

Thermodynamic similarity of the correlation times of rotational motion of molecules in a liquid

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It is shown that the dependences of the relative values of the angular momentum correlation time τ_{JR} and of the reorientation correlation time $\tau_{\theta,R}$ on the relative temperature T/T_c , measured by the method of NMR relaxation method along the liquid-vapor coexistence line, coincide in the case of molecules that are rigid rotators with symmetry O_h , T_d , and C_{3v} . For the liquid phase, an exponential dependence of $\tau_{\theta,R}$ on $1/T$ is observed, with an "activation energy" $U_\theta = (1.3 \pm 0.1)T_{cr}$ (T_{cr} is the critical temperature).

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The validity of the thermodynamic-similarity method for the description of the temperature dependence of thermodynamic parameters in liquid and in vapor has been well confirmed by experiment. This method can be used also for kinetic characteristics such as viscosity, thermal conductivity, and the speed of sound. [1,2]

It is of interest to consider the possibility of applying this method to kinetic coefficients that depend directly on the anisotropic part of the intermolecular-interaction potential. Such coefficients are, in particular, the correlation times τ_θ of the orientation and τ_J of the angular momentum—the zero moments of the corresponding correlation functions.

The correlation times τ_J and τ_θ can be determined from data on nuclear magnetic relaxation, and the most reliable values of the correlation times are obtained in the case when the predominant contribution to the measured rate of NMR relaxation is given by the spin-rotational (τ_J) or quadrupole (τ_θ) interaction. [3]

In a liquid far from the critical temperature, and in a rarefied gas, the correlation time τ_J is connected with the spin-lattice NMR relaxation time T_{1sr} due to the interaction of the nuclear spin with the angular momentum of the molecule, and with the temperature, by the relation

$$1/\tau_J \sim C_{ef}^2 TT_{1sr} \quad , \quad (1)$$

where C_{ef}^2 is the effective constant of the spin-rotational interaction and is practically the same for a liquid and a gas, [4,5] and T is the temperature. It is usually assumed that (1) is satisfied also in the region of the critical temperature. [4]

The correlation time τ_θ of the molecule reorientation is determined from the quadrupole contribution made to the rate of the NMR relaxation T_{1q}^{-1}

$$1/\tau_\theta \sim T_{1q} \quad , \quad (2)$$

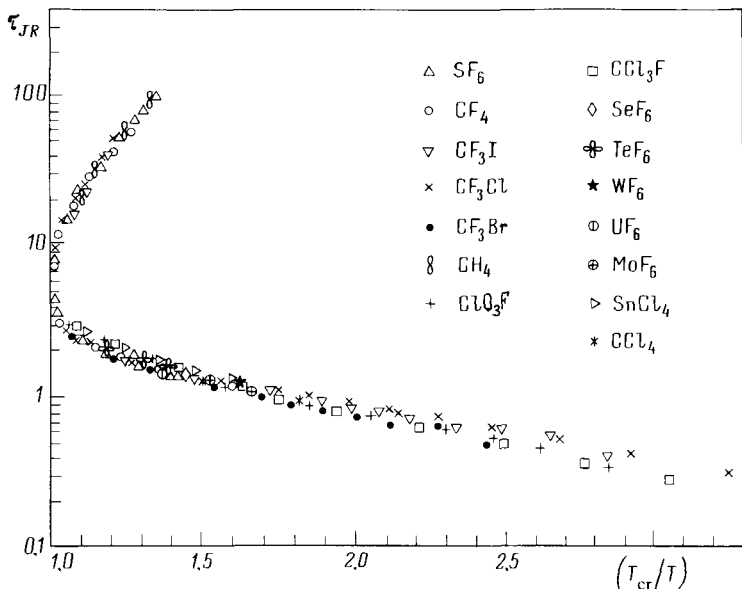


FIG. 1.

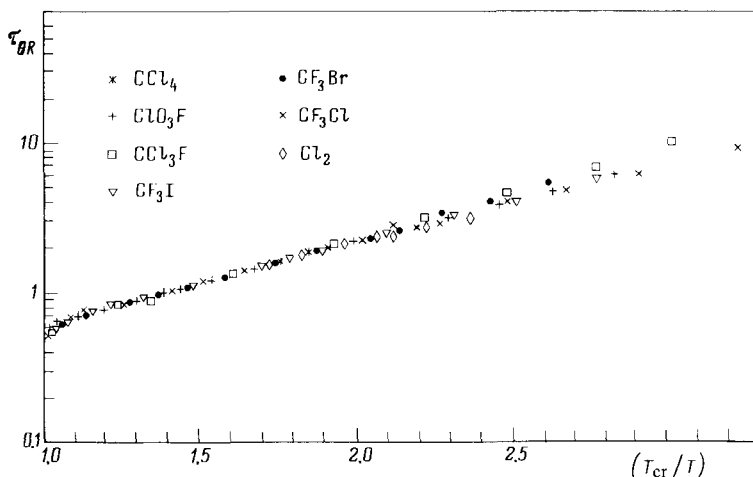


FIG. 2.

where the proportionality is a constant for each of the substances.

Experimental data on the temperature dependence of the NMR relaxation times on the liquid-vapor coexistence line, for a number of simple liquids for which the contributions due to τ_J and τ_θ can be distinctly separated, are given in^[6] for $S^{19}F_6$, in^[7] for $C^{19}F_4$, $C^{19}F_3Cl$, $C^{19}F_3Br$, and $C^{19}F_3I$ for the liquid and vapor phases, in^[8] for $Mo^{19}F_6$, $W^{19}F_6$, and $U^{19}F_6$, in^[9] for $Se^{19}F_6$, $Te^{19}F_6$, in^[5] for $ClO_3^{19}F$, in^[10] for $C^{35}Cl_3^{19}F$, in^[11] for $Sn^{35}Cl_4$, in^[12] for $C^{35}Cl_4$, in^[13] for $^{35}Cl_2$ for the liquid phase, and in^[14] for C^1H_4 for vapor. (The atomic numbers are given for nuclei for which the rate of the NMR relaxation was measured).

The symmetry of the molecules of these compounds is O_h , T_d , or C_{3v} . The nonsphericity of molecules with C_{3v} symmetry, characterized by the parameter $\xi = (I_{\perp} - I_{\parallel})/I_{\parallel}$, where I_{\perp} and I_{\parallel} are the principal moments of inertia of the molecules, is equal respectively to 0.73, 1.76, 2.77, -0.30, and 0.07 for the series CF_3Cl , CF_3Br , CF_3I , CCl_3F , and ClO_3F . When the thermodynamic-similarity method is used, the reference parameters are chosen to be the values of the investigated quantities at critical temperature. However, in view of the fact that some of the cited papers do not give measurement data in the critical region, we choose these parameters to be the values of τ'_J and τ'_θ in the liquid phase at the temperature $0.7T_{cr}$. Figures 1 and 2 show the obtained plots of the relative correlation times of the angular momentum τ_{JR} and of the reorientation $\tau_{\theta R}$. It is seen from the figures that these plots coincide for the indicated substances within 10%. It follows also from Fig. 2 that in the liquid phase we have up to the critical temperature

$$\ln \tau_{\theta, R} = (U_\theta / T), \text{ where } U_\theta = T_{cr}(1.3 \pm 0.1).$$

The results offer evidence of thermodynamic similarity of the correlation times τ_J and τ_θ measured along the liquid-vapor coexistence line for molecules with different symmetries and dimensions.

We are presently readying for print the results of an analysis of the connection between the observed similarity and the molecular and thermodynamic characteristics of individual substances.

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Erratum: Thermodynamic similarity of the correlation times of rotational motion of molecules in a liquid [JETP Lett. 23, 11-13 (5 January 1976)]

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On page 11, line 4 of the article should read “viscosity and thermal conductivity^[1,2]” instead of “viscosity, thermal conductivity, and the speed of sound. [1,2]”