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## EVIDENCE OF THE COLLECTIVE TRANSPORT IN ATOMIC LIQUIDS AND LIQUID METALS

*The behavior of the effective radii of “particles” (molecules and ions) as a manifestation of the collective components of their thermal motion in atomic liquids and liquid metals has been studied. The specific form of the temperature dependence of the effective radii of molecules and ions is established in good agreement with the results obtained for the hydrodynamic radii according to the Stokes–Einstein formula. Attention is drawn to the differences between the values of the radii of particles that are used to describe the thermodynamic and kinetic properties of liquids.*

*Keywords:* thermal motion of molecules, collective transport, self-diffusion coefficient of molecules in liquids.

### 1. Introduction

The existence of a collective transport in liquid water was predicted in work [1]. The extended theory of collective mass transfer was initiated by I.Z. Fisher in work [2]. The works [3–6] were devoted to the further development and improvement of theoretical ideas about the nature of collective transport. An extremely important role in the formation of ideas concerning the collective transport in liquids was played by the works of Bulavin *et al.* [7–11]. In those works, as well as in the works by Mykhailenko and *et al.* [12, 13] dealing with computer simulations, it was proved that the collective component in the self-diffusion coefficient can reach a quarter of its total magnitude.

However, no complete agreement between theoretical and experimental data has been attained, because the so-called “single-particle” component (see works [2, 14]) of the self-diffusion coefficient remained unknown. Moreover, it was assumed that the temperature dependence of this component may have an activation character, similar to what takes place in solids. The falsity of such ideas has been emphasized many times in works [6, 14–19]. In works [6, 16, 18], it was ultimately proved that the so-called “single-particle” component of the self-diffusion coef-

ficient emerges owing to the swings of small molecular groups at small angles. A typical molecular group of this kind is formed by a certain molecule and its immediate molecular environment. Of course, the group swing motions have no activation character, but a collective one.

As was shown in work [16], the “single-particle” component is described by the Stokes–Einstein formula in which the radius of the molecule is determined from the analysis of the shear viscosity. As a result, the self-diffusion coefficient of a molecule is expressed by the sum (see also works [14, 17])

$$D_s = D_r + D_c, \quad (1)$$

where

$$D_c = \frac{k_B T}{10\pi\eta\sqrt{\nu\tau_M}} \quad (2)$$

is a collective component associated with the nanoscopic hydrodynamic vortex modes, and

$$D_r = \frac{k_B T}{6\pi\eta r_p^{(\nu)}} \quad (3)$$

is a contribution from the swing motions of small molecular groups. Here,  $k_B$  is the Boltzmann constant,  $T$  the temperature,  $\eta$  the dynamic shear viscosity,  $\nu$  the kinematic shear viscosity, and  $\tau_M$  the Maxwell relaxation time.

Table 1. Values of the parameters in formula (1)

Parameter	Ar	Ne	Kr	Xe	C <sub>6</sub> H <sub>6</sub>	N <sub>2</sub>	Sn	Bi	Pb
$\tilde{v}_0$	0.984	0.978	0.985	0.982	0.976	0.977	0.993	0.960	0.981
$\zeta_0$	0.263	0.278	0.264	0.296	0.285	0.294	0.211	0.342	0.310
$(1 - \tilde{v}_0)^{1/3}$	0.251	0.279	0.243	0.261	0.288	0.284	0.190	0.342	0.272

Writing the molecular self-diffusion coefficient in the form

$$D_s(T) = \frac{k_B T}{6\pi\eta r_p^{(D)}},$$

we obtain the following formula for the hydrodynamic radius of a molecule:

$$r_p^{(D)}(T) = \frac{k_B T}{6\pi\eta D_s(T)}. \quad (4)$$

The temperature dependence  $r_p^{(D)}(T)$  was the subject of research in a lot of works [19–22]. First of all, this concerns liquid metals, where  $r_p^{(D)}$  has to be identified with the ionic radius,  $r_I(T) = r_p^{(D)}(T)$ . However, there are a lot of misunderstandings about the temperature dependence of  $r_I$ .

In the framework of our approach, the corresponding radius of a particle, which will be called its effective radius, is determined by the relations

$$\frac{1}{r_p^{(\text{eff})}(T)} = \frac{1}{r_p^{(\nu)}} + \frac{3}{5\sqrt{\nu(T)\tau_M(T)}}, \quad (5)$$

where  $r_p^{(\text{eff})}(T)$  is a known temperature dependence. In this work, the temperature dependences of the radii  $r_p^{(\text{eff})}$  and  $r_p^{(D)}$  will be studied in detail for argon-like liquids and liquid metals. Under argon-like liquids, we understand all low-molecular liquids for which the averaged potentials of intermolecular interaction possess the argon-like structure. This class of liquids includes argon and other atomic liquids according to Bulavin’s classification [23], liquids with dumbbell-like molecules of the N<sub>2</sub> type and disc-like molecules of the C<sub>6</sub>H<sub>6</sub> type, and some other liquids. A good numerical agreement between the values of  $r_p^{(\text{eff})}(T)$  and  $r_p^{(D)}(T)$  is considered as a clear criterion for the existence of the collective transport in liquids. A direct equivalent of this criterion is the agreement between the experimental values of the self-diffusion coefficient and the values calculated by formula (1).

## 2. Shear Viscosity in Argon-Like Liquids and the Determination of the Molecular and Ionic Radii

As was shown in works [24–27], the kinematic shear viscosity of liquids is mainly determined by the effects of friction between molecular layers that move relative to one another. This parameter is described by the equation

$$\tilde{\nu}(\tilde{v}, t) \approx \left[ \frac{1 - \tilde{v}_0^{(i)}}{\tilde{v} - \tilde{v}_0^{(i)}(t)} \right]^{1/3} \quad (6)$$

for  $i = \text{Ar, Kr, C}_6\text{H}_6, \text{C}_6\text{H}_5\text{NO}_2, \text{N}_2$ , and so forth, where  $\tilde{\nu}(t) = \nu(t)/\nu_{\text{tr}}$ ;  $\nu_{\text{tr}}$  is the kinematic shear viscosity at the triple point,  $t = T/T_{\text{tr}}$  and  $\tilde{v} = v/v_{\text{tr}}$  are the dimensionless temperature and specific volume, respectively ( $T_{\text{tr}}$  and  $v_{\text{tr}}$  are the temperature and the specific volume, respectively, at the triple point);  $\tilde{v}_0^{(i)} = v_0^{(i)}/v_{\text{tr}}^{(i)}$ , and  $v_0^{(i)}$  is the excluded volume of the system, which corresponds to its shear viscosity. Formula (6) successfully describes the shear viscosity in all liquids for which the averaged intermolecular potentials are similar to the Lennard-Jones potential in argon. It reproduces the temperature dependence of the shear viscosity with a high accuracy in such liquids as benzene, nitrobenzene, and nitrogen [25], as well as in liquid alkali [28] and transition metals [29].

Table 1 contains the values of the parameters entering formula (6) for various liquids. As one can see, the values of the excluded volume  $\tilde{v}_0$  are almost identical to the values of the specific volume in the indicated liquids at the corresponding triple point. Such a situation also takes place for alkali and post-transition metals. In the following calculations, we will assume that  $v_0 \approx v_m$ .

In work [25], it was shown that formula (6) also well reproduces the shear viscosity of water almost within the entire temperature interval of its liquid

state:  $315 \text{ K} < T < 620 \text{ K}$ . We emphasize once more that the values of the excluded volume almost coincide with the values of the specific volume at the triple point for liquids or the melting point for metals. This fact is another confirmation that there is no activation mechanism of the shear viscosity and self-diffusion processes in liquids.

The analysis of the kinematic shear viscosity makes it possible to determine the radii  $r_p^{(\nu)}$  of molecules or ions in liquid metals. As it is in the van der Waals equation, the excluded volume of a particle is equal to four times its proper volume. Therefore, the particle radius  $r_p^{(\nu)}$  can be calculated using the formula

$$r_p^{(\nu)} = \left( \frac{3}{16\pi} v_m \right)^{1/3}.$$

In liquid metals, an important role is played by the parameter of dense packing of ions,  $\delta$ , which is defined as the ratio between the intrinsic volume of the ion and the volume per ion in the system, i.e. as the ratio between the intrinsic volume of the ion and the volume of the sphere whose radius coincides with the position of the maximum in the binary correlation function for the system of solid spheres [30, 31]. For alkali metals, this parameter takes the values  $\delta = 0.46 \div 0.48$  [32]. Therefore, the ionic radius turns out related to the specific volume as follows:

$$r_p^{(\nu)} = \left( \frac{3}{16\pi} \delta v_m \right)^{1/3}.$$

The values of the radii  $r_p^{(\nu)}$  of molecules and ions together with the corresponding values for the gas phase of the corresponding liquid,  $r_p^{(\text{gas})}$ , and the values used in the Lennard-Jones potentials,  $r_p^{(\text{LJ})}$ , are quoted in Tables 2 and 3, respectively. As one can see, the molecular radii determined from the equation of state and from the analysis of the kinematic shear viscosity are appreciably different from each other (e.g.,  $r_p^{(\text{LJ})}/r_p^{(\nu)} \approx 1.21$  for argon). A similar situation is also typical of the radii  $r_p^{(\nu)}$ , which are determined from the shear viscosity of gases [33], but the corresponding difference between  $r_p^{(\text{LJ})}$  and  $r_p^{(\nu)}$  is smaller.

Let us illustrate the origin of this situation by estimating the radius that is responsible for the values of thermodynamic quantities and the radius that determines the kinetic characteristics. The former roughly

corresponds to the position of the minimum in the intermolecular potential,  $U'(r_p) = 0$ , whereas the latter is determined by the value of the potential core radius at which  $U(r_p) \approx k_B T_{\text{tr}}$ . In the case of argon, the ratio between those two radii  $r_p^{(\text{LJ})}/r_p^{(\nu)} \approx 1.16$ .

The ionic radii in liquid metals, which are determined from the equation of state and by analyzing the kinematic shear viscosity, differ from each other, as it is for molecular liquids, but the difference is somewhat larger. This situation arises due to a “softer” repulsion between the ions. It can be demonstrated using the general view of the potential from works [36, 37]. In particular, the ratio  $r_p^{(\text{LJ})}/r_p^{(\nu)}$  between those two radii is approximately equal to 1.2 for liquid Na, and 1.29 for liquid Rb, which approximately corresponds to the ratio of radii taken from Table 3 [28].

### 3. Estimation of the Maxwell Relaxation Time in Liquids and Liquid Metals and Its Temperature Dependence

By definition, the Maxwell relaxation time (MRT) equals [38, 39]

$$\tau_M = \eta/G, \quad (7)$$

where  $\eta$  is the dynamic shear viscosity in a liquid, and  $G$  the high-frequency shear modulus in the liquid

**Table 2. Molecular radii (in Å units) obtained from the equation of state,  $r_p^{(\text{LJ})}$ , and by analyzing the kinematic shear viscosity,  $r_p^{(\nu)}$**

Radii of molecules	Ar	Kr	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	N <sub>2</sub>
$r_p^{(\nu)}$	1.411	1.55	2.19	2.38	1.49
$r_p^{(\text{LJ})}$	1.701	1.77	2.62	2.80	1.85
$r_p^{(\text{gas})}$	1.73	1.80	2.63	–	1.82

**Table 3. Ionic radii (in Å units) obtained from the equation of state,  $r_p^{(\text{LJ})}$ , and by analyzing the kinematic shear viscosity,  $r_p^{(\nu)}$**

Radii of molecules	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Pb <sup>+</sup>	Sn <sup>+</sup>	Bi <sup>+</sup>
$r_p^{(\nu)}$	0.79	1.01	1.23	1.52	1.18	1.24	1.27
$r_p^{(\text{LJ})}$	1.27 [34]	1.13 [34]	1.62 [35]	2.02 [20]	1.7 [34]	–	–

Table 4. The upper limits  $T_u$  of the temperature interval  $T_m < T < T_u$ , where the calculated MRT has physically correct values

	Ar	Kr	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	N <sub>2</sub>	Na <sup>+</sup>
$T_u$	$1.19T_m \approx 100$ K	$1.14T_m \approx 132$ K	$1.42T_m \approx 400$ K	$1.33T_m \approx 375$ K	$1.31T_m \approx 83$ K	$1.10T_m \approx 1132$ K

system. Making use of the kinematic shear viscosity  $\nu = \eta/\rho$  and the relationship  $G = \rho c_t^2$ , we obtain

$$\tau_M = \nu/c_t^2,$$

where

$$\tau_M = \nu/c_t^2$$

is the high-frequency velocity of transverse sound in liquids. Taking the inequality  $c_t < c_l$  into account, we obtain

$$\tau_M > \nu/c_l^2 \tag{8}$$

for the lower MRT limit. Making allowance for the approximate relationship  $c_t^2 \approx \frac{2}{3}c_l^2$  between the velocities of transverse and longitudinal sounds [40, 41], we get

$$\tau_M = \frac{3\nu}{2c_l^2}.$$

For atomic and low-molecular liquids, the temperature dependence of the longitudinal sound velocity is known, so the fulfillment of inequality (8) is mandatory. For liquid metals, the temperature dependence of the longitudinal sound velocity has not been studied so well, so Eq. (7) was used to calculate  $\tau_M$  with an acceptable accuracy. In the latter case, the MRT equals

$$\tau_M(T) = \tau_M(T_m) \frac{\eta(T)}{\eta(T_m)}, \tag{9}$$

where

$$\tau_M(T_m) = \frac{\eta(T_m)}{G_{cr}}$$

is the MRT value at the melting point. The scope of MRT applications is limited from above by the temperature  $T_u$  determined from the equation

$$\frac{\nu(T_u)}{c_l(T_u)} = \sqrt{\frac{3}{2}} r_p. \tag{10}$$

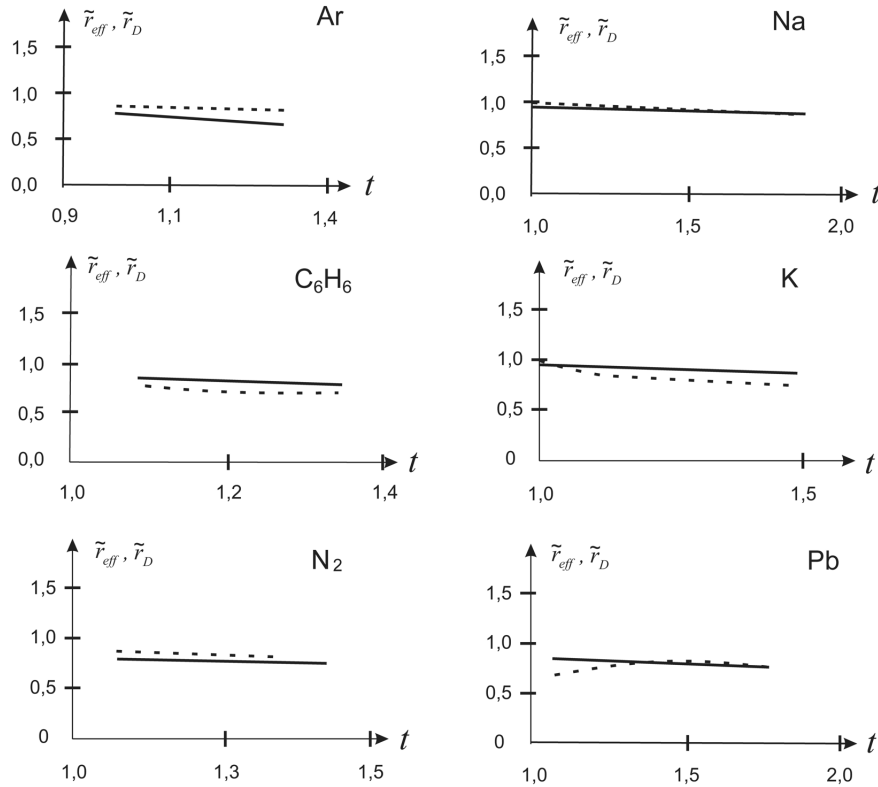
Here, the argument was used that the radius of the Lagrangian particle,  $r_L = 2\sqrt{\nu\tau_M}$  has to be not smaller than the radius of the molecular complex consisting of the selected molecule and its immediate environment. The values of the temperature  $T_u$  are quoted in Table 4.

#### 4. Comparison of the $r_p^{(eff)}(T)$ - and $r_p^{(D)}(T)$ -Values for Lliquids and Liquid Metals

Let us compare the values of the effective and hydrodynamic molecular (ionic) radii making use of formulas (4) and (5). In Fig. 1, the temperature dependences of those parameters are illustrated for some liquids.

For all liquids, the effective and hydrodynamic radii of particles demonstrate a similar temperature behavior. Taking the collective contribution to the self-diffusion coefficient of particles in liquids into account exhaustively explains the necessity of the artificial introduction of the particle radius dependence on the temperature when comparing the theoretical and experimental values of  $D_s(T)$  on the basis of the Stokes–Einstein formula. However, the  $r_p^{(eff)}$ - and  $r_p^{(D)}$ -values also reveal some difference. First of all, this is a result of the measurement accuracy of self-diffusion coefficients, which amounted to about 10% or less in most experiments. Approximately the same discrepancy takes place between the  $r_p^{(eff)}$ - and  $r_p^{(D)}$ -values. For liquid Na and Pb, the measurement accuracy of the corresponding self-diffusion coefficients was about 6%. So, as one can see, the  $r_p^{(eff)}$ - and  $r_p^{(D)}$ -values are practically identical, within the measurement error for  $D_s(T)$  in the temperature interval, where the collective motion of particles must be taken into account.

Another origin of the discrepancies between  $r_p^{(eff)}$  and  $r_p^{(D)}$  is the calculation error for the MRT parameter, which is determined by the transverse sound velocity. There are experiments, where the trans-



**Fig. 1.** Dependences of  $\tilde{r}_{\text{eff}} = r_p^{(\text{eff})}/r_p^{(\nu)}$  (solid curves) and  $\tilde{r}_D = r_p^{(D)}/r_p^{(\nu)}$  (dotted curves) on the normalized temperature  $T/T_{\text{tr}}$  ( $T/T_m$  for liquid metals) for argon-like liquids and liquid metals

verse sound velocity was measured for highly viscous liquids [42]. For atomic and low-molecular liquids, the MRT was calculated using molecular dynamics [6, 43, 44]. However, we do not know about such experiments or theoretical calculations for liquid metals. Nevertheless, despite the indicated uncertainties, the  $r_p^{(\text{eff})}$ -values practically coincide with the  $r_p^{(D)}$ -ones to the measurement error of the self-diffusion coefficient and correctly describe the temperature dependence of the hydrodynamic particle radius. Thus, taking the component  $D_c$  of the self-diffusion coefficient into account is crucial for a wide scope of liquids: atomic, low-molecular ones, and pure liquid metals.

## 5. Discussion of the Results Obtained

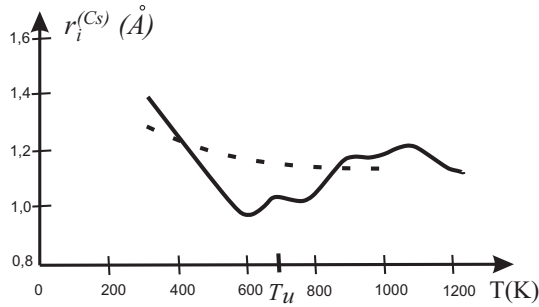
In this work, a clear definition of the effective radius  $r_p^{(\text{eff})}$  of molecules and ions was given, and, on the basis of many liquids taken as examples, it was shown that  $r_p^{(\text{eff})}(T) \approx r_p^{(D)}(T)$ . This relationship is a strong evidence of the existence of a collective transport in

liquids and liquid metals. It was shown above that the accuracy of this approximate equality depends, first of all, on the measurement accuracy of the self-diffusion coefficient values, as well as on the determination accuracy of the Maxwell relaxation time.

Let us discuss the comparison of our results with those obtained in works [20, 45] for alkali metals Rb and Cs in more detail. According to work [45], main attention at the first stage was paid to the calculation of the effective interaction potential between two ions. For this purpose, the cited authors used the Schommers algorithm [46]. Then, using the molecular dynamics method, the mean-square displacement of the ion,  $\langle(\Delta\mathbf{r})^2\rangle$ , was calculated and, with the help of the relation

$$D_s = \lim_{t \rightarrow \infty} \frac{\langle(\Delta\mathbf{r})^2\rangle}{6t},$$

the values of the ionic self-diffusion coefficient were determined. This circumstance is especially impor-



**Fig. 2.** Temperature dependences of  $r_D^{(\text{Cs})}$  (solid curve) and  $r_{\text{eff}}^{(\text{Cs})}$  (dotted curve). The marker  $T_u$  denotes the upper limit of the temperature interval, where the MRT values for liquid Cs are physically correct

tant, because the experimental values of the self-diffusion coefficient  $D_s$  were obtained only for three temperatures: 301.8, 573, and 773 K. The  $D_s^{(\text{Cs})}$ -values calculated in work [45] correspond to a rather wide temperature interval  $306 \text{ K} < T < 1400 \text{ K}$ , being in a quite satisfactory agreement with experimental data.

Below, we used the values  $D_s$  for Cs that were obtained in work [45]. The radius  $r_D^{(\text{Cs})}$  of a  $\text{Cs}^+$  cation was determined with the help of the Stokes–Einstein relation  $r_p^{-1} \sim D_s \eta / T$ . The values of the radius  $r_D^{(\text{Cs})}$  obtained in this way and the radius  $r_{\text{eff}}^{(\text{Cs})}$  calculated using formula (5) are compared in Fig. 2. When calculating  $r_{\text{eff}}^{(\text{Cs})}$ , the value  $r_p^{(\text{Cs})} = 1.495 \text{ \AA}$  corresponding to the shear viscosity of the melt was used instead of  $r_p^{(\text{Cs})}$ , and the MRT was calculated by formula (7). The temperature dependence of  $r_{\text{eff}}^{(\text{Cs})}$  becomes appreciable only in the temperature interval  $306 \text{ K} < T < 700 \text{ K}$ , where the collective contribution to  $D_s$  has to be taken into account. In what follows, we took  $r_{\text{eff}}^{(\text{Cs})} \rightarrow r_p^{(\text{Cs})}$ .

As one can see, the calculated ion radii agree with one another by the order of magnitude, but the temperature dependence of  $r_D^{(\text{Cs})}$  is substantially nonmonotonic, although there are no physical grounds for such nonmonotonic behavior. From the comparison made above, it follows that the temperature dependence of  $r_{\text{eff}}^{(\text{ion})}$  is completely governed by the collective drift of a molecule or ion in the field of thermal hydrodynamic nanoscopic fluctuations.

In work [21], the temperature dependences of the self-diffusion coefficients of  $\text{Al}^+$  and  $\text{Ni}^+$  cations in Al–Ni melts were studied. It was shown that there

are intervals, where the temperature dependences of  $r_D^{(i)}$  ( $i = \text{Al}^+$  and  $\text{Ni}^+$ ) are strong. Unfortunately, our results cannot yet be compared with the results of work [21] because of the lack of reliable values for the shear viscosity coefficient obtained at various temperature and melt concentration values.

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#### ПРОЯВИ ІСНУВАННЯ КОЛЕКТИВНОГО ПЕРЕНОСУ В АТОМАРНИХ РІДИНАХ ТА РІДКИХ МЕТАЛАХ

В роботі досліджується прояв колективних складових теплового руху “частинок” (молекул та іонів) у поведінці їх ефективних радіусів. Встановлено конкретний вигляд температурної залежності ефективних радіусів молекул та іонів. Демонструється їх добре узгодження з гідродинамічними радіусами, що визначаються за формулою Айнштейна–Стокса. Звертається увага на відмінності між значеннями радіусів частинок, що використовуються для опису термодинамічних та кінетичних властивостей рідин.

*Ключові слова:* тепловий рух молекул, колективний перенос, коефіцієнт самодифузії молекул рідини.