20]. The molecule is in electronic ground state. The energy of the electronic ground-state energy levels is zero, and then the electronic partition function is equal to the energy level degeneracy of the electronic ground state.

$$z_e = g_{e,0} \tag{13}$$

For most diatomic molecule ground state spectra is singlet state and it is not excited at normal temperature. So the electronic partition function z_e has no contribution to the total partition function and can be regarded as $z_e = 1$, except O_2 ($g_{e,0} = 3$) and NO ($g_{e,0} = 2$).

2.2. The nuclear partition function

As for the nuclear partition function, the core is always in the ground state in general physical and chemical changes except nuclear reactions, and the contribution to the changes in nuclear partition function is just offset, so z_n can be regarded as 1.

Table 1
The characteristic rotational temperature Θ_r of diatomic molecules.

Molecules	H_2	D_2	Br_2	N_2	O_2	CO	HCl	NO	HBr	Cl_2	I_2
Θ_r/K	87.5	43.8	0.116	2.89	2.08	2.78	15.2	2.45	12.2	0.351	0.0537

Table 2
The characteristic vibrational temperature Θ_v of diatomic molecules.

Molecules	H_2	N_2	O_2	CO	NO	HCl	HBr	HI
Θ_v/K	6320	3390	2278	3120	2745	4330	3820	3200

2.3. The translational partition function

The translational partition function is the sum of Boltzmann factor in the space motion of the molecular center. It can be proved [19,20] that for system of any shape, the translational partition function of the molecule is

$$z_t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V \tag{14}$$

where m is the molecular mass and h is the Planck constant.

2.4. The rotational partition function

All of the diatomic molecules are linear molecules and can be regarded as linear rigid rotor. The characteristic rotational temperature of ordinary diatomic molecules is very low as shown in Table 1 [19].

We can see from Table 1 that at ambient temperature, for ordinary diatomic molecules, $\Theta_r/T \ll 1$, therefore, we can describe the internal rotation of molecules with the classical method for most gases. The expression of rotational partition function of linear molecules is [19]:

$$z_r = \frac{8\pi^2 IkT}{h^2} \tag{15}$$

It should be noted that Eq. (15) only applies to heteronuclear diatomic molecules (say CO) for which when the molecule rotates 180 degrees around its symmetry axis the number of the same configurations is one. According to [19], its symmetry number equals one ($\sigma = 1$). For homonuclear diatomic molecules (say H_2) this number is two ($\sigma = 2$) [19,20]. Then Eq. (15) can be modified as follows:

$$z_r = \frac{8\pi^2 IkT}{\sigma h^2} \tag{16}$$

where I is rotational inertia of linear molecular, h is the Plank constant.

2.5. The vibrational partition function

A diatomic molecule has only one vibrational degree of freedom. The spacing between vibration energy levels is very large, and the characteristic vibrational temperature is much higher compared with characteristic rotational temperature, generally reaching to thousands of Celsius degrees. The characteristic vibrational temperatures of common diatomic molecule are shown in Table 2 [19].

In low temperature, it can be thought that the internal vibration of the molecules is in the ground state, and the high energy level almost has no contribution to partition function. Similar to the electronic partition function, the vibrational partition function is

a constant, which is equal to the degeneracy of ground-state energy level. So the vibrational partition function can be approximately regarded as $z_v = 1$ at normal temperature.

To sum up, the partition function of the diatomic molecule at normal temperature is

$$Z = z_t z_r z_v z_e z_n = \frac{V}{h^3} (2\pi m)^{3/2} (kT)^{5/2} \frac{8\pi^2 I}{\sigma} g_{e,0} \quad (17)$$

Substituting Eq. (17) into Eq. (10), the expression of microstate number is obtained as follows:

$$\Omega = (V/N)^N (8\pi^2 I g_{e,0} / \sigma h^3)^N \cdot (2\pi m)^{3N/2} (kT)^{5N/2} \exp(5nN/2) \exp(N) \quad (18)$$

From Eq. (18), the relation between temperature T and microstate number Ω can be found as follows:

$$T = [h^2 (\sigma N)^{2/5} / ((2\pi m)^{3/5} V^{2/5} k (8\pi^2 I g_{e,0})^{2/5} \exp(n))] \Omega^{2/(5N)} = \alpha \Omega^{2/(5N)} \quad (19)$$

where

$$\alpha = h^2 (\sigma N)^{2/5} / ((2\pi m)^{3/5} V^{2/5} k (8\pi^2 I g_{e,0})^{2/5} \exp(n)) \quad (20)$$

Combining Eqs. (2), (7b) and (19), the microscopic expression of entransy for the ideal gas system with diatomic molecule at normal temperature is obtained

$$G = \kappa \Omega^{4/(5N)} \quad (21)$$

where

$$\kappa = n C_v \alpha^2 / 2 = \beta \cdot \frac{N^{14/5}}{m^{6/5} (IV)^{4/5} \exp(2N/N_A)} \quad (22)$$

$$\beta = \frac{5h^4 \sigma^{4/5}}{2^{28/5} k N_A \pi^{14/5} (e g_{e,0})^{4/5}} \quad (23)$$

When a diatomic molecule system is given, its symmetry number σ , and degeneracy $g_{e,0}$ are determined, therefore, β can be regarded as a constant. In addition, κ is only related to the particle number, particle mass, rotational inertia and volume of system. Hence κ is a constant when these four quantities are given. Thus Eq. (20) shows that for an ideal gas system of diatomic molecules entransy is a single-valued function of temperature when the particle population, particle mass and volume are given.

Compared with the micro expression of entransy in monatomic molecule ideal gas system, it can be seen that coefficient and index of microstate number are different. This is mainly because when determining the partition function of diatomic molecule systems, the rotational and vibrational function of diatomic molecules should be taken into account.

3. Conclusion

The micro expression of entransy for an diatomic molecule ideal gas system has been derived in this paper based on the

approximate calculation of the molecular partition function. In the approximate non-interaction particle system, entransy is a single-valued function of the microstates number just like entropy. Thus the micro expression parallelism between entropy and entransy has been verified for the diatomic molecule ideal gas system.

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Conflict of interest

The authors declare that they have no conflict of interest.

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