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# Specific-heat relaxation in glycerol

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The frequency dependence of the specific heat observed by Birge and Nagel in supercooled glycerol is found to obey fractional power laws in the high- and low-frequency limits. The relaxation of the specific heat has been interpreted in terms of the Dissado-Hill many-body theory. The evaluated values of the exponents suggest a relatively high degree of local correlations ($n=0.43$) and a low degree of long-range correlations ($m=0.73$) of the motions responsible for the relaxation observed. Agreement of the $n$ and $m$ parameters with those calculated from dielectric and acoustic relaxation data is found. The possibility of introducing fractal concepts into the description of relaxation phenomena in glycerol is pointed out.

Specific-heat spectroscopy is a technique recently invented by Birge and Nagel[1,2] and, independently, by Christiansen.[3] The frequency dependence of the real and imaginary parts of the specific heat $c_p^*(\nu)=c_p'(\nu)-ic_p''(\nu)$ was detected for glycerol in the temperature region near the glass transition. The $c_p(\nu)$ spectrum of glycerol was obtained by applying to the sample a heat flux in the form of small-amplitude sinusoids with frequencies ranging from 0.2 Hz to 6 kHz and by measuring the temperature response as a function of frequency. The details of the experiment are presented in Ref. 2.

In this paper an interpretation of the above data of the specific-heat relaxation in glycerol[2] is given in terms of the many-body approach.[4] Introduction of two correlation parameters describing the dynamical properties of glycerol in many-body terms allows for comparison of the parameters evaluated from $c_p''(\nu)$ data in the literature with those obtained with the help of other techniques, i.e., the dielectric[5] and the acoustic[6] relaxations. The dielectric relaxation has been studied by Shablakh, Hill, and Dissado[5] on a Salatron frequency response analyzer in the frequency range from $10^{-4}$ to $10^4$ Hz. Studies of the acoustic speed and damping relaxation have been performed by Yong-Xin Yan, Lapp-Tak Cheng, and Nelson[6] at frequencies from 20 MHz to 3 GHz using time-domain light scattering at angles from 1° to 90°.

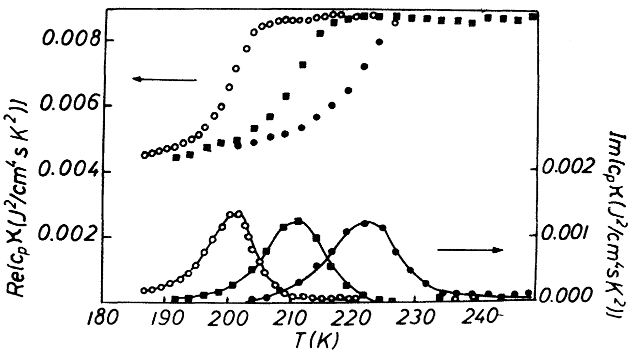

FIG. 1. Temperature dependence of the real and imaginary parts of $c_p^*\kappa$ for three frequencies $\nu$: (○) 0.62 Hz, (■) 34 Hz, (●) 1100 Hz, after Birge and Nagel (Ref. 2).

In Fig. 1 the real and imaginary parts of $c_p^*\kappa$ as a function of temperature are presented after Birge and Nagel[2] for three frequencies. $\kappa$ is the thermal conductivity, whose frequency dependence was not found in Ref. 2.

For an interpretation of the relaxation observed, the $c_p^*(\nu,T)\kappa$ data shown in Fig. 1 are presented in a compact form using a double-logarithmic scale. At first, for each temperature marked in Fig. 2, both $\log_{10}c_p''\kappa$ versus $\log_{10}\nu$ and $\log_{10}c_p'\kappa$ versus $\log_{10}\nu$ response curves were constructed. Then, they were shifted along the two coordinates to have the pair of single master curves coincide with the pair of curves observed for the scaling temperature chosen in Fig. 2 as 206.5 K.[7] Owing to the superimposing of the experimental points from subsequent runs

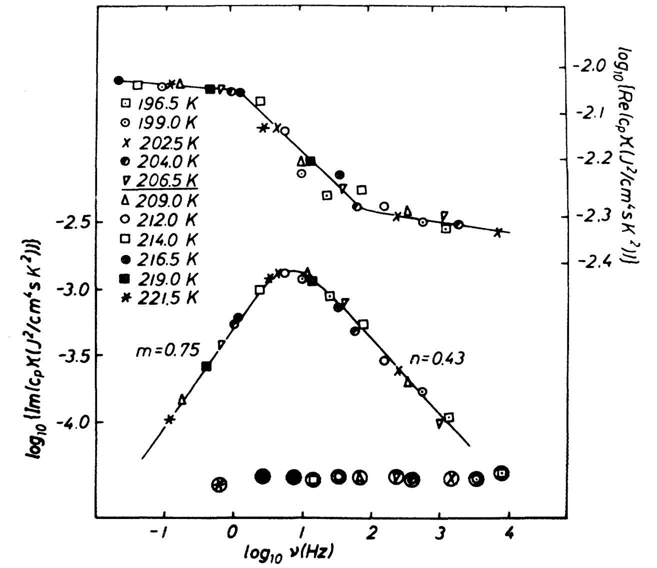

FIG. 2. Master curves $\log_{10}c_p'\kappa(\log_{10}\nu)$ and $\log_{10}c_p''\kappa(\log_{10}\nu)$ normalized at 206.5 K. The encircled points are the trace of the reference point (⊗).

TABLE I. Dissado-Hill correlation parameters for glycerol.

| Type of relaxation | Temperature range (K) | Relaxation rates $\omega_{\max}$ (kHz) | Correlation parameters | |
|---|---|---|---|---|
| | | | $n$ | $1-m$ |
| Specific heat | 180–213 | 1.1 (223 K) | 0.43 | 0.27 |
| Dielectric | 186.5–221.5 | 1 (213 K) | 0.41 | 0.09 |
| Acoustic | 241–355 | 1000 (241 K) | 0.42 | 0.15 |

of different temperatures, the effective frequency range of the relaxation is broadened and the experimental errors are reduced. The scaling procedure was performed for the whole frequency range from 0.1 Hz to 10 kHz. The encircled points at the bottom of Fig. 2 are a trace of the reference point (the upside-down triangle in the circle) and help visualize how the scaling procedure was performed. The master $c_p''(\nu,T)\kappa$ curve exhibits linear wings for both limits of frequency. The slopes of the wings define two extra parameters $n$ and $m$, giving information about the $c_p''(\nu)\kappa$ [and $c_p'(\nu)\kappa$] shape. The possibility of performing the scaling procedure results from the fact that the $n$ and $m$ values are constant in the whole temperature range investigated.

The relaxation of the specific heat in glycerol[2] seems to possess the features of the "universal response" observed by Jonscher[8] in various not perfectly ordered materials for the electric susceptibility $\chi^*(\nu)$ relaxation:

$$\chi''(\nu)\sim[\chi'(\nu)-\chi'(\infty)]\sim(\nu/\nu_{\max})^{n-1} \quad \text{for } \nu>\nu_{\max}\ ,$$

$$\chi''(\nu)\sim[\chi'(0)-\chi'(\nu)]\sim(\nu/\nu_{\max})^{m} \quad \text{for } \nu<\nu_{\max}\ .$$

The $m$ and $n$ exponents, called the Dissado-Hill correlation parameters, have values in the range (0,1). In terms of the Dissado-Hill theory,[4,9] the single-particle Debye relaxation is characterized by $n=0$, and $1-m=0$. The case with the greater $n$ and $1-m$ values corresponds to the growing influence of the short- and long-range correlations of motions, respectively, on the process observed. The parameters $n$ and $1-m$ are a measure of the structural order in the sample on the local and long-range levels, respectively.

The values of the $n$ and $1-m$ correlation parameters estimated from the slopes of the master $c_p''(\nu)\kappa$ curve presented in Fig. 2 are collected in Table I. The analogous values estimated from the acoustic data available in the literature[6] and those characterizing the frequency dependence of the electrical complex capacity in Ref. 5 are also given.

The characteristic feature of the relaxation observed by the three techniques is a wide range of the time scale involved.[5,6,10] Nevertheless, there seems to be a single relaxation mechanism, the same in liquid and in superliquid glycerol.[10] The dielectric data for various alcohols[11] allows us to consider the relaxation observed as connected with the overall rotation of glycerol molecules mainly. The small $1-m$ values show that the long-range correlations of motion of glycerol molecules are relatively weak. The highest $1-m$ value is the one estimated from the $c_p''(\nu)\kappa$ data. This seems reasonable, as the unique advantage of the $c_p$ relaxation is that it gives information about the dynamics of all degrees of freedom, not only about those coupled to the electrical field or mechanical stress.[1,2] The $n\sim 0.4$ recorded by all the experimental methods shows that the orientational cooperativity of glycerol molecules on the local scale is rather strong.

The molecular-dynamics study of glycerol[12] shows that both the stable liquid (303 K) and the supercooled liquid (203 K) reveal a variety of asymmetrical molecular conformations and an irregular network of the intermolecular and intramolecular hydrogen bonds. Similarly, the intermolecular distribution function, calculated for $D$ glycerol at 293 K from neutron-diffraction measurements,[13] shows strong local correlations due to hydrogen bonding lost at distances larger than 10 Å and long-range correlations due to molecular packing.

The existence of the O—H bonds results in some forms of ordering in the molecular system which have to influence the relaxation process. The patterns of hydrogen-bonded molecules evolve as the system tends to equilibrium but, on the whole, they keep their ramified shapes. This feature, i.e., a certain time invariance of the geometry of growing and reducing molecular ensembles, seems to be typical of fractallike structures.[14] For the glass-forming materials, the system could be self-similar in connectivity although being homogeneous from the point of view of density.[15] The $n$ and $m$ correlation parameters can thus be regarded as the fractallike scaling exponents[16] quantitatively describing the relation between dynamical and structural properties of the system under study.

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that of Cole-Cole $\tilde{c}_p''/\tilde{c}_p'$ type, where

$$\tilde{c}_p^*(\omega,T)=[c_p^*(\omega,T)-c_p'(\infty,T)]/[c_p'(0,T)-c_p'(\infty,T)] .$$

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