

Universal behavior of shear viscosity near freezing point

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We study dynamics of liquids above freezing point. It is demonstrated that available experimental data on shear viscosity of simple liquids can be described in the framework of the so-called weak crystallization theory. Theory predicts that in the main approximation shear viscosity is proportional to the $(T/T_* - 1)^{-3/2}$, where T_* is a temperature close to freezing temperature. This prediction is in a good agreement with experimental data for many substances.

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It is well known that crystallization of a liquid is a first order phase transition. It means that fluctuations are not very strong and critical behavior is not expected near freezing point. However shear viscosity of a liquid significantly increases if the temperature tends to the freezing point. The qualitative behavior of the viscosity for different substances is similar. For example, the viscosity of water at atmospheric pressure at the temperature 273.2 K equals to 1.79 cps, whereas at the temperature 373.2 K it equals to 0.28 cps, i.e. the viscosity changes in 6 times in the temperature range of 100 K.

Usually the temperature dependence of the viscosity is described by Arrhenius formula $\eta \propto \exp(E/T)$. In article [1] it was shown that power-law dependence of the viscosity $\eta \propto 1/(T - T_0)^x$ is more adequate for most of considered systems. For different substances considered in [1] fitting gave the exponent value x between $1.7 \div 2.5$.

The shear viscosity diverges in the liquid-glass transition point. Corresponding problem was studied in large number of articles. Usually singular behavior of viscosity is described by Voger-Fulcher formula $\eta \propto \exp(E/(T - T_g))$ [2]. In paper [3] the dynamical theory of the liquid-glass transition based on the microscopic theory, developed by the author, was constructed. For both shear and longitudinal viscosities author has predicted the power-law behavior $\eta \propto (n - n_g)^{-1.765}$, where n is the density. Similar exponent value for both viscosities was obtained in modified theory, which takes into account the dependence of relaxation time on the wavevector value [4]. In these articles the exponent value was calculated in close vicinity of the liquid-glass transition point.

The basic mechanism for the increase of the viscosity is the interaction between hydrodynamic flow and density fluctuations of liquid. In the vicinity of the freezing

point the main maximum of the static structure factor of the liquid is significantly greater than the others [5]. The value of this maximum at nonzero wavevector q_0 increases as temperature tends to the freezing point, which corresponds to the growth of density fluctuations with $q \sim q_0$. In present paper we study dynamics of a liquid in the vicinity of the freezing point taking into account the fluctuations of short-scale density $\varphi(\mathbf{r})$ with wavevectors close to q_0 . We restrict ourselves by one-loop approximation which means that the obtained results are valid only near freezing point and can not be applied in the vicinity of liquid-glass transition point.

Since we are interested in dynamics of non-ordered liquid phase and fluctuation contributions to its dynamical characteristics it is possible to apply the approach, developed in [6] to our problem. The Landau functional of the system can be written as

$$\mathcal{F} = \int d\mathbf{r} \left(\frac{\mathbf{j}^2}{2\rho} + E(\rho, \varphi, \sigma) \right), \quad (1)$$

$$E = \epsilon(\rho, \sigma) + \frac{\tau}{2}\varphi^2 + \frac{\alpha}{8q_0^2}(D\varphi)^2 + \frac{\mu}{6}\varphi^3 + \frac{\lambda}{24}\varphi^4.$$

Here ρ is the long-wavelength density of mass, σ is the density of entrophy, \mathbf{j} is the momentum density $\mathbf{j} = \rho\mathbf{v}$, $D = \nabla^2 + q_0^2$. Parameters τ , α , μ and λ are some functions of the temperature and pressure. As usual we suppose that in the vicinity of the phase transition all parameters of Landau functional can be treated as constants except parameter τ which is proportional to $T/T_* - 1$, where T is absolute temperature and T_* is some temperature close to freezing point.

Similar formulation of the problem for the liquid-glass transition has been studied by Das [7]. He considered the problem numerically and predicted that the both viscosities have power-law behavior with the exponent value 0.9. The region of applicability for this result was badly determined.

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Thermodynamic properties of the model described by the static part of the functional (1) were considered in [6]. In the mean field approximation the phase transition takes place at $T = T_*$, provided triple vertex $\mu = 0$. For non-zero value of the triple vertex the transition temperature increases, $\tau_{tr} \propto \mu^2/\lambda$. Thermal fluctuations decrease the transition temperature. The static correlation function of the field φ is

$$\langle \varphi(\mathbf{q})\varphi(-\mathbf{q}) \rangle = \frac{k_B T}{\Delta + \alpha(q - q_0)^2}, \quad (2)$$

where k_B is the Boltzmann constant. Parameter Δ in (2) is the gap in the spectrum of the field φ . As it was shown in [8] in the main approximation the gap Δ can be found as a solution of the transcendent equation

$$\Delta = \tau + \beta \Delta^{-1/2}, \quad \beta = \lambda k_B T q_0^2 / 4\pi \alpha^{1/2}. \quad (3)$$

It follows from (3) that the gap Δ is positive even for negative τ , i.e. liquid state remains metastable in this region.

The Eq. (3) was obtained provided condition $\tau \ll \ll \alpha q_0^2$ is valid. This condition is correct in the vicinity of the freezing point which is of our interest. In the region $\beta^{2/3} \ll \tau$, i.e. if the temperature is not very close to the T_* , it is possible to neglect the term produced by the thermal fluctuations in (3) and to use mean field expression $\Delta \approx \tau$.

To study dynamical behavior we will use the general approach described in [9]. Since dynamics of the order parameter is purely relaxational the dynamic equation for φ can be written as

$$\Gamma \partial_t \varphi = -\delta \mathcal{F} / \delta \varphi, \quad (4)$$

where Γ is a kinetic coefficient. As far as we are interested in the region near the freezing point, it is possible to consider the parameter Γ as a constant.

We will study the influence of dynamic fluctuations of the field φ on the parameters of the diffusion and sound modes of the system. Calculating correction for diffusion mode we obtain the following expression for the fluctuational part of the shear viscosity

$$\eta_{fl} = \frac{k_B T \Gamma \sqrt{\alpha} q_0^4}{240\pi} \Delta^{-3/2}. \quad (5)$$

Let us estimate this fluctuational correction. Expression (5) can be rewritten as

$$\eta_{fl} = \frac{1}{240\pi} \frac{\Gamma}{\Delta} \sqrt{\frac{\alpha q_0^2}{\Delta}} k_B T q_0^3. \quad (6)$$

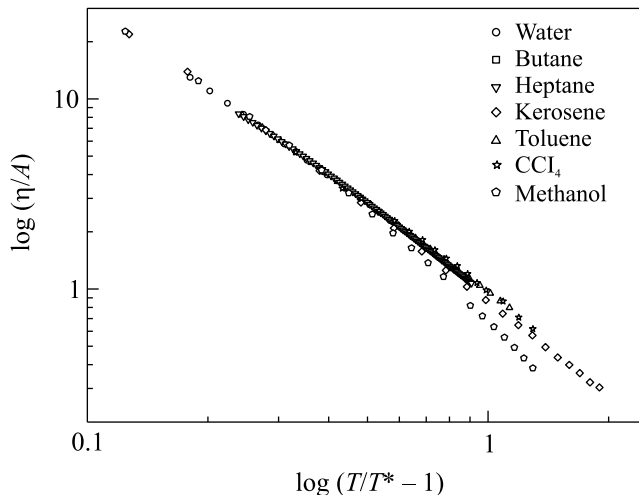
As it follows from Eq. (3) in the mean field approximation $\Delta \approx \tau$. Dimensionless parameter $\sqrt{\alpha q_0^2/\tau}$

changes from unity far from transition point up to 20 near transition point. Parameter $k_B T$ is of the order of $400 \div 600 \cdot 10^{-16}$ erg, $q_0 \sim 3 \cdot 10^8$ cm⁻¹. As it follows from (4) the ratio Γ/τ is equal to the relaxation time of the density fluctuations with the wave vector $q \sim q_0$, which is of the order of 10^{-12} s. As a result we obtain $\eta_{fl} \sim 0.01 \div 0.1$ cps, so that the fluctuational correction (6) is of the same order of magnitude as the shear viscosity itself.

To verify the obtained prediction we took experimental data for the shear viscosity of seven different substances from NIST chemical webbook [10] and reference book [11]. The data for toluene were taken from [12]. These data were fitted to the expression

$$\eta = \frac{A}{(T/T_* - 1)^{3/2}}, \quad (7)$$

with two fitting parameters for each substance: amplitude A and temperature T_* . Figure presents corresponding results for the scaled viscosity η/A as a function of



Log-log plot of shear viscosity as a function of a reduced temperature

$T/T_* - 1$. It is seen that in the region $\log(T/T_* - 1) < 0.7$ all experimental points are situated near universal curve, determined by the expression (7).

In general some regular part must be added to the right-hand side of formula (7). To decrease the number of fitting parameters it is possible to take this regular part as some constant. In this case such constant value turns out non-relevant and was omitted for all substances in Figure.

Table contains parameters for the substances presented in Figure. Second and third columns present the parameters obtained from the fitting, fourth column contains the reference freezing temperatures.

Substance	T_* , K	A , cps	T_{fr} , K
Water	231.39	0.1375	273.15
Butane	98.4	0.52	135.0
Heptane	149.36	0.422	178.65
Kerosene	197.85	0.526	213.
Toluene	168.86	0.378	183.15
CCl_4	197.54	0.325	250.
Methanol	154.33	0.675	175.5

For all substances the difference $T_{fr} - T_*$ is positive and lies in the interval $20 \div 40$ K. It means that the increase of the transition temperature induced by the triple vertex μ is larger than the negative fluctuational shift of the transition temperature. Therefore thermal fluctuations are in some sense weak, which makes our approximation self-consistent and allows us to use the mean field approximation for the gap Δ . In close vicinity of T_* it is necessary to use Eq. (3) for the calculation of the gap Δ .

The agreement between the experimental data and theoretical expression for chosen substances is very good. For example, the average relative deviation for water is 0.7%, whereas for Arrhenius formula, which also has two fitting parameters, it is 5.5%. For some substances, for example, alcohols or glycerol, a systematic deviation appears in the region $0.7 < \log(T/T_* - 1)$ analogously to the behavior of methanol, presented in Figure. The addition of a regular part to the right-hand side of expression (7) can eliminate this deviation.

The longitudinal sound mode can be considered in the similar way. As a result we find corrections to the sound speed and damping coefficient. The main correction to longitudinal mode arises due to the dependence of parameter τ of the density ρ . This dependence was neglected in article [7]. Taking into account this dependence we obtain the following correction to the longitudinal viscosity ζ

$$\zeta_{fl} = \frac{3T\Gamma\tau_\rho^2 q_0^2}{128\pi\sqrt{\alpha}} \Delta^{-5/2}, \quad (8)$$

where $\tau_\rho = \rho\partial\tau/\partial\rho$. Therefore the correction to the longitudinal viscosity is proportional to the $\Delta^{-5/2}$ and is more singular than the correction to the shear viscosity (5). This correction was obtained in [6]. Unfortunately the accurate measurements of the sound spectrum for low frequencies are difficult, corresponding experimental studies are not known to us.

Thus, the correction to the shear viscosity of the liquid produced by the short-scale density fluctuations provides good description of the experimental data for real liquids. To test our predictions more thoroughly it is necessary to study the viscosity behavior in the region where fluctuations are highly developed, i.e. in the close vicinity of T_* . However unlike a second order phase transition this region corresponds to the metastability region of the liquid phase and is hardly available for the experimental investigation.

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