MOLECULAR ROTATION AND VOLUME DEPENDENCE OF THE THERMAL CONDUCTIVITY IN LIQUID N$_2$

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The influence of molecular rotation on the volume dependence of thermal conductivity in liquid nitrogen was evaluated. A modified method of reduced coordinates has been used to calculate components of the isochoric heat capacity of liquid nitrogen. A difference in the behavior of temperature dependences of the Bridgman coefficient at pre-crystallization temperatures in liquid Ar, CH$_4$ and N$_2$ is explained by the influence of rotational motion of molecules.

Key words: thermal conductivity, Bridgman coefficient, molecular rotation in liquids.

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I. INTRODUCTION

In the general case, the total energy of the molecules in a liquid is due to their random translational motion as well as their vibrational and rotational motions. As indirect, but in no case secondary, experimental data on the thermal conductivity Λ can serve as a source of information on the thermal motion in liquids [1]. A thorough analysis of the thermal conductivity features in liquids allows one to compare them with the results of structural and thermodynamic studies. The specific features of the dynamics of translational and rotational subsystem of molecular liquids affect their thermodynamic properties and must manifest themselves in one way or another in the relaxation processes [2]. This is primarily related to the coupling (known as translation-rotation coupling) between translation displacements and molecular rotations and it is characteristically reflected in the kinetic properties of molecular liquids and, in particular, on the thermal conductivity. In the majority of cases, this coupling is most apparent for liquids at pre-crystallization temperatures in which the formation of orientational subsystem is accompanied by a change of structural ordering. Often this change is preceded by anomalous thermodynamic properties.

In the present paper, we perform a detailed analysis of heat transfer in liquid nitrogen, paying special attention to the influence of molecular rotation on volume dependence of the thermal conductivity. With that purpose, we carried out a comparison of the isochoric thermal conductivity of liquid Ar, CH$_4$ and N$_2$. The distinctions between the volume dependence of liquid Ar, CH$_4$ and N$_2$ are explained by the influence of rotational motion of molecules. Finally, we give an additional argument by the calculation of the isochoric heat capacity components of liquid nitrogen.

II. CALCULATION RESULTS AND DISCUSSION

The liquid that contains molecules or molecular ions is more complex than one containing only atoms or atomic ions because the individual species have orientation as well as position. This allows the existence of additional types of thermal motion (as compared with that in atomic liquid) and makes the interpretation of thermal conductivity data more difficult. It is necessary to consider in molecular liquids, along with translation oscillation of molecules, the orientational motion of molecules as a whole, intramolecular rotation of molecular segments, and intramolecular oscillations. At the same time, by choosing corresponding liquids, we can exclude one or other type of thermal motion from consideration. For example, intramolecular rotation of molecular segments in simple molecular liquids can be disregarded, owing to the simplicity of the molecular structure. In most cases the energy of intramolecular coupling in simple molecular liquids exceeds considerably the energy of intermolecular interactions. Respectively, intramolecular coupling makes no significant contribution to the kinetic properties of simple molecular liquids. Thus, while considering the thermal conductivity of simple molecular liquids, we may restrict ourselves to the account of translation oscillations and the orientational motion of molecules as a whole. The peculiarities of translation-rotation coupling depend on molecular structure and are determined by the relationship between central and non-central intermolecular interaction forces. In the general case, the transition of molecular motion from low-amplitude librations to weakly hindered rotation is accompanied by a decrease in the thermal resistance $W = 1/\Lambda$ [3]. Translation-rotation coupling also leads to a softening of elastic constants and affects the molecular translation oscillation. Our previous studies of high-temperature thermal conductivity of simple molecular crystals [4–7] have revealed the peculiarities of heat transfer which are due to molecular rotation. The influence of this type of molecular motion on the heat transfer in molecular liquids is not yet completely clear. The liquid N$_2$ is the convenient object for such a kind of investigations. As temperature rises, the orientational disordering (OD) processes in N$_2$ start to intensify in the high-temperature solid β-phase and increases further intensively in liquid phase immediately above melting temperature (63.15K [11]). The direct evidences for these OD processes came from the exper-

iments cited in [8–13]. In the solid β-phase of N_2 the frequency of reorientations varies with the temperature from 9.5×10^{11} s^{-1} to 5.5×10^{12} s^{-1} immediately before melting [8]. According to [9,10], a negative jump of the spin-lattice relaxation time in N_2 is observed at the melting temperature testifying that the rotation of nitrogen molecules in the liquid phase is more hindered than that in the solid one. This is due to the formation of a structure, where molecules can make free precession in the β-phase of solid N_2; such a structure is not implemented in the liquid phase because of an irregular particle arrangement and thermal fluctuation effects [11]. Data from the consideration of the molecular volume have yielded a picture that showed for nitrogen to 48.1×10^{-24} cm^3 in the solid β-phase and to 57.7×10^{-24} cm^3 in the liquid state, whereas the value of this quantity calculated from the observed distance of closest molecule approach in the solid β-phase at 4 K amounts to 64.7×10^{-24} cm^3, provided the assumption of free molecular rotation is made [12].

How is it possible to observe the influence of molecular rotations on experimental thermal conductivity dependence? In this paper, we perform our study of molecular rotation effect by way of comparison of thermal conductivity of liquid N_2 with the behavior of thermal conductivity of atomic liquids or molecular liquids in which the character of molecular rotations does not vary with temperature. The liquid Ar and CH_4 were chosen for this purpose. The reasons for this choice are as follows: i) in argon there are no rotational degrees of freedom and a simply comparison with molecular liquids shows features of influence of orientational subsystem; ii) in CH_4 molecular rotation becomes close to free at temperatures above 50 K in the high-temperature solid phase [11,13]. In this case, comparison between thermal conductivity dependences of liquid CH_4 and N_2 shows direct influence of change in the character of nitrogen molecules rotations on thermal conductivities of liquid N_2. iii) the isochoric thermal conductivity of liquid Ar, CH_4 and N_2 were measured under identical conditions on the same setup [14, 15].

The analysis of thermal conductivity data of liquids under saturated vapor pressure or under isobaric conditions does not allow revealing the influence of molecular rotation on thermal conductivity due to thermal expansion. Therefore, for comparison the isochoric thermal conductivity data must be used to exclude the thermal expansion effect.

The experimental isochoric thermal conductivity Λ_v of liquid Ar, CH_4 and N_2 according to data [14, 15] is shown in Fig. 1,a. From Fig. 1,a it can be seen that the behavior of the thermal conductivity of liquid N_2 differs essentially from the thermal conductivity of liquid Ar and CH_4. In liquid Ar and CH_4, the isochoric thermal conductivity increases with temperature. At the same time Λ_v of liquid nitrogen is practically constant up approximately to 90 K, and then begins to increase with temperature. The volume dependences of thermal conductivity $\Lambda(V)$ are best suited for studying the influence of molecular rotation on the heat transfer. It is known that volume dependence of the thermal conductivity can be described

by the Bridgman coefficient [16, 17]:

$$g = -\left(\frac{\partial \ln \Lambda}{\partial \ln V}\right)_T, \qquad (1)$$

The Bridgman coefficients for liquid Ar, CH_2 and N_2 were calculated according to Eq. (1) using experimental data [14,15].
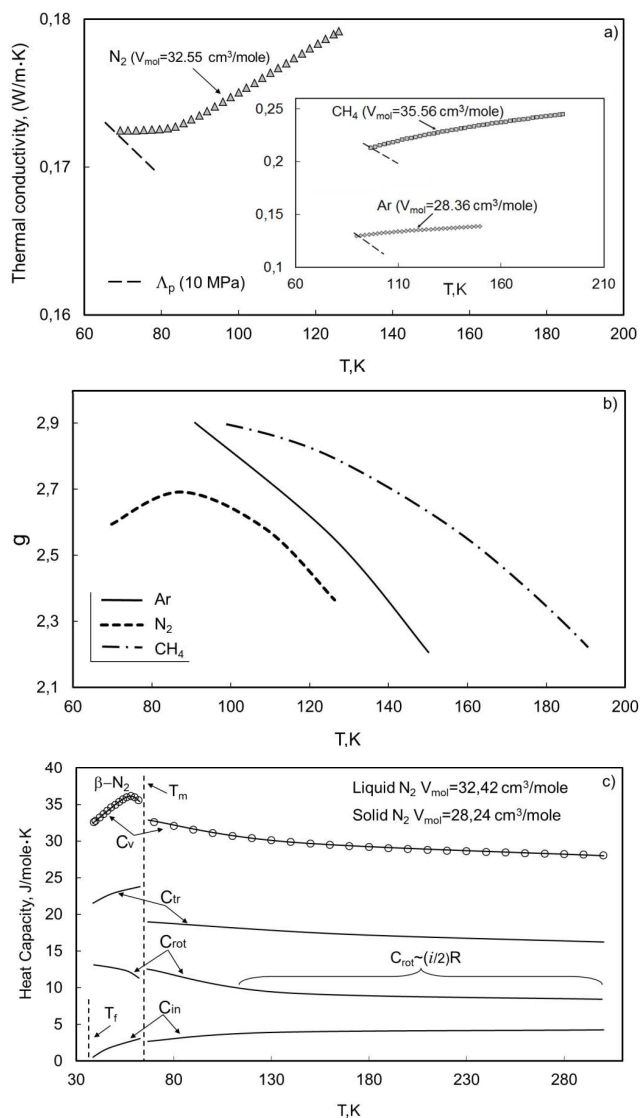

Fig. 1. a) Isochoric Λ_v thermal conductivity in liquid Ar, N_2 and CH_4. b) Temperature dependences of the Bridgman coefficient for liquid Ar, N_2 and CH_4. c) Isochoric heat capacity components for liquid and solid (β-phase [11]) N_2. T_m is the melting temperature of N_2, and T_f is the temperature of $\alpha \rightarrow \beta$ phase transition in solid N_2.

Fig. 1,b shows the calculated results for $g(T)$. The curves of $g(T)$ for liquid methane and argon are similar testifying that there is no effect of the rotational motion of methane molecules. It can be seen from Fig. 1,b that the behavior of the Bridgman coefficient of liquid N_2 differs essentially from the Bridgman coefficient of liquid

Ar and CH_4. In liquid Ar and CH_4, the Bridgman coefficient decreases with temperature. At the same time, the Bridgman coefficient in liquid N_2 initially increases with increasing temperature, then passes through a smooth maximum and starts to decrease. In our opinion, the distinctions observed between the volume dependence of liquid Ar, CH_4 and N_2 can be attributed to the influence of molecular rotation. The last assertion requires at least simplified explanations. In the course of gradual transition of molecules to the hindered rotation, the contribution of this type of thermal motion to heat capacity tends asymptotically to the heat capacity of a system of free rotators, and the relevant contributions to thermal expansion and thermal conductivity tend to zero [11]. An increase in the angular amplitude of librations cannot occur without an increase in the effective molecular volume. As a result this leads to an additional contribution to thermal expansion. Free molecular rotations means the absence of the interaction with translational oscillations and rotations of other molecules. At free molecular rotations, translation-rotation coupling can be neglected, and it leads to negligibly small effect of molecular rotation on thermal conductivity (for example, in liquid methane).

A study of the influence of molecular rotation on the heat transfer is a rather complex problem due to the fact that, rather than being independent of one another, the translation and rotation motions in liquids occur as coupled translation-rotation vibrations. Therefore, to support our point of view and to elucidate the reasons for different behavior of $g(T)$ in liquid Ar, CH_4 and N_2, we have calculated the translational, intramolecular and rotational contributions to the isochoric heat capacity of liquid N_2. In general, the isochoric heat capacity C_v of simple molecular liquids can be written as a sum of contributions from the translational C_{tr}, intramolecular C_{in} and rotational C_{rot} vibrations:

$$C_v = C_{tr} + C_{in} + C_{rot}, \qquad (2)$$

Despite evidence for that molecular translation oscillations in liquids can be collective, it is uncertain whether Debye approximation is generally applicable to liquids. Therefore, the translational component C_{tr} was determined using a modified method of reduced coordinates [18]. It is important that with this method there is no need to involve any approximate model. As a rule, the reduction parameters are $T_{mol} = \varepsilon/k_B$, $\Lambda_{mol} = k_B/\sigma^2\sqrt{\varepsilon/\mu}$, and $V_{mol} = N\sigma^3$, where σ and ε are the parameters of Lennard-Jones potential, μ is the molar weight, and N is the total number of particles. As the reduced parameters T_{mol} and V_{mol} we used the values of critical temperatures T_{cr} and molar volumes V_{cr} of N_2 and Ar were used [19] (Table 1). The choice of the given parameters is explained as follows. For simple molecular substances, T_{cr} and V_{cr} are proportional to ε and σ^3, respectively. However, the accuracy of determination is much higher for critical parameters than for the parameters of the binomial potential. It should be noted, that the quantities σ and ε depend substantially on the choice of binomial potential and the method used to determine it. According to this method, if the contributions of various vibration mechanisms to the total heat capacity C_v are additive, the translational heat capacity of N_2 is considered equal to the isochoric heat capacity of liquid Ar [20], provided that the reduced temperatures $T^* = T/T_{mol}$ and volumes $V^* = V/V_{mol}$ are identical in both cases.

The contribution of intramolecular vibrations C_{in} to the total heat capacity C_v was calculated in the Einstein approximation; the required values of characteristic temperature Θ_E were taken from [21, 22]. The rotational heat capacity was determined as $C_{rot} = C_v - C_{in} - C_{tr}$. The values of the isochoric heat capacity C_v of liquid N_2 were taken from [23].

Substances	T_{cr}, K	V_{cr}, cm^3/mole	ε, K	σ 10^{-10}, m	V, cm^3/mole	Ref.
Ar	150.71	75.2	119.5	3.41	29.12	[19]
N_2	126.25	90.1	95.0	3.70	32.42	[19]

Table 1. Reduced parameters and molar volumes of liquid Ar and N_2.

The temperature dependences of contributions to isochoric heat capacity of liquid and crystalline (β-phase [11]) nitrogen calculated for samples with molar volumes of 32.42 and 28.24 cm^3/mole, respectively, are shown in Fig. 1,c. To determine partial contributions of C_v for solid β-N_2, the same calculation procedure was engaged as in the liquid N_2 case; in so doing, the data cited in [11] were used. It is convenient to judge the nature of orientational molecular motion by analyzing the temperature dependence of rotational heat capacity. In the temperature range from the melting temperature to 85–90 K, C_{rot} decreases considerably (from 12.1 to 9.6 J/(mole × K), which testifies to intensive processes of orientational disordering. With further temperature growth, C_{rot} decreases weakly approaching the value of 8.75 J/(mole × K). At $T > 90$ K, the rotational component of heat capacity tends to the value of $(i/2)R$ (Fig. 1,c), typical for free i-dimensional rotators. From the foregoing it seems reasonable to conclude that at temperatures higher than about 90 K, the processes of orientational disordering terminate, and molecules of liquid nitrogen start to move in the weakly-hindered rotation mode. The calculations carried out for the components of the heat capacity C_v reveal a jump of C_{rot} towards its increasing at the point of crystal–liquid phase transition. This is in good agreement with data of references [10, 11, 24, 25], indicating that the orientational ordering of molecules in liquid N_2 in the range above the melting temperature is higher than in the β-phase of crystalline N_2 at premelting temperatures.

III. CONCLUSIONS

The data provided by this study add to our general understanding of heat transfer processes features in molecular liquids. On the basis of the results obtained in the

present investigation it seem justified to conclude that distinctions in the volume dependences of thermal conductivity for liquid Ar, CH_4 and N_2 are connected with the influence of rotational molecular motion in N_2 at pre-crystallization temperatures (64–85 K). Above 85–90 K, nitrogen molecules rotation becomes "weakly-hindered", and this influence disappears, so that the volume dependence of thermal conductivity in liquid N_2 behaves similarly to thedependence for Ar and CH_4.

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ОРІЄНТАЦІЙНИЙ РУХ МОЛЕКУЛ І ОБ'ЄМНА ЗАЛЕЖНІСТЬ ТЕПЛОПРОВІДНОСТІ РІДКОГО N_2

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Досліджено вплив орієнтаційного руху молекул на об'ємну залежність теплопровідності рідкого N_2. На основі модифікованого методу наведених координат розраховано компоненти ізохорної теплоємності рідкого N_2. Відмінності в поведінці температурних залежностей коефіцієнта Бріджмена рідких Ar, CH_4 і N_2 в області температур безпосередньо вище від температури кристалізації пояснено впливом орієнтаційного руху молекул.