



Research paper

An approach to the averaged intermolecular potential field of methane from viscosity



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ABSTRACT

A novel approach to averaged intermolecular potential field (AIPF) of methane from viscosity was developed. Using symmetric molecular interaction approximation and Maxwell-Boltzmann distribution function of velocity, equations relating the AIPF and viscosity have been derived. Applying the equations to methane, good agreements were found between high quality viscosity data and the equations via fitting method. Then a formula for methane's AIPF as a function of temperature and density was determined. Obtained results not only give a new method to estimate the AIPF for fluidic system, but also may form a novel base to study the viscosity of other alkane mixtures.

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1. Introduction

Intermolecular interactions have always received noticeable attention because they are responsible for the properties of substance. Since each interaction can be represented with a potential, the precise knowledge of the interaction potential among molecules has theoretical and practical importance in studying the substance properties. For this reason, investigations on the intermolecular potential have been conducted more than a hundred years, and a milestone could be traced back to the well-known potential proposed in 1924 by John Lennard-Jones [1]. Since then, articles on this topic were continuously reported in many famous journals [2–9]. Today it is still a very interesting and essential subject that needs to be explored via emerging innovative method, although considerable progresses have been made regarding the relationship between macroscopic properties and the microscopic interaction potential. The first example of the progresses is the virial coefficient which has been calculated using the intermolecular potential for interesting substances [10–12]. The second is the transport property such as viscosity, diffusion coefficient, or collision integral, whose links with the intermolecular potential have been determined via referred methods [13–20]. The final are other macroscopic properties and new calculation method that associate the intermolecular potentials [21–23].

Methane is the first and simplest alkane as well as the main constituent of natural gas. The knowledge about methane has not only the theoretical importance, but also the practical value in natural gas science and technology. The intermolecular potentials between methane molecules have interested a lot of scientists and engineers for many years. Matthews and Smith [24] reported a numerical spherically averaged intermolecular pair potential energy function by data inversion technique in 1976. Via relevant methods, Szczesniak et al. [25], Rowley and Pakkanen [26], Goharshadi and Abbaspour [27] determined this function again after the year. In 2004, Chen et al. [28] reported an intermolecular interaction potential of the methane dimer from the local density approximation. In recent years, molecular dynamics simulation method has enabled computation of thermodynamics, transport, structural properties, and new equation of state for fluid methane from the intermolecular interaction potential [29]. In order to improve results for the entire system, not only the three-body intermolecular potential was incorporated, but also the intermolecular potential for methane was refined [30].

The above stated efforts traditionally focus on the pair molecular potential, although little has been put on the three-body intermolecular potential. In a real physical system, there is a huge number of molecules, so the molecular interaction can be described in terms of intermolecular potential field (IPF). The IPF in the real system is obviously not as simple as the pair molecular potential. Actually it should relate a lot of macroscopic structures and behaviors more directly than the pair potential. However, the knowledge on this important issue remains a large gap. Just like the studies on the pair potential, an exploration on the IPF in the system containing

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huge number of molecules has both academic and practical significance, especially in understanding the properties like viscosity, diffusion, thermal conductivity, and so on.

The aim of this study is to develop a novel theoretical approach to the averaged intermolecular potential field (AIPF) of methane from viscosity. For this target, the rest of the article is structured as follows: first, an approach to intermolecular distance from density is established, and then equations relating the AIPF to viscosity is derived, finally binary term of the AIPF and contributions of triple and higher terms are determined.

2. Theoretical approach

2.1. Approaching intermolecular distance from density

An intermolecular distance between two molecules is usually defined as the distance between their centers. When the shape of molecules is ignored, it is referred as site-to-site intermolecular distance. Considering a N -body system containing N molecules restricted in volume V , the averaged volume occupied by each molecule is V/N . If the averaged volume is modeled as a sphere of diameter d , it yields,

$$V = N \frac{\pi}{6} d^3 \quad (1)$$

Or representing via density,

$$\rho = \frac{Nm}{V} = \frac{m}{\frac{\pi}{6} d^3} \quad (2)$$

where m denotes the molecular mass, ρ the density of the system. The parameter d not only represents a dimension for the averaged volume occupied by each molecule, but also gives a measure to an averaged intermolecular distance for the N -body system. Therefore, the averaged intermolecular distance can be estimated by Eq. (2) from the density of the system.

By defining a reduced density $\rho_r = \rho/\rho_{ref}$ and reduced averaged intermolecular distance $d_r = d/d_{ref}$, upon their reference values, Eq. (2) is rewritten as

$$\rho_r = \frac{1}{d_r^3} \quad (3)$$

These reduced variables may bring a lot of benefits. For instance, when the reference values take the amounts at which the binary potential crosses zero, Eq. (3) then may mean a strict relation between the reduced variables rather than merely an estimation with the model. And hence, the d_r should be the variable using a hard molecule diameter as the unit.

2.2. Approaching intermolecular potential field from viscosity

Intermolecular potential energy is defined as the work of intermolecular forces. It depends on the magnitude of intermolecular forces and the position the molecules have. For a system of N molecules, the total potential function $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ describes how the potential energy of the system depends on the coordinates of the molecules, $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$. The force on the i -th molecule is expressed by $\mathbf{F}_i = \nabla_i U$.

If we introduce an averaged potential u on each molecule, then the total potential function $U = Nu$. When the number of N is so large that the system can be approximated as continuous media, the intermolecular potential transforms to an intermolecular potential field (IPF), which means the magnitude of intermolecular potential acting on the molecule at a given position \mathbf{r} .

The total potential function can also be expanded in a many-body expansion,

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_i U_1(\vec{r}_i) + \sum_i \sum_{j>i} U_2(|\vec{r}_i - \vec{r}_j|) + \sum_i \sum_{j>i} \sum_{k>j} U_3(|\vec{r}_i - \vec{r}_j|, |\vec{r}_j - \vec{r}_k|) + \dots \quad (4)$$

here, U_1 denotes one-body term due to an external field, U_2 two-body term or binary potential that depends only on the pair distance and is not affected by the presence of other molecules, U_3 three-body term or triple potential that presents three molecules simultaneously interact with each other, and so on.

Let

$$d = |\vec{r}_i - \vec{r}_j| \quad (5)$$

and assuming there is no external field ($U_1 = 0$), we then have

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = Nu = Nu_2(d) + Nu_3 + \dots \quad (6)$$

where u_2 is the averaged binary potential field (ABPF), and u_3 the averaged triple potential field.

Based on the above considerations, we can loosely separate the potentials into two classes: binary potentials (only U_2 is present) and many-body potentials (U_3 and higher terms are included). Then the averaged intermolecular potential field (AIPF) for the molecular system is represented as

$$u = u_2 + u_m \quad (7)$$

here, u_m stands for the total contributions of triple and higher terms.

With regard to interaction, the efficiency for an interaction transition should be considered. A binary interaction mechanism merely transits a molecular event to the other one through the pair interaction. For a system containing N molecules, the binary mechanism requires $N - 1$ transitions for the event to reach the whole system. Comparing to the binary mechanism, a triple interaction mechanism transits a molecular event to two molecules each time. To reach the entire system, the triple mechanism only needs $\ln(N - 1)/\ln 2$ transitions, which is much lower than the number of binary transitions. For a mole molecules ($N = N_A = 6.02 \times 10^{23}$), the transition numbers for the binary mechanism are approximately 6.02×10^{23} corresponding to $\ln(6.02 \times 10^{23})/\ln 2 = 79$ for the triple mechanism. Similar results are easily found for the quadruple and higher interaction mechanisms. The huge difference in the size of the number (more than 21 orders of magnitude) suggests that the triple and higher interaction mechanisms actually transit a molecular event simultaneously to the entire system against the binary interaction mechanism. In another word, the effect of the triple and higher mechanisms effectively appears as the bulk effect of all molecules. For this reason, we can consider their contribution to the AIPF as a variable independent of intermolecular distance. Therefore, u_m does not rely on density that relates to the averaged intermolecular distance through Eq. (2).

To approach the AIPF in fluidic system, we use the symmetric molecular interaction approximation [31,32]. This approximation considers the molecule in the fluidic system accepts symmetric forces around it due to the uniformity, therefore the total force (\mathbf{F}) is approximately zero. At the boundary, however, the molecule receives unsymmetric forces from its half neighbor to restrict it inside the system. According to $\mathbf{F} = -\nabla u \approx 0$, the intermolecular potential field u on each molecule in the system is thus simplified as a variable independent of molecular spatial coordinates, and a step function at the boundary. This feature behaves just like a potential well, whose depth equals the AIPF and reflects the degree to restrict each molecule inside the symmetric molecule system. For the independence of spatial coordinates, the variable u inside the system should be a function of state (e.g., a function of temperature and density), and equal the AIPF.

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