

Correlations between the shear viscosity and thermal conductivity coefficients of dense simple liquids

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Motivated by the excess entropy scaling of transport coefficients, we look for correlations between the properly reduced shear viscosity and thermal conductivity coefficients of dense liquids. We demonstrate that correlations exist and this can be considered as an analogue of the Stokes-Einstein relation between the self-diffusion and shear viscosity coefficients. Results presented for four simple model systems with different pairwise interaction potentials (Lennard-Jones, Coulomb, inverse sixth power, and hard-sphere) as well as for six real atomic and molecular liquids (Ar, Kr, Xe, CH₄, O₂ and N₂) support this conclusion and allow to identify several universality classes. Practical fits relating shear viscosity and thermal conductivity coefficients are proposed.

I. INTRODUCTION

Considerable progress in understanding transport properties of liquids has been achieved over decades [1–4]. Nevertheless, our understanding of these processes remains incomplete and fragmented as compared to gases and solids. Difficulties with theoretical description of liquid state dynamics have been recently very well formulated by Brazhkin [5]. Solids and gases can be considered in some (dynamical) sense as “pure” aggregate states. In solids the motion of atoms is purely vibrational, while in dilute gases atoms move freely along straight trajectories between collisions. This simplifies the development of transport theories. On the other hand, liquids constitute a “mixed” aggregate state. Both vibrational and ballistic atomic motions are present. Their relative contribution to atomic dynamics depends on the thermodynamic state. Near the liquid-solid phase transition vibrational motion dominates and solid-like approaches to transport properties are more relevant. At lower densities and higher temperatures ballistic motion dominates and transport is similar to that in non-ideal gases.

In the absence of general theory, we often have to rely on phenomenological approaches, semi-quantitative models, and scaling relationships. Among the most useful relationships proposed so far is the relation between transport coefficients and internal entropy of simple systems put forward by Rosenfeld [6]. He demonstrated that properly reduced transport coefficients are approximately exponential functions of the reduced excess entropy $s_{\text{ex}} = (S - S_{\text{id}})/Nk_{\text{B}}$, where S is the system entropy, S_{id} is the entropy of the ideal gas at the same temperature and density, N is the number of particles and k_{B} is the Boltzmann’s constant. The system-independent normalization for the transport coefficients used by Rosenfeld reads:

$$D_{\text{R}} = D \frac{\rho^{1/3}}{v_{\text{T}}}, \quad \eta_{\text{R}} = \eta \frac{\rho^{-2/3}}{m v_{\text{T}}}, \quad \lambda_{\text{R}} = \lambda \frac{\rho^{-2/3}}{v_{\text{T}}}, \quad (1)$$

where D , η , and λ are the self-diffusion, shear viscosity, and thermal conductivity coefficients and the subscript R denotes the Rosenfeld’s normalization. Here ρ is the atom density, $v_{\text{T}} = \sqrt{T/m}$ is the thermal velocity, T is temperature in energy units ($\equiv k_{\text{B}}T$), and m is the atomic mass. The scaling proposed by Rosenfeld is [7]

$$D_{\text{R}} \simeq 0.6e^{0.8s_{\text{ex}}}, \quad \eta_{\text{R}} \simeq 0.2e^{-0.8s_{\text{ex}}}, \quad \lambda_{\text{R}} \simeq 1.5e^{-0.5s_{\text{ex}}}. \quad (2)$$

Note that s_{ex} is negative because interactions between atoms enhance the structural order compared to non-interacting ideal gas. It has been demonstrated that many simple and not so simple systems conform to the approximate excess entropy scaling, although counterexamples also exist. For a recent review of the excess entropy scaling see e.g. Ref. [8].

Another very useful relationship is the Stokes-Einstein (SE) relation between the self-diffusion and shear viscosity coefficients of simple liquids. For dense simple liquids it reads

$$D\eta(\Delta/T) = \alpha_{\text{SE}}, \quad (3)$$

where $\Delta = \rho^{-1/3}$ is the mean interatomic separation and α_{SE} is a weakly system-dependent SE coefficient. Equation (3) is also known as the Stokes-Einstein relation without the hydrodynamic diameter (in fact, interatomic separation plays the role of hydrodynamic diameter) [9].

Equation (3) is satisfied for many simple model and real liquids near the liquid-solid phase transition [9–11]. Theoretical models explaining why it should be approximately so have been proposed [12–14]. In particular, the theory developed by Zwanzig, based on the vibrational character of liquid state atomic motion on short time scales [12, 15], predicts the SE coefficient as $\alpha_{\text{SE}} \simeq 0.13(1 + \eta/2\eta_{\text{l}}) = 0.13(1 + c_{\text{t}}^2/2c_{\text{l}}^2)$, where η_{l} is the longitudinal viscosity, and $c_{\text{t(l)}}$ is the transverse (longitudinal) sound velocity. As a result, the SE coefficient is allowed to vary theoretically between $\simeq 0.13$ and $\simeq 0.18$, which is consistent with the results from simulations and experiments of many simple liquids [9–11].

Other useful approximations include different variants of freezing-temperature scaling of transport coefficients

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(see e.g. Refs. [16–22]). In a recent paper we have demonstrated that the reduced transport coefficients of Lennard-Jones liquids exhibit a freezing-density scaling and this scaling is closely related to the density scaling of transport coefficients of hard-sphere fluids [23]. The dynamical equivalence between the Lennard-Jones liquid and hard sphere fluids has been also recently discussed [24]. Various simple models for individual transport coefficients (self-diffusion, viscosity, and thermal conductivity) have been proposed in the literature.

The purpose of this paper is to examine correlations between the coefficients of shear viscosity and thermal conductivity for dense simple liquids. We demonstrate that correlations indeed exist. This allows us to put forward an approximate relationship between shear viscosity and thermal conductivity coefficients, resembling the Stokes-Einstein relation. The approach potentially allows to estimate all transport properties from only one known (self-diffusion, viscosity, or thermal conductivity).

II. MOTIVATION

In dilute gases the transport properties are determined by collisions between the constituent atoms. The transport coefficients can be evaluated using the Chapman-Enskog theory [25]. In the first approximation

$$D = \frac{3\sqrt{\pi}}{8} \frac{v_T}{\rho\Omega_1}, \quad \eta = \frac{5\sqrt{\pi}}{8} \frac{mv_T}{\Omega_2}, \quad \lambda = \frac{75\sqrt{\pi}}{32} \frac{v_T}{\Omega_2}, \quad (4)$$

where Ω_1 and Ω_2 are the transport integrals (momentum and energy transfer cross sections integrated with the Maxwellian velocity distribution function). The latter depend on the mechanism of the interaction between the atoms. Since both, the shear viscosity and the thermal conductivity coefficients are inversely proportional to Ω_2 , the relation between these coefficients is independent of the exact interaction mechanism:

$$\frac{\lambda m}{\eta} = \frac{15}{4}. \quad (5)$$

This relation is a consequence of the same processes behind the momentum and energy transport in dilute gases and does not hold in the liquid state [26].

On the other hand, using the Rosenfeld's normalization (1) with the SE relation without the hydrodynamic diameter we get

$$D\eta(\Delta/T) = D_R\eta_R. \quad (6)$$

The excess entropy scaling (2) then predicts the SE coefficients as $\alpha_{SE} = D_R\eta_R \simeq 0.12$. This is a reasonable prediction although the actual values of the SE coefficient are slightly higher ($\simeq 0.14$ for one-component plasma and Yukawa fluids, $\simeq 0.15$ for Lennard-Jones liquids, and $\simeq 0.17$ for hard-sphere fluids [11]).

Excess entropy scaling arguments applied to the relation between the shear viscosity and thermal conductivity coefficients yield

$$\lambda_R \simeq 4.10\eta_R^{5/8}. \quad (7)$$

This points out to an analogue with the Stokes-Einstein relation, although the analogy is incomplete. The mechanisms of diffusion and shear viscosity in dense liquids remain intimately related, while the mechanism of thermal conductivity is different. The dominant contribution to thermal conductivity in dense liquids is due to collective excitations (we do not consider liquid metals, where the dominant contribution comes from transport and scattering of electrons) [27]. Despite this difference, the thermal diffusivity and kinematic viscosity coefficients of some noble and molecular liquids exhibit similar (system-dependent) temperature dependence and their minima are relatively close for different substances [27]. The ratio $m\lambda/\eta$ (equal to 15/4 in an ideal gas) exhibits non-monotonous dependence on density, but is not very much different from $\simeq 4$ (the deviations of $\sim 50\%$ were reported for a Lennard-Jones liquid and $\sim 30\%$ for a one-component plasma models [26]). The Prandtl number $Pr = c_p\eta/m\lambda$ (where c_p is the specific heat at constant pressure) increases on approaching the freezing point, but even there is not much different from unity [28]. Thus, it is not very unreasonable to look for some interrelations between the thermal conductivity and viscosity coefficients.

Below, using literature data on the shear viscosity and thermal conductivity data of several real and model systems we will verify the following: (i) is there a convincing correlation between these transport coefficient; (ii) whether the scaling is universal; and (iii) whether the form suggested by Eq. (7) is appropriate.

III. RESULTS

We have analysed the literature data for the viscosity and thermal conductivity coefficients of several real and model systems. Among the real systems investigated are the liquified noble gases (argon, krypton and xenon), methane, oxygen and nitrogen. Model systems considered in this work are Lennard-Jones (LJ) liquids, one-component plasma (OCP), a fluid with inverse power law $\propto 1/r^6$ (IPL6) repulsive interaction, and the hard-sphere (HS) model.

If one consider density dependence of the reduced transport coefficients D_R , η_R and α_R of simple liquids, a qualitative difference will become apparent. The self-diffusion coefficient decreases monotonically with density towards the freezing point. On the contrary, the shear viscosity and thermal conductivity coefficients depend non-monotonically on the density. They exhibit minima at approximately the same system density, indicating the crossover between the gas-like and liquid-like scalings of

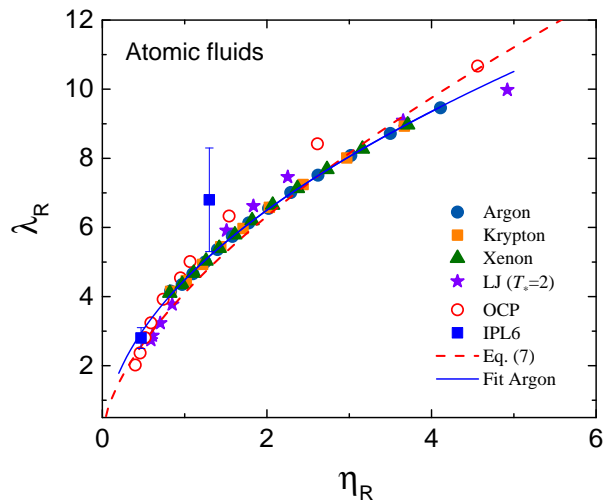


FIG. 1. (Color online) Correlations between the reduced thermal conductivity coefficient λ_R and the shear viscosity coefficient η_R of simple atomic fluids. The symbols correspond to the available data for various real and model fluids (see the legend). The dashed curve denotes the excess entropy based scaling of Eq. (7). The solid curve denotes a fit based on the data for argon.

the transport coefficients with density. A good illustrative example can be found for instance in Ref. [23], which discusses a freezing density scaling of transport coefficients in LJ liquids. In this paper we consider sufficiently dense liquids at densities higher than those corresponding to the minima in η and λ . This corresponds to the liquid-like regime on the phase diagram. In this regime both η and λ increase monotonically towards the freezing point.

The data for liquified noble gases as well as oxygen and nitrogen are taken from Ref. [29]. The data for methane are taken from Refs. [30]. There exist extensive datasets on transport properties of LJ liquids. Since the reduced transport coefficients of LJ liquids along isotherms exhibit quasi-universal freezing-density scaling [23], it is sufficient to consider one isotherm. We chose an isotherm $T_* = T/\epsilon = 2$ (ϵ is the energy scale of the LJ potential) and employ the viscosity and thermal conductivity coefficients tabulated in Refs. [31, 32]. For a strongly coupled OCP fluid we use the data from MD simulations in Refs. [33, 34]. In addition, we add two points for IPL6 repulsive potential that are available from Ref. [35]. Finally, the transport data for the hard-sphere (HS) systems are taken from recent MD simulations reported in Refs. [36, 37].

The results for the liquified noble gases, LJ, OCP and IPL6 fluids are shown in Fig. 1. We observe that the viscosity and thermal conductivity coefficients are indeed well correlated. The data points for various monoatomic liquids considered tend to group around a quasi-universal curve. The excess entropy based dependence of Eq. (7) is plotted by the dashed curve. Overall, a fairly good agree-

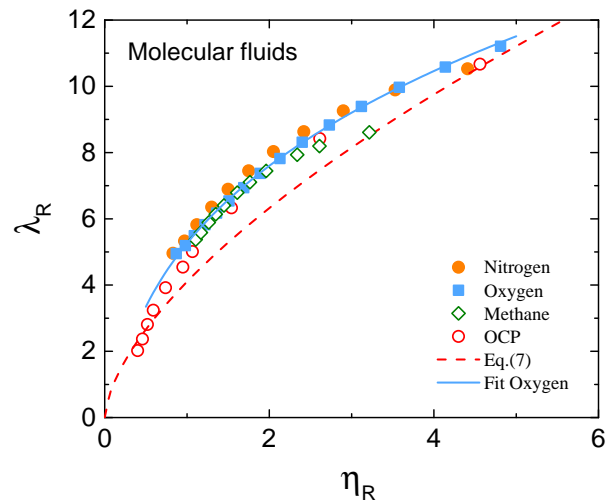


FIG. 2. (Color online) Correlations between λ_R and η_R for N_2 , O_2 , and CH_4 . The symbols correspond to the available experimental data from Refs. [29, 30]. Open circles denote the numerical results for the OCP. The dashed curve denotes the excess entropy based scaling of Eq. (7). The solid curve is a fit based on the data for oxygen.

ment with the data points is observed. For liquified noble gases argon, krypton and xenon the universal correlation between λ_R and η_R is particularly striking. Based on the excess entropy scaling outcome, Eq. (7), the functional form

$$\lambda_R \simeq \alpha \eta_R^\beta + \gamma \quad (8)$$

can be expected. Fitting the data for argon we have obtained $\alpha \simeq 4.88$, $\beta \simeq 0.50$, and $\gamma \simeq -0.40$. This fit is also representative for krypton and xenon. The LJ data points are close to those for the liquified noble gases. The OCP thermal conductivity is slightly higher at strong coupling. Nevertheless, all the data points are grouped relatively close, and we can consider them as belonging to the same universality class.

In Fig. 2 we plot the dependence of λ_R on η_R for molecular liquids: liquid nitrogen, oxygen, and methane. A clear universality is again observed, but the universality class is different from that of liquid noble gases. The excess entropy based scaling of Eq. (7) is not perfect in this case. At the same time the functional form of Eq. (8) remains appropriate. Based on the data for oxygen we have obtained $\alpha \simeq 10.51$, $\beta \simeq 0.29$, and $\gamma \simeq -5.25$. This fit remains relevant for nitrogen. The data for methane show some deviation as the density grows and the reduced transport coefficient increase. Interestingly, the data points for the OCP fluid lie relatively close to those of molecular liquids considered.

A canonical reference system in condensed matter physics is a system of hard spheres. It is often assumed that certain structural and dynamical properties of soft interacting particle systems can be mapped into those of HS systems, even though there exists a soft-to-hard-

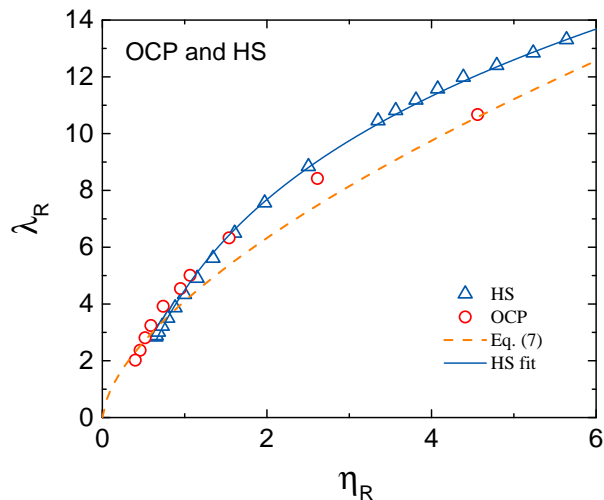


FIG. 3. (Color online) Correlations between λ_R and η_R for the HS and OCP systems (see the legend). The dashed curve denotes the excess entropy based scaling of Eq. (7). The solid curve is the fit based on HS data from Refs. [36, 37].

sphere crossover in fluid excitations and thermodynamics [38]. Recent results on the freezing density scaling of the transport properties of Lennard-Jones liquids demonstrated that while the diffusion and shear viscosity coefficients can be rather well mapped into those of the HS fluid, the thermal conductivity coefficient of dense HS fluids is systematically larger than that of LJ liquid [23]. For this reason we show the comparison of the dependence of λ_R on η_R of the extremely soft OCP fluid and

HS fluid separately, see Fig. 3. The thermal conductivity of the HS fluid is systematically higher as expected. The fit using Eq. (8) yields in the HS limit $\alpha \simeq 22.62$, $\beta \simeq 0.19$, and $\gamma \simeq -18.14$. This defines the HS universality class.

IV. CONCLUSION

Our main conclusions can be formulated as follows. There are certain correlations between properly reduced shear viscosity and thermal conductivity coefficients of dense liquids. This provides us with an analogue of Stokes-Einstein relation between the diffusion and viscosity coefficients. The relationship between the viscosity and thermal conductivity is, however, not truly universal. Certain system-dependence has been documented (and this resembles situation with the Stokes-Einstein relation, too [10, 11]). Different systems may belong to different universality classes. We have identified three universality classes in this study: argon (atomic fluids), oxygen (molecular fluids), and hard-sphere. If the universality class is known, knowledge of one transport coefficient allows to estimate the other two. This can be a very useful simplification in describing various phenomena pertinent to the liquid state.

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