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The transport coefficients described in the dense gas-like model

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ABSTRACT

The transport coefficients of shear viscosity, diffusion, thermal conductivity and bulk viscosity are described systematically in the dense gas-like model that adopts the concepts of both the kinetic theory and the reaction rate theory. The activation energy is assumed to be the sum of the excess energy and the excess pressure with the fraction $1/3\,f_c$, where the factor of three represents the kinetic freedom of a point particle, and f_c its deviation in a fluid. Analyzing the simulation data for the hard-sphere and Lennard–Jones fluids, the form of f_c is prescribed as a simple function of density and temperature with three parameters for each transport coefficient, and these parameters are sought by fitting the simulation data. In addition, a term is implemented in f_c so as to describe the anomaly experimentally observed for the thermal conductivity as well as for the bulk viscosity of the Ar fluid near the critical point. The form of this term is adopted from the cubic model that has been frequently employed to describe the static critical anomalies. The physical properties as well as the dynamic processes of a fluid are featured in f_c that may indicate signals of the anomaly near the critical point by the analysis of the simulation data.

1. Introduction

The transport coefficients of fluids are the important factors in processing materials. Interest in the transport coefficients of fluids stems not only from practical considerations, but also from microscopic considerations for the transport phenomena to test various models of fluids with elaborate experimental as well as simulation data for the transport coefficients of fluids. Our goal is to provide a practical and yet microscopically descriptive model for transport phenomena applicable for various kinds of fluids, from which one will be able to extract microscopic properties of fluids.

As a practical model for a dense fluid like a liquid, the one expressed in a simple exponential form (the Arrhenius type) is most well-known. For instance, the shear viscosity of a liquid is written as

$$\eta = A\exp\left(\frac{E}{RT}\right), \tag{1}$$

where R is the gas constant, T is the absolute temperature, A is constant or slightly of temperature-dependence associated with some additional factors suggested by the reaction rate theory [1], and E is a constant, called the activation energy which is regarded, in the viscous activation picture, as an energy for molecules to move over a potential barrier from one layer to another. Various forms for A and E have been proposed, for example, Refs. [2,3], and most of them involve adjustable parameters to the experimental shear viscosity. Since there are no confirmed regulations for these parameters, the model loses the general application for various kinds of liquids.

Seeking certain regulations for parameters to describe the transport coefficients for a dense fluid, Rosenfeld proposed a universal scaling model [4,5] where the excess entropy of a dense fluid is employed instead of E/T in the exponential form of Eq. (1). The model factorizes the transport coefficients by the appropriate kinematics to get universal constants to describe the transport coefficients of a dense fluid. While the universal constants are adjustable parameters to the simulation data, the universality of these parameters would be of great advantage for practical usage. This model rather resembles to the one that will be presented in this report in a sense that both of them employ the simple exponential form as in Eq. (1), and seek appropriate parameters adjusting to the simulation data or experimental data.

There exist some models free of adjustable parameters. Among them, the Green–Kubo (GK) formulas for the transport coefficients based on the fluctuation dissipation theorem [6,7] are most well-known. Since these formulas require the knowledge of the trajectories of the constituent molecules, it needs lengthy computational simulations to evaluate the transport coefficients especially for a dense fluid like a liquid. Assuming some approximations for the GK formulas, the mode-coupling theory (MCT) [8,9] provides a model capable to evaluate the transport coefficients free of adjustable parameters as well as free of lengthy computational simulations. Nevertheless, the model still has considerable complications, so that its practical use for various kinds of fluids must await further simplifications [10].

Recently, adopting the concepts of both the kinetic theory and the reaction rate theory, a model for the shear viscosity was proposed [11,12]. To use the kinetic theory for a liquid, the Enskog formula of shear viscosity for a dense gas [13] was modified so as to involve the exponential form of the Arrhenius type – an activation energy for a viscous flow – the concept in the reaction rate theory. The Enskog formula

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stands on the firm microscopic picture, and yet possesses a simple analytical form so that the evaluation of the transport coefficients is much easier than using the MCT.

Initially, the model was designed to describe the shear viscosity for a liquid, and applied for liquid metals [11,14]. Then, using some experimental data of the Ar fluid, the model was extended [12] from the liquid region to the dilute-gas and the supercritical regions. This model was termed as the dense gas-like model (DGLM) [11], since it is entirely based on the Enskog formula for a dense gas as explained in the next section.

In the present work we shall re-examine the DGLM for all the transport coefficients of shear viscosity, diffusion, thermal conductivity and bulk viscosity to complete the model. In order to do so, it is unavoidable to consider the anomaly of transport coefficient near the critical point, since the large enhancement near the critical point of the Ar fluid is experimentally observed for the thermal conductivity [15] as well as for the bulk viscosity [16]. This subject is difficult for modeling a practical formula applicable in the entire fluid region, since the anomaly appears only in a narrow range near the critical point. We shall, therefore, treat the anomaly separately from the other fluid region, and combine them in a systematic way by introducing a concept of the freedom factor in the DGLM as presented in the following sections.

As those based on the reaction rate theory, the DGLM also involves adjustable parameters to the experimental transport coefficients. These parameters are all put in the freedom factor, and its form and the parameters will be determined by employing two sets of comprehensive molecular dynamic (MD) simulation data for the transport coefficients: one is obtained for the hard-sphere fluid by Alder et al. [17], and the other for the Lennard–Jones fluid by Meier [18].

It should be noted that the anomalies near the critical point are induced by a long-range fluctuation [19] which would require to consider the kinetics of $\sim 10^9$ molecules in that range [20]. It is thus believed impossible to reproduce these anomalies by the MD simulation with a limited number of molecules. Controversially, however, Meier [18] found some anomaly around the critical point for the bulk viscosity by the MD simulation with only $\sim 10^3$ molecules. The peak of the anomaly shifts according to temperature, and yet the maximum one is not at the nearest temperature to the critical point. This is a striking result, and certainly deserves attention for further investigation. We shall discuss this issue in detail in Section 5.

The layout of this paper is as follows. Section 2 explains the dense gas-like model and introduces the freedom factor. Then we proceed to Section 3 for implementing a term to describe an anomaly of transport coefficient near the critical point. The model is examined with the simulation data for the hard-sphere and Lennard–Jones fluids in Section 4, and with the experimental data in Section 5. We conclude the present model in Section 6.

2. The dense gas-like model

In this section, we explain the DGLM, and newly introduce a concept of the freedom factor in the model. In order to do so, let us start with the Enskog formulas [13] of the transport coefficients of shear viscosity η, diffusion D, thermal conductivity λ, and bulk viscosity η_b, assuming a fluid of the hard-sphere constituents:

$$\eta = \eta_g\left[\frac{1}{\chi} + 0.8b\rho + 0.761(b\rho)^2\chi\right], \tag{2}$$

$$D = \frac{D_g}{\chi}, \tag{3}$$

$$\lambda = \lambda_g\left[\frac{1}{\chi} + 1.2b\rho + 0.757(b\rho)^2\chi\right], \tag{4}$$

$$\eta_b = 1.002\eta_g(b\rho)^2\chi, \tag{5}$$

with $b = 2\pi\sigma^3/3$, where ρ is the number density, σ is the diameter of the hard-sphere molecule, and χ is a correction factor due to the sizable molecules. The transport coefficients for a dilute hard-sphere fluid are denoted by the suffix g, and they are respectively written as

$$\eta_g = \frac{5}{16\sqrt{\pi}}\frac{\sqrt{MRT}}{N_A\sigma^2}, \tag{6}$$

$$D_g = \frac{3}{8\sqrt{\pi}}\frac{\sqrt{MRT}}{M\sigma^2\rho}, \tag{7}$$

$$\lambda_g = \frac{75}{64\sqrt{\pi}}\frac{R\sqrt{MRT}}{MN_A\sigma^2}, \tag{8}$$

where N_A is Avogadro's number, and M is the mass of a molecule.

The first terms in the Enskog Eqs. (2) and (4) are called the kinetic terms, corresponding to the momentum and the energy transportations respectively by bodily movements of the molecules from one layer to another, whereas the last terms are called the collisional terms, corresponding to those transformed directly from one layer to another by collisions at the separated distance over these two layers due to the size of the hard-sphere molecules. The second terms in Eqs. (2) and (4) are called the cross terms, partly made up by the kinetic and collisional terms. The collisional term is conventionally called the potential term [21].

The correction factor χ represents the increase of collisions of molecules at the surface of the hard-sphere molecule due to an excluded volume in the region where the size of the molecules is comparable to this volume. Hence χ ranges from 1 for a dilute fluid to infinite for a packed fluid where movements of the molecules are impossible. Let us then call χ the collision factor hereafter. Conventionally, one replaces χ by the value of the radial distribution function $g(\sigma)$ at the surface of the hard-sphere molecule, which is equivalent to χ in a steady fluid. The DGLM extended [11,12] the collision factor from a hard-sphere fluid to a realistic fluid by relating to the activation energy for a molecule to overcome the potential barrier for its movement as

$$\chi = exp\left(\frac{E}{RT}\right). \tag{9}$$

Since the potential barrier against a molecule is resulted by a force due to the interatomic potential between the molecules in a fluid, the DGLM employed the thermodynamic quantities for E by the following consideration:

In an ordinary liquid where the contribution from the attractive (negative) part of interatomic potential dominates, the force imposing on a molecule to maintain a liquid structure may be related to the excess internal energy, U^{ex}, defined in the scheme of binary additive interactions by

$$U^{ex}(T,\rho) = 2\pi\rho N_A\int_0^\infty u(R)g(R)R^2dR, \tag{10}$$

where $u(R)$ is the pair potential representing an interatomic potential between a pair of molecules with the separation distance R.

As pressure on a liquid becomes higher, the density and the temperature of the liquid increase. Accordingly, the position of the first peak in $g(R)$ approaches the strong repulsive part of the pair potential, and eventually the sign of the excess energy changes from negative to positive due to the form of Eq. (10). The positive excess energy can no longer be regarded as a force imposing the potential barrier on a molecule moving to another layer. In such a case, the pressure acting on a liquid from the outside takes the place of the