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Transport coefficients of soft sphere fluid at high densities

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Molecular dynamics computer simulation has been used to compute in wide pressure–temperature region the self-diffusion coefficient and shear viscosity of soft-sphere fluids, in which the particles interact through the inverse power pair potential. The limitations of the previous empirical approaches and models for the description of the kinetic coefficients is shown. On the basis of the simulations the universal functions for diffusion coefficient and shear viscosity of soft spheres are constructed which allow to compute these quantities for any density and temperature. We show that the behavior of shear viscosity at high temperatures is more complex than the one of diffusion coefficient and give quantitative explanation of this result.

Knowledge of transport properties of matter at high pressures and high temperatures is extremely important. One of obvious examples of liquid at high pressure and high temperature is Earth outer core which is supposed to be liquid. However, nowadays it is not possible to carry out any experiments at such extreme conditions. The extreme conditions region is also hard for theoretical investigations and simulation studies. Importantly, all theoretical models are developed for normal conditions, and we can never be sure that the same models are applicable at high pressure and temperature. Basing on this speculation it becomes important to carry out a systematic study of some simple model in wide range of pressures and temperatures in order to see the most important effects induced by pressure and temperature. Such investigation will give a solid base for studies of more complex and more realistic systems.

In this work we choose a soft spheres system as a generic model for high pressure atomic systems. This system is defined by the interaction potential

$$U(r) = \varepsilon \left(\frac{\sigma}{r}\right)^n, \tag{1}$$

where ε and σ are energy and length scales. This system is convenient for our goals since its thermodynamic quantities follow well known scaling laws [1–5]). An important consequence of this scaling is that the soft spheres phase diagram is one dimensional, and it is known at all temperatures. This allows us to carry out simulations up to very high temperatures and pressures being sure that the system is in stable liquid phase.

Obviously, soft sphere system is a toy model of a real liquid. However, at high pressures and temperatures the behavior of substances is mostly governed by repulsive cores atoms. This makes soft spheres one of the simplest qualitative models of matter at extremely high temperatures and pressures.

It is well known that the thermodynamic properties of the soft-sphere system can be expressed in terms of a reduced parameter, $\gamma = \rho\sigma^3(k_B T/\varepsilon)^{-3/n}$, where ρ is the reduced number density ($\rho = N/V$, for N particles in volume V), k_B is Boltzmann's constant and T is the temperature (Klein theorem [1–3]). It may be shown [1–5] that the following scaling laws are valid along the melting line (we skip the Boltzmann constant in the formulas below for the sake of brevity):

$$T = V_0 \left(\frac{T}{T_0}\right)^{-3/n}, \tag{2}$$

$$P = P_0 \left(\frac{T}{T_0}\right)^{1+3/n}, \tag{3}$$

where V_0, T_0 and P_0 are some arbitrary values of volume, temperature and pressure.

The exponents in (2) and (3) were known before (see, for example, [3]). However, in [5] the method was developed which can be applied to any physical quantity of the form $F = \langle f(q_i, p_i, t)\rangle$ under the transformation which preserves the form of Hamiltonian equations. This transformation conserves geometric relations on a phase trajectory, thereby preserving the scaling of the individual trajectories of each of the N particles and, hence, it conserves the multiphase nature of the whole system. The simplest example of a phase equilibrium curve is the two-phase melting curve. Using the Green–Kubo relation for the diffusion $D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}(t)\mathbf{v}(0)\rangle dt$, it may be shown, that:

$$D \sim T^{1/2-1/n}; D \sim P^{\frac{n-2}{2(n+3)}}. \tag{4}$$

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Similarly, the viscosity has the form:

$$\eta = \frac{1}{Vk_BT}\int_0^\infty \langle\sigma^{xy}(t)\sigma^{xy}(0)\rangle dt, \qquad (5)$$

where σ^{xy} is a stress tensor component. In this case one can derive the scaling relations for viscosity:

$$\eta \sim P^{\frac{n+4}{2n+6}}; \eta \sim T^{\frac{n+4}{2n}}. \qquad (6)$$

Below we show that transport properties of soft spheres – diffusion coefficient and shear viscosity – can be transformed to fall in the same master curve and construct the fitting functions to these curves.

In our simulations we use the soft sphere potential (1) with $n = 12$. The potential is cut at the distance $r_c = 2.5$ as in standard simulations of Lennard–Jones systems. Reduced units ($\varepsilon = 1$ and $\sigma = 1$) are used in the paper.

For calculation of the transport properties of soft spheres the system of 1000 particles was simulated in the microcanonical (constant N, V and E) ensemble. Equations of motion were integrated by the velocity Verlet algorithm. The equilibration time was set to $5 \cdot 10^5$ time steps and the production time – $3.5 \cdot 10^6$ steps. The time step we used was $dt = 0.0005$. During equilibration the velocity rescaling was applied to keep the temperature constant. During the production cycle, the NVE-ensemble was used. The diffusion coefficient was calculated from the mean square displacement via Einstein relation, while the viscosity was determined by the integration of the stress correlation function (Eq. (5)) [6].

Many data points were simulated in order to get good statistics on the diffusion coefficient and viscosity of the system independently on any scaling assumptions. The data were collected along the isotherm $T = 1.0$, a set of eleven isochors ($\rho = 0.65$; 0.95; 1.15; 1.51; 2.43; 2.69; 2.89; 3.06; 3.2; 3.33; 3.44) and along the melting line. The temperature along isochors was varied from the melting temperature up to $T_{\max} = 100.0$.

As we saw above, there are some reasons to think that soft spheres transport coefficients follow some scaling law. Furthermore, even if it is valid we are not aware with any calculations of coefficients of the scaling functions in literature. Here we analyze our set of data for diffusion coefficient and viscosity of soft spheres with $n = 12$ and construct universal functions for theirs description. These universal functions are used to analyze the transport coefficients behavior under extreme conditions – at high temperatures and high pressures which is the topic which did not get sufficient attention in the literature.

The transport properties of soft spheres system were widely studied by many authors. The most intensive investigations were carried out by D.M. Heyes and A.C. Brańka, whose main results are summarized in [7]. Basing on theirs results these authors proposed the approximation formulas for the diffusivity of soft spheres.

In D.M. Heyes and A.C. Brańka publications they studied only one isotherm with $T = 1.0$. In order to obtain the diffusion coefficient and viscosity for other $\rho - T$ points they propose to use the values with the same γ as at $T = 1.0$ isotherm. However, the validity of this assumption is questionable. Furthermore, it is not clear from [7] which function of diffusion and shear viscosity one should consider as invariant at constant γ: pure D and η or $\frac{D}{(k_BT)^{2/n}}$ and $\frac{\eta}{(k_BT)^{2/n}}$. As a result even if extremely detailed study was carried out along a single isotherm it is difficult to generalize these results to other temperatures.

As we discussed in above, for the case of thermodynamic quantities the scaling rule defines the behavior of nonideal part of the quantity. One can expect that we should seek for an universal function for transport properties in terms of nonideal part.

In order to exclude the ideal gas contribution from the diffusion coefficient and shear viscosity of soft spheres we do the following procedure. It is well known from kinetic theory of gases that the diffusion coefficient of gases is proportional to $T^{1/2}/(\rho\sigma_1^2)$ and viscosity is proportional to $T^{1/2}/\sigma_1^2$ where σ_1 is the size of the particles (do not confuse with the soft spheres potential parameter σ!) [8]. Basing on this fact one can suppose that the quantities $D\frac{\rho\sigma_1^2}{T^{1/2}}$ and $\eta\frac{\sigma_1^2}{T^{1/2}}$ are universal.

Figs. 1a and b show the diffusion coefficient and shear viscosity divided by the kinetic theory ones as functions of soft spheres parameter γ for a large set of data points which includes melting line, several isochors and isotherm $T = 1.0$. The size of the particles σ_1 was computed as the location of the first peak of radial distribution function. It is evident from these figures that diffusion coefficient and shear viscosity do demonstrate universal behavior in this representation.

In [9] it was shown that for soft spheres with $n = 12$ the location of the first maximum of radial distribution function at constant γ follows the relation $\sigma_1 \sim T^{-1/12}$. Using this relation one can rewrite the universal functions of diffusion coefficient and viscosity in the form $\tilde{D} = D\frac{\rho}{T^{2/3}}$ and $\tilde{\eta} = \eta/T^{2/3}$. The corresponding plots are given in Figs. 2a and b [2]).

[2])These expressions for the universal functions of diffusion coefficient and viscosity were already reported in [10]. However, the conclusions of this publication were based on the reduction of Newton motion equations. However, it may be shown that this procedure can not be considered as self consistent.

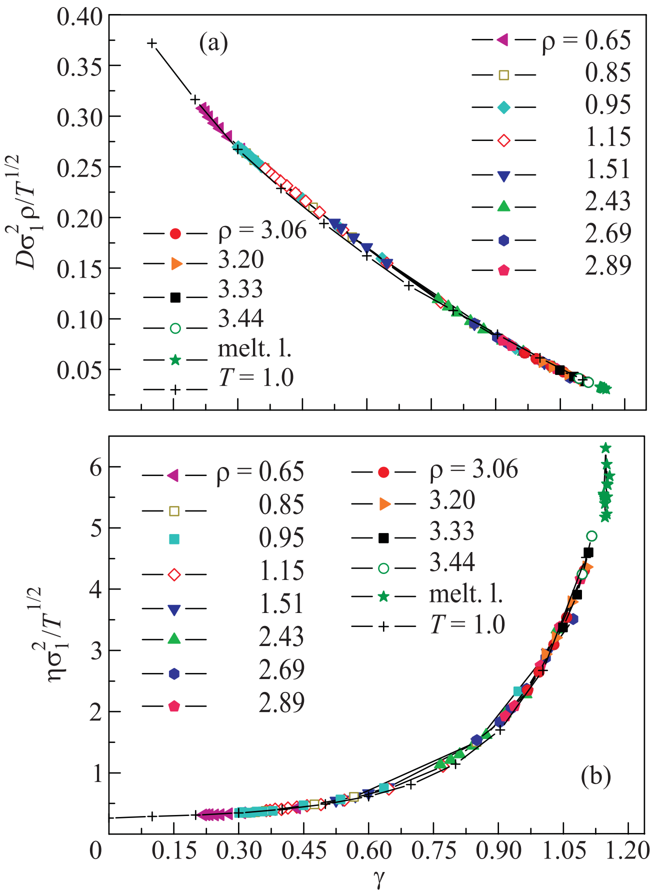

Fig. 1. Universality of (a) diffusion coefficient and (b) shear viscosity reduced by the kinetic theory ones

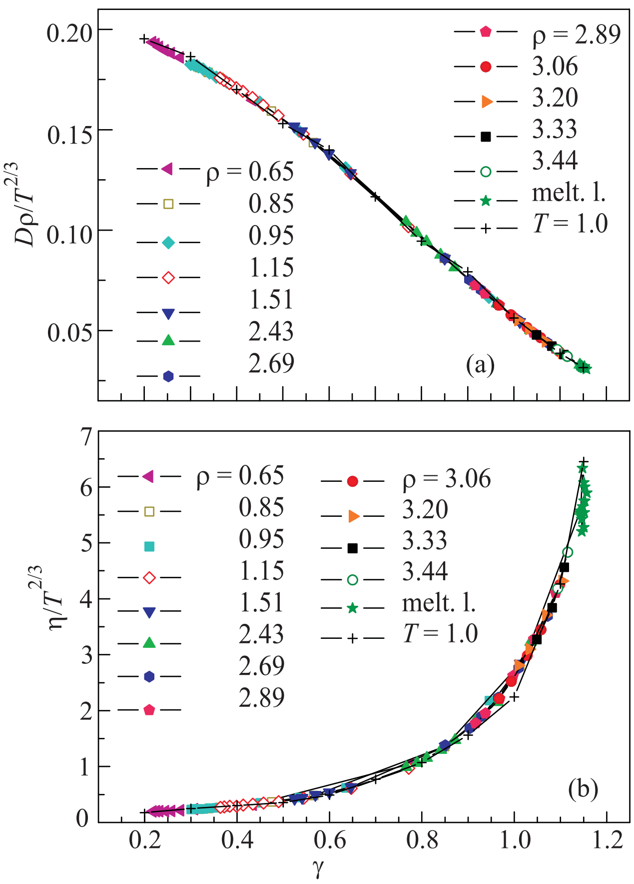

Fig. 2. Universality of (a) diffusion coefficient and (b) shear viscosity scaled in accordance with the kinetic theory with $\sigma_1 \sim T^{-1/12}$

Taking into account the universality of the functions $D\rho/T^{2/3}$ and $\eta/T^{2/3}$ for soft spheres with $n = 12$ one can construct some approximative formulas for these quantities. This would allow to find the diffusion coefficient and shear viscosity for any given density and temperature.

Examining the phenomenological formulas from [7] we find that they describe the system qualitatively, however, they show large errors in the case of quantitative comparison. We propose to approximate both diffusion coefficient and shear viscosity by polynomial of 8-th order:

$$\frac{D\rho}{T^{2/3}} = \sum_{k=0}^{k=8} b_k \gamma^k \tag{7}$$

and

$$\frac{\eta}{T^{2/3}} = \sum_{k=0}^{k=8} c_k \gamma^k. \tag{8}$$

The coefficients b_k and c_k are given in Table.

Several equations of state were proposed in literature [11]. However, none of them give good description of simulation data in wide range of γ parameters. In publication [7] the problem of equation of state was discussed briefly, and it was proposed that 4-th order polynomial approximation of $Z = \frac{P}{\rho k_{\mathrm{B}} T} - 1$ can be sufficient. In our work we use 8-th order polynomial to be consistent with the transport coefficients approximation:

$$\frac{P}{\rho k_{\mathrm{B}} T} = \sum_{k=0}^{k=8} d_k \gamma^k. \tag{9}$$

Coefficients d_k are given in Table.

An intermediate conclusion is that we have constructed fitting functions for equation of state, diffusion coefficient and shear viscosity of soft spheres with $n = 12$.

As was stated above, soft spheres can serve as a generic model for studying properties of atomic systems at high pressures and high temperatures. Using the approximations proposed above we can carry out detailed studies of transport coefficients of soft spheres at

Fitting parameters for $D\rho/T^{2/3}$ (Eq. 7), $\eta/T^{2/3}$ (Eq. 8) and compressibility $Z = P/\rho k_B T$ (Eq. 9)

k	b_k	c_k	d_k
0	0.20826	0.09213	1.0
1	0.00151	0.36805	2.73384
2	−0.50037	5.74477	0.61191
3	0.77922	−55.19641	25.55162
4	1.0733	222.45565	−73.44559
5	−6.40928	−461.66584	142.91181
6	9.58519	529.4369	−149.02936
7	−6.16766	−316.90574	81.74545
8	1.4866	78.27714	−18.29821

arbitrary temperatures and pressures. Below we discuss some examples of interesting soft spheres behavior. These results can be generalized to more complex systems including the models for simulation and experimental systems.

The first point we would like to discuss is related to the behavior of transport coefficients along isochors. As we found in our simulations, the viscosity along an isochor develops a minimum. (Fig. 3a). At the same

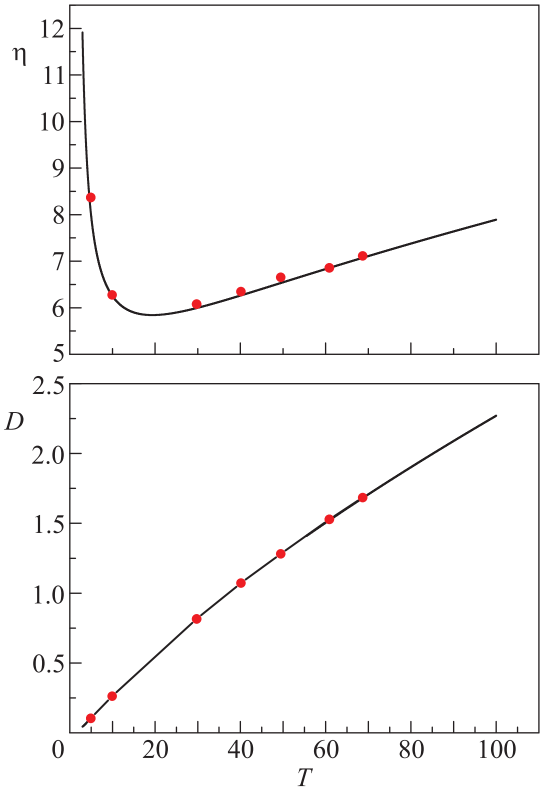

Fig. 3. Viscosity (a) and diffusion coefficient (b) along $\rho = 1.51$ isochor. Continuous lines – from Eqs. (7), (8), symbols – simulation results

time diffusion coefficient is monotonous along isochors. Figs. 3a and b give examples of the transport coefficients along isochor $\rho = 1.51$. Other isochors look qualitatively the same. The location of viscosity minimum corresponds to $\gamma = 0.734$.

A possibility of viscosity minimum was mentioned by Rosenfeld [12]. However, a strict explanation of this minimum was not given in this publication. To explain this viscosity minimum we use the following reasoning. If we consider the viscosity as an integral over the stress correlation function (Eq. (5)), we can split it to the three contributions: kinetic–kinetic (kk), kinetic–potential (kp) and potential–potential (pp)[6, 13]:

$$\eta = \int_0^\infty C_{kk}(t)dt + \int_0^\infty C_{kp}(t)dt + \int_0^\infty C_{pp}(t)dt, \tag{10}$$

where

$$C_{kk}(t) = \frac{m^2\rho}{Nk_{\rm B}T}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle v_{x,i}(0)v_{y,i}(0)v_{x,j}(y)v_{y,j}(y)\rangle, \tag{11}$$

where $v_{x,i}(t)$ denotes x component of the velocity of the particle i at time t,

$$C_{pk}(t) = \frac{2m\rho}{Nk_{\rm B}T}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1,k\neq j}^{N}\langle v_{x,i}(0)v_{y,i}(0)\times \tag{12}$$

$$\times\frac{x_{jk}(t)y_{jk}(t)}{r_{jk}(t)^2}F[r_{jk}(t)]\rangle,$$

where $x_{jk}(t)$ and $y_{jk}(t)$ are Cartesian components of $\mathbf{r}_{jk}(t)$ and $F(r) = -\frac{r}{2}\frac{\partial\Phi[r]}{\partial r}$ – force between particles j and k.

Finally

$$C_{pp}(t)=\frac{\rho}{Nk_BT}\sum_{i=1}^{N}\sum_{j=1,j\neq i}^{N}\sum_{k=1}\sum_{l=1,l\neq k}^{N}\langle\frac{x_{ij}(0)y_{ij}(0)}{r_{ij}(0)^2}\times$$

$$\times F[r_{ij}(0)]\frac{x_{kl}(t)y_{kl}(t)}{r_{kl}(t)^2}F[r_{kl}(t)]\rangle. \tag{13}$$

One can expect [12, 14] that close to the melting line the main contribution to the viscosity comes from the potential–potential correlation, while at high temperatures the kinetic–kinetic part should be dominant. Having the pp-correlation decreasing and the kk one increasing, one can expect that a crossover between these regimes appears which brings to a minimum on the total viscosity curve.

In order to verify this suggestion we carried out the calculations of the different contributions to the viscosity for the density $\rho = 1.51$ and a set of temperatures (Fig. 4). As one can see from this figure the suggestion

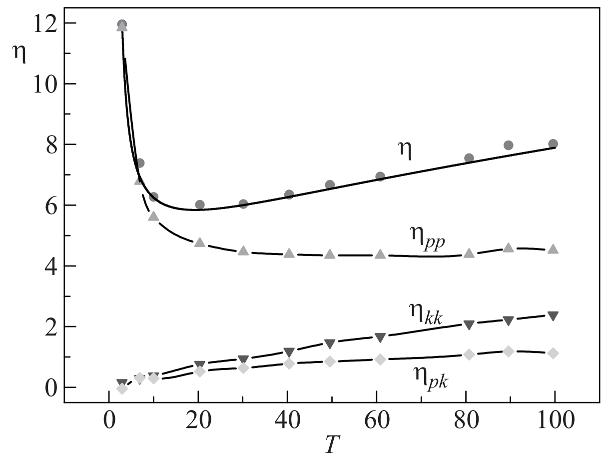

Fig. 4. Different contributions to viscosity as a function of pressure and temperature along the isochore $\rho = 1.51$. Continuous line – viscosity from Eq. (8) circles – full viscosity (Eq. (5)), up triangles – pp-contribution (Eq. (13)), down triangles – kk-contribution (Eq. (11)) and diamonds – kp-contribution (Eq. (12))

is correct: while the pp-contribution decreases with increasing temperature both the kk and kp ones increase. Because of this one can expect the further increase of the viscosity with increasing temperature.

Note that the qualitative behavior of viscosity along isochors preserves the same form for more complex systems where the fitting formulas (Eqs. (7–9)) can not be applied [15, 16].

Recently [15, 16] it was shown that the existence of the minima on the temperature dependance of the viscosity is related with the crossover of the dynamic line (Frenkel line) which separates the rigid and non-rigid states of a liquid.

In [7] the authors claim that η^{-1} behaves qualitatively analogous to D. In the present study we observe the qualitative difference in the behavior of the diffusion coefficient and inverse viscosity: the diffusion coefficient is monotonous function of temperature while viscosity passes through a minimum (inverse viscosity passes through a maximum).

From the above discussion, we conclude that the change in the qualitative behavior of viscosity is related to the crossover from the potential dominated to kinetic dominated regimes.

If we apply the same Green–Kubo formalism to diffusion coefficient we obtain: $D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}(\tau)\mathbf{v}(0)\rangle dt$. One can see that this corresponds to the kk-term in viscosity calculations. This means that diffusion coefficients is totally defined by kinetic term only which monotonically increases with temperature.

The second point to be discussed here is related to behavior of the transport coefficients at high pressures. Experiments by Gulik [17] proposed that at sufficiently high densities shear viscosity and inverse diffusion coefficient are almost linear functions of pressure if considered along isotherms. This idea was used later in [7]. However, this approach has obvious limitations. For example, if we consider a liquid close to the glass transition line the diffusivity is negligibly small and therefore the inverse diffusivity is divergent at finite pressure which is inconsistent with linear law. Although one can expect that the linear relation between shear viscosity and inverse diffusion coefficient as a function of pressure can held true at high enough densities but far from glass transition point, i.e., the dependence is almost linear only in some intermediate pressures range. In Figs. 5a and b the shear viscosity and inverse diffusion coefficient

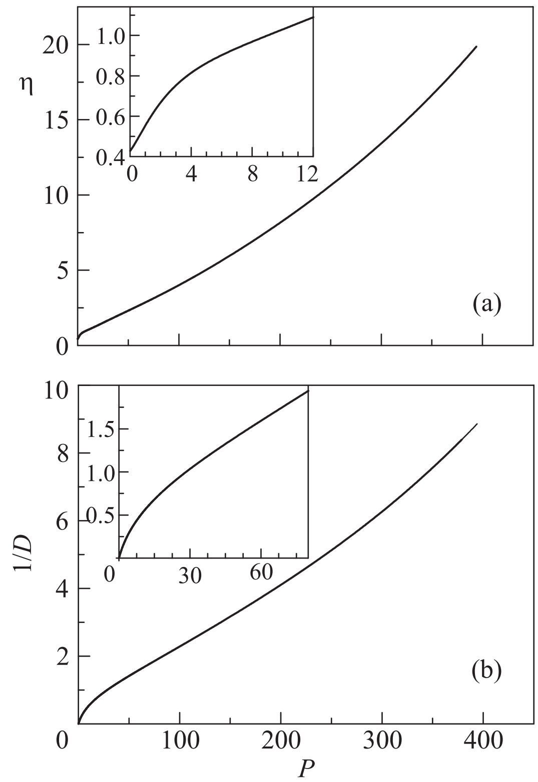

Fig. 5. Viscosity (a) and inverse diffusion coefficient (b) along $T = 10.0$ isotherm. The insets enlarge the low pressure region

are shown calculated via Eqs. (7)–(9) along $T = 10.0$ isotherm. One can clearly see from these figures that the curves do become almost linear at sufficiently high pressures. However, on further increasing the pressure an obvious deviation from linearity is observed.

Having in mind the discussion described above one can speculate on the applicability of linear relation between shear viscosity and inverse diffusion coefficient in real liquids. In Gulik's paper [17] mostly simple liquids (neon, argon, krypton and some more) were considered. These liquids are difficult to supercool and vitrify in experiment and therefore linearity can be observed. However, if one considers some liquids which are easy to glassify (for instance, glycerol) one should not observe linear transport coefficients behavior as a function of pressure. This qualitative picture corresponds to experimental observations.

In conclusion, the paper discusses the transport properties of soft spheres at high densities. The soft spheres system can be considered as a generic system to study atomic substances at high pressures and temperatures. This topic is important for understanding of many fundamental questions ranging from Geophysics and Physics of planets till industrial applications. However, because of both experimental and theoretical difficulties this topic did not have much attention in the literature.

Basing on our simulation results we construct the universal functions for diffusion coefficient and shear viscosity of soft spheres which allow to compute these quantities for any given density ρ and temperature T. Using these approximations we show that the behavior of shear viscosity at high temperatures is more complex then the one of diffusion coefficient and give the explanation of this phenomena. We also consider the pressure dependence of the transport coefficients of soft spheres and find the bend from linear behavior of shear viscosity and inverse diffusivity proposed in literature.

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