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SELF-DIFFUSION CROSSOVERS IN LIQUIDS

Regions of characteristic contributions to the self-diffusion coefficient have been determined on the $P - T$ phase diagram of low-molecular-weight liquids. The main role is played by two crossover curves that divide the region of liquid states, L, into three subregions. It is shown that, in the subregion SL, the self-diffusion coefficient is determined by two contributions, both of which are collective in nature. In the central part of the region L, the self-diffusion coefficient is also collective in nature, but it can be described with regard for only one contribution. In the subregion LG, the self-diffusion coefficient is again determined by two contributions, one of which is collective in nature, and the other is single-particle, which is characteristic of gaseous states.

K e y w o r d s: self-diffusion, crossover, phase diagram, collective contributions, low-molecular liquids.

1. Introduction

The years 1971 and 1986 are inscribed in gold in the annals of outstanding achievements of Ukrainian physics. In 1971, Josyp Z. Fisher first in the world formulated the concept of the collective component in the self-diffusion coefficient in liquids [1]. Fifteen years later, in 1986, Leonid A. Bulavin, together with his colleagues, became the first in the world who experimentally proved the existence of collective transport in liquids and solutions, and also estimated the magnitude of the corresponding contributions to the self-diffusion coefficients [2,3]. Those achievements reraised the issue of the physical nature of self-diffusion processes in liquids, which had long been considered completely resolved.

In the years that have passed since then, substantial progress has been achieved in both the development of theoretical ideas regarding the origin of self-diffusion processes and the experimental study of self-diffusion regularities in various types of liquids and solutions; see works [4–12]. Both then and now, these works deserve the highest appreciation at the national and international levels. But, in what follows, we will not present the most important results achieved in this area. Instead, we will consider the very important issue concerning the relation between various components of the self-diffusion coefficient and the characteristic regions of the temperature and pressure values on the phase diagrams of low-molecular-weight substances.

2. Discussion of the Results

Standard pressure (P)–temperature (T) phase diagrams [13] that describe condensed systems formed by atoms (e.g., argon) or small molecules (e.g., water) conditionally include three characteristic regions corresponding to the solid (S), liquid (L), and gaseous (G) states (Fig. 1). Two main specific states are distinguished as a rule: the triple point T_{tr} and the critical point T_{c}.

However, this picture seems too simplified for many specific systems. In some cases, a relatively narrow subregion of liquid states (SL) appears at the boundary separating the solid and liquid phases,
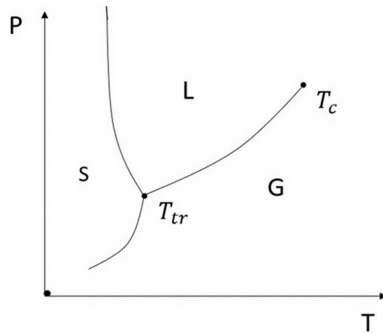
Fig. 1. Typical $P - T$ phase diagram for condensed media formed by atoms or small molecules
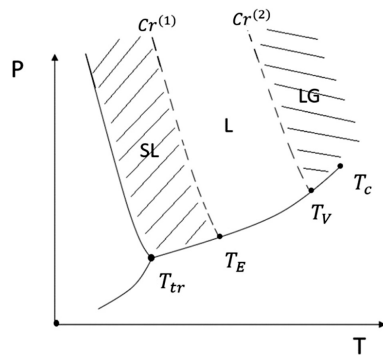

Fig. 2. Generalized solid–liquid–gas $P - T$ phase diagram for condensed matter with specific interparticle interactions

where metastable superheated solid states can be observed in the form of clusters, associates, or aggregates with a certain degree of short-range positional ordering. Together with similar ideas expressed in Frenkel's *Kinetic Theory of Liquids* [14], one can mention numerous examples for liquids formed by relatively large molecules with a complicated structure (the pre-transition region between the cholesteric and A-smectic mesophases [15], or the so-called "deep eutectics" in organic mixtures [16]). Somewhat less common examples can be noted for the boundary region LG between the liquid and gaseous phases, where some features typical of a gas can manifest themselves in a generally ordinary liquid [17].

Thus, a generalized form of the "solid–liquid–gas" phase diagram can be proposed (Fig. 2). Along with the traditional T_{tr} and T_c parameters, one may talk about two other specific states, TE and TV, with the corresponding crossover lines $Cr^{(1)}$ and $Cr^{(2)}$. The curve $Cr^{(1)}$ on the $P - T$ plane has a finite crossover value separating the metastable solid-liquid (SL) states and stable liquid states. Similarly, the location

of the boundary $Cr^{(2)}$ separating the L and LG regions is determined from the physical condition that the elastic shear modulus tends to zero.

Our idea is to consider a specific aspect of the SL and LG systems described above, namely, various types of self-diffusion that can be realized under those conditions. Let us proceed from the fact that the main characteristic of the viscoelastic properties of liquids is the Maxwell relaxation time (MRT) τ_M [14, 18], which can be evaluated from the values of viscosity and elastic moduli experimentally measured for shear deformation ($\tau_M = \eta/G$). For a large number of various liquids, the values of the shear viscosity, as well as the high-frequency shear modulus, can be easily found in reference books; see, in particular, book [19]. To get a better comprehension of this characteristic, here are some examples of τ_M-values for liquids of different chemical nature. In particular, τ_M is approximately equal to 3.3×10^{-13} s for water, 5×10^{-13} s for ethanol, 2×10^{-13} s for non-polar n-hexane, $(1.0 \div 1.1) \times 10^{-11}$ s for liquid argon and nitrogen, 0.5–1.5 s for glycerol (a high-viscosity trihydroxyalcohol), 0.01–1 s for nematic liquid crystals, 0.0025–0.15 s for deep eutectic solvents, and $\sim$10–1000 s for glass and polymer melts. One can see that the MRT values can differ qualitatively by many orders of magnitude, but there is little information about any qualitatively different properties, because all basic formulas for viscoelastic properties are similar for substantially different classes of liquids. Therefore, we assume that the formation of SL states, which can be observed experimentally in liquid crystals (LC), deep eutectic solvents (DES), and other complicated liquids, can be theoretically predicted for simpler systems, including water or argon, and the manifestations of those SL states will be detected in the future using more sophisticated methods and equipment.

The self-diffusion of a Brownian particle of radius r_B, which is known to be governed by collective effects, is described by the Einstein formula with the known coefficient [20],

$$D_B = \frac{k_B T}{6\pi\eta r_B}. \tag{1}$$

It can be shown (see works [10,11]) that, for the SL region, this formula should be somewhat modified,

$$D_m = \frac{k_B T}{6\pi\eta r_\nu}, \tag{2}$$

where r_ν is the effective molecular radius, which is determined from the kinematic shear viscosity. This modification is based on the assumption that the self-diffusion process in the substance in the liquid state in the region close to the "liquid–solid" transition is driven by small simultaneous displacements of molecules, which stimulate the re-mixing of neighboring molecular groups. As a result, the corresponding contribution to the self-diffusion coefficient should be collective by character.

Another contribution to the SL region can be made by elastic Lagrangian particles, i.e., effective groups of molecules that can change their shape and size under flow conditions. (This concept becomes especially clear and simple, if we directly consider liquids of complicated types with various clusters, complexes, and associates formed owing to universal and specific intermolecular interactions.) In this case, the corresponding contribution D_c to self-diffusion is given by either the expression

$$D_c^{(F)} = \frac{k_B T}{16\pi\eta(\nu\tau_M)^{1/2}} \qquad (3)$$

obtained in work [1] or the expression

$$D_c^{(BLM)} = \frac{k_B T}{10\pi\eta(\nu\tau_M)^{1/2}} \qquad (4)$$

found in work [4].

Hence, the self-diffusion coefficient of liquids can be represented as follows:
• in the SL region,

$$D_s = D_c + D_m, \qquad (5)$$

where D_c and D_m are collective contributions, as was defined above;
• in the L region located between the crossover curves $Cr^{(1)}$ and $Cr^{(2)}$ (Fig. 2),

$$D_s = D_m; \qquad (6)$$

• in the LG region (to the right of $Cr^{(2)}$),

$$D_s = (1-x)D_m + xD_G, \qquad (7)$$

where x is the fraction of voids in the liquid state (their presence substantially changes the self-diffusion mechanism), and D_G is the self-diffusion coefficient in the gaseous state, which has a single-particle nature (see work [21]).

The correspondence of those formulas to experimental data in water and argon was discussed in detail in works [10,11]. The application of this approach to liquids of other types now seems to be a rather simple task.

3. Conclusions

In this short article, it is found that the features of self-diffusion of molecules in low-molecular-weight liquids, such as argon, are closely related to their thermodynamic properties on the standard $P - T$ phase diagram. First of all, it is necessary to distinguish the SL region where the system can be in both a stable liquid state and a metastable superheated solid state. Accordingly, two independent contributions to the self-diffusion coefficient arise. The boundary of the SL region from the liquid side is confined by a crossover, whose position can be determined by analyzing the Maxwell relaxation time. Another crossover on the phase diagram naturally arises as the boundary between the L and LG regions, where self-diffusion occurs due to small rotations of molecular groups and the translational motion of molecules along voids that naturally arise, when approaching the gaseous state.

A further analysis of self-diffusion processes in supercooled liquids, where two independent contributions to the self-diffusion coefficient should also be observed, is essential. This problem becomes especially interesting for supercooled water and glycerin, where an anomalous increase in the viscosity of those liquids is observed. This issue will be dealt with in a separate paper.

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КРОСОВЕРИ САМОДИФУЗІЇ У РІДИНАХ

На фазовій P, T–діаграмі низькомолекулярних рідин встановлено області характерних внесків у коефіцієнт самодифузії. Основну роль відіграють дві криві кросовера, які розділяють область рідинних станів на три підобласті. Показано, що в підобласті SL коефіцієнт самодифузії визначається двома внесками, обидва з яких мають колективний характер. У центральній частині L між двома кривими кросовера коефіцієнт самодифузії також має колективний характер, але він описаний з урахуванням лише одного внеску. В області LG, праворуч від області L, коефіцієнт самодифузії знову визначається двома внесками, один з яких має колективний характер, а інший – одночастинковий, характерний для газоподібних станів.

К л ю ч о в і   с л о в а: самодифузія, кросовер, фазова діаграма, колективні внески, низькомолекулярні рідини.