

The role of the isothermal bulk modulus in the molecular dynamics of super-cooled liquids

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Elastic models imply that the energy expended for a flow event in ultra-viscous matter coincides with the elastic work required for deforming and re-arranging the environment of the moving entity. This is quite promising for explaining the strong non-Arrhenius behavior of dynamic quantities of fragile super-cooled liquids. We argue that the activation volume obtained from dielectric relaxation and light-scattering experiments for super-cooled liquids should scale with the Gibbs free energy of activation, with a proportionality constant determined by the isothermal bulk modulus and its pressure derivative, as described by an earlier thermodynamic elastic model. For certain super-cooled liquids the bulk compression transpiring in the local environment, as governed by the isothermal bulk modulus, play a significant role in the reorientational dynamics, with far-field density fluctuations and volume changes avoided by shear deformation. © 2011 American Institute of Physics. [doi:10.1063/1.3666008]

I. INTRODUCTION

Super-cooled liquids represent an exceptional state of matter, exhibiting physical properties such as the strong temperature dependence of the activation enthalpy, extraordinarily large viscosities, and scaling of the dynamic quantities with density and temperature.^{1–6} The strong non-Arrhenius dependence of the structural relaxation time, the viscosity, and the diffusivity observed on approach to the glass transition by cooling has been interpreted by identifying the activation enthalpy with the elastic energy required for a flow event to occur. Ultra-viscous liquids, close to the glass transition, share characteristics of both solid (e.g., jumps to neighboring sites only rarely) and liquid (e.g., inability to resist persistent shear forces) states.³ Thus, both solid and liquid-state approaches are employed to address the properties of the super-cooled state (“solid that flows”).³ Dyre and co-workers developed the idea that the shear modulus controls flow events, by performing calculations based on the theory of elasticity^{3,7,8} in combination with extensive experimental work.^{9–11} They showed that various dynamic quantities and the (high-frequency) shear modulus share common temperature dependences and may mutually correlate.

While shear modes are obviously important in normal liquids, the situation is more complex in “solids that flow”. Recent work indicates that the fragility of super-cooled liquids is related to the bulk modulus¹² and the isochoric fragility,¹³ may be correlated to Poisson’s ratio,¹⁴ and is linked with both the bulk and shear modulus of the glassy state.¹⁵ It seems that the complex state of ultra-viscous materials obscures inherent solid-like features. The utility of elastic

models in addressing the physics of strongly non-Arrhenius behaviour inspired¹⁶ the derivation of density scaling functions of the diffusivity based on an earlier thermodynamic elastic point defect model;¹⁷ subsequently, correlation of the density scaling exponent with the pressure derivative of the isothermal, static bulk modulus was demonstrated.^{17–19}

II. THEORETICAL BACKGROUND, RESULTS AND DISCUSSION

The relative contribution of the bulk or shear modulus in the activation, formation, and migration of defects in solids has been debated over the past decades. Different approaches appeared in the literature, including that of Wert and Zener²⁰ (shear modulus), Flynn²¹ (combination of proper elastic compliance), Granato²² (shear modulus), and Varotsos and Alexopoulos²³ (bulk modulus). The latter, $cB\Omega$ model,^{23–26} was successful for various types of processes in many different classes of solids, ranging from silver halides,²⁷ super-ionic conductors,²⁸ and diamond,²⁹ to rare gas solids³⁰ (whose inter-atomic Lennard-Jones potential resembles that of ultra-viscous liquids, with a steep repulsive term), ionic crystals under gradually increasing uniaxial stress³¹ (in which electric signals are emitted before fracture, similar to signals detected prior to earthquakes^{32–35}), and disordered polycrystalline materials.³⁶ The experimental validation of the $cB\Omega$ model supports the idea that, even if a flow event induces far-field shear, compression can happen locally.⁸ The notion of local density fluctuations suggests an investigation of the role of bulk compression in structural relaxation in super-cooled liquids. Since dielectric relaxation and light scattering experiments probe short-range motion of the atoms (molecules), they should be sensitive to local bulk compression accompanying a relaxation or flow event.

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Elastic models usually imply proportionality between some dynamic quantity (such as the activation enthalpy or the Gibbs free energy for activation) and an elastic quantity. For example, the Zener model assumes that the Gibbs free energy for diffusion is proportional to the shear modulus,²⁰ the showing model^{6,10} assumes that the activation enthalpy for a flow event is proportional to the (high-frequency) shear modulus, and in the $cB\Omega$ model the Gibbs free energy for defect formation, migration, or activation is proportional to the product of the isothermal bulk modulus and the mean atomic volume.²³ In all these cases, the proportionality constant is in principle unknown, preventing direct validation of these models from a single experiment. For example, an equivalent common temperature variation of the dynamic variable and an elastic quantity does not guarantee a linear relation between dynamic and elastic quantities.

The $cB\Omega$ model^{21,22,24} asserts that the Gibbs free energy for activation is

$$g^{\text{act}} = cB\Omega, \quad (1)$$

where B and Ω are the isothermal bulk modulus and the mean atomic volume, respectively, while c is essentially a constant. (The atomic volume is roughly the volume divided by the number of atoms, provided the material consists of a single type of atom, otherwise, Ω is a mean atomic volume.) Differentiating Eq. (1) with respect to pressure we get

$$v^{\text{act}} = B^{-1}[(\partial B/\partial P)_T - 1]g^{\text{act}}, \quad (2)$$

where $v^{\text{act}} \equiv (\partial g^{\text{act}}/\partial P)_T$ denotes the activation volume. According to the rate theory, the dielectric structural relaxation time (α relaxation time) is related to microscopic quantities as

$$\tau(P, T) = (\lambda\nu)^{-1} \exp(g^{\text{act}}/k_B T), \quad (3)$$

where ν is the attempt frequency and λ a geometrical constant. Partial differentiation of Eq. (3) yields

$$(\partial \ln \tau / \partial P)_T = -\frac{\gamma}{B} + \frac{v^{\text{act}}}{k_B T}, \quad (4)$$

where $\gamma \equiv -(\partial \ln \nu / \partial \ln V)_T$ is the Grüneisen parameter (V denotes the volume) and

$$(\partial \ln \tau / \partial (1/k_B T))_P = h^{\text{act}}. \quad (5)$$

The Gibbs free energy is given by $g^{\text{act}} \equiv h^{\text{act}} - Ts^{\text{act}}$, where h^{act} and s^{act} are the respective activation enthalpy and entropy. In a non-Arrhenius isobar the logarithm of the relaxation time plotted versus inverse temperature is non-linear;¹⁶ thus, the slope is temperature dependent and, according to Eq. (5), h^{act} is also temperature dependent being related to the local slope in a $\ln \tau$ vs. $1/(k_B T)$ plot, at a given temperature. By plotting the tangent to the Arrhenius curve, the slope (“local” as it refers to a selected temperature) and its intercept $\tau_0 \equiv \tau(T \rightarrow \infty)$ are obtained. The latter value (which is temperature-dependent) provides an estimate of the activation entropy $s^{\text{act}} = -k_B \ln(\nu \tau_0)$ (for $\lambda = 1$) and g^{act} at a given temperature. In the present work, a typical value of 10^{12} Hz was taken for ν (the exact value of the attempt frequency is unknown and thus ν must be identified with an arbitrary phonon frequency). Alternative approaches for describing the pressure

dependence of the dielectric relaxation time can be found in Refs. 37 and 38. We note that the activation volume obtained from Eq. (4) is defined through the thermodynamic equation $v^{\text{act}} = (\partial g^{\text{act}}/\partial P)$. When γ/B is small, Eq. (4) resembles the Williams formula³⁹ $\Delta v/k_B T = (\partial \ln \tau / \partial P)_T$, where Δv is the activation volume defined as the molar volume difference between an activated state and a ground state.

To examine whether g^{act} is controlled by the isothermal bulk modulus (according to Eq. (1)), it is adequate to check whether Eq. (2) is validated by the experimental data. The modification of the original Eq. (1) to the equivalent Eq. (2) has two advantages: (i) the unknown factor c , assuming to be constant, is eliminated, and, (ii) combined isobaric and isothermal experiments (providing values for g^{act} and v^{act} , respectively) can be used. In Table I relaxation and elastic data for phenylphthalein-dimethylether (PDE), cresolphthalein-dimethylether (KDE), ortho-terphenyl (OTP), glycerol, salol, chlorinated biphenyl (PCB62), 1,1-di(4'-methoxy-5'-methylphenyl)-cyclohexane (PMMPC), and propylene carbonate (PC) are collected. Using the isothermal (relaxation) results for the lowest available pressure, the ambient pressure activation volume v_0^{act} was calculated from the slope of $\ln \tau$ vs P isotherms in together with γ/B_0 (B_0 denotes the isothermal bulk modulus at ambient pressure) Eq. (4). We note that, in viscous liquids, the contribution of the term γ/B_0 is usually negligible compared with the change of the relaxation time with pressure. For example: For PC in the ambient pressure limit $(\partial \ln \tau / \partial P)_T = 8.7 \text{ GPa}^{-1}$. Taking $\gamma = 1.4$ (Ref. 40) and $B_0 = 2770 \text{ MPa}$ (Table I), $\gamma/B_0 = 0.5 \text{ GPa}^{-1}$, which is 6% of the corresponding slope. For PDE in the ambient pressure limit $(\partial \ln \tau / \partial P)_T = 47.4 \text{ GPa}^{-1}$, while $\gamma/B_0 = 0.4 \text{ GPa}^{-1}$ ($\gamma = 0.87$ (Ref. 41) and $B_0 = 2110 \text{ MPa}$ (see Table I)), which is 0.8% $(\partial \ln \tau / \partial P)_T$. For OTP, $\gamma/B_0 = 0.5 \text{ GPa}^{-1}$ ($\gamma = 1.2$ (Refs. 41 and 42) and $B_0 = 2168 \text{ MPa}$ (Table I)), which is 0.4% of $(\partial \ln \tau / \partial P)_T = 139.1 \text{ GPa}^{-1}$. In these example calculations the thermodynamic Grüneisen parameter was used, which corresponds to a mean value of the phonon frequencies. Although using the Grüneisen parameter for the specific vibrational mode responsible for the activation process would be more accurate, it is in principle unknown. This uncertainty about the proper γ value does not affect these estimates, since liquids usually exhibit large values of the bulk modulus.

The corresponding activation enthalpy h_0^{act} , entropy s_0^{act} , and Gibbs free energy g_0^{act} were obtained from tangents (at a given temperature) to the ambient pressure isobars. In Figure 1 the quantity $B_0^{-1}[(\partial B/\partial P)_T - 1]g_0^{\text{act}}$ is plotted against v_0^{act} , together with the prediction of the $cB\Omega$ model (Eq. (2)). Data for glycerol, PC, salol, and PDE are very close to the theoretical prediction. Data points for PCB62, OTP, and BMMPC scatter around the predicted line (the maximum deviation does not exceed $\sim 30\%$). Finally, the result for KDE clearly deviates from the prediction. Thus, the $cB\Omega$ model seems to be validated for small activation volumes; however, for large activation volumes, the correspondence between experiment and model is modest. The deviations in materials with large activation volumes likely reflect the fact that when a large volume is swept out during the relaxation process, bulk compression of the surroundings has to be supplemented with additional mechanisms. It is the contribution of the latter

TABLE I. Relaxation data are from dielectric measurements, unless indicated otherwise. All relaxation and isothermal bulk modulus data are the low-pressure limiting values. The values in the table were obtained from published data or graphs in the cited papers: From the numerical values as reported: (I); from $\ln\tau$ (P) plots in the ambient pressure limit (see text): (II); from the tangent of Arrhenius plots (see text): (III); by analytical (fitting) functions given in the original papers: (IV); from isothermal compressibility (or bulk modulus) isotherms vs pressure: (V).

Viscous liquid	T (K)	v_0^{act} (cm ³ /mole)	h_0^{act} (eV)	s_0^{act} ($\times 10^{-4}$ eV/K)	g_0^{act} (eV)	B_0 (MPa)	$(\frac{\partial B}{\partial P})_T$	$\frac{1}{B_0} [(\frac{\partial B}{\partial P})_T - 1] g_0^{\text{act}}$ (cm ³ /mole)
Salol	316	66.2 ^{a,II}	0.39 ^{a,III}	5.95 ^{a,III}	0.21 ^{a,III}	2054.7 ^{b,IV}	8.9 ^{b,IV}	77.7
PC	273	19.8 ^{a,II}	0.16 ^{c,II}	1.18 ^{c,II}	0.13 ^{c,II}	2770 ^{d,V}	7.0 ^{d,V}	27.2
KDE	363	230 ^{e,II}	2.18 ^{e,III}	9.1 ^{e,III}	1.87 ^{e,III}	2479 ^{f,g,IV}	9.69 ^{f,g,IV}	630
Glycerol	243	19.3 ^{h,II}	0.92 ^{i,III}	27.9 ^{i,III}	0.25 ^{i,III}	6270 ^{j,I}	6.11 ^{j,I}	19.5
OTP	268	310 ^{k,I}	6.0 ^{l,IV}	160 ^{l,IV}	1.11 ^{l,IV}	2168 ^{m,I}	9.97 ^{m,I}	442.8
PDE	363	140.2 ^{n,III}	1.25 ^{g,III}	24.9 ^{g,III}	0.35 ^{g,III}	2110 ^{m,I}	9.76 ^{m,I}	140
BMMPC	285	325 ^{o,II}	2.7 ^{o,III}	69.4 ^{o,III}	0.72 ^{o,III}	2478 ^{g,IV}	9.9 ^{g,IV}	249.1
PCB62	334.5	178 ^{p,II}	1.31 ^{p,III}	30.4 ^p	0.295 ^p	2299 ^{q,IV}	10.1 ^{q,IV}	112.6

^aReference 43.

^bReference 44.

^cReference 45.

^dReference 46.

^eReference 47.

^fReference 48.

^gReference 49.

^hReference 50.

ⁱReference 51.

^jValues estimated from a second-order polynomial extrapolation based on the experimental isothermal compressibility data within the temperature range from 273 K to 398 K.

Reference 52.

^kReference 53.

^lReference 54.

^mReference 55.

ⁿReference 56.

^oReference 57.

^pReference 58.

^qReference 59.

that underlies the deviations in Figure 1. Thus, the results in Figure 1 divide into two classes: (a) liquids with relatively small activation volume for relaxation, with behavior in accordance with the $cB\Omega$ model, and (b) liquids with large activation volumes, for which other processes are involved in the (more complex) relaxation process.

Comparison of the temperature dependence of the activation volume with that predicted through Eq. (2) is of in-

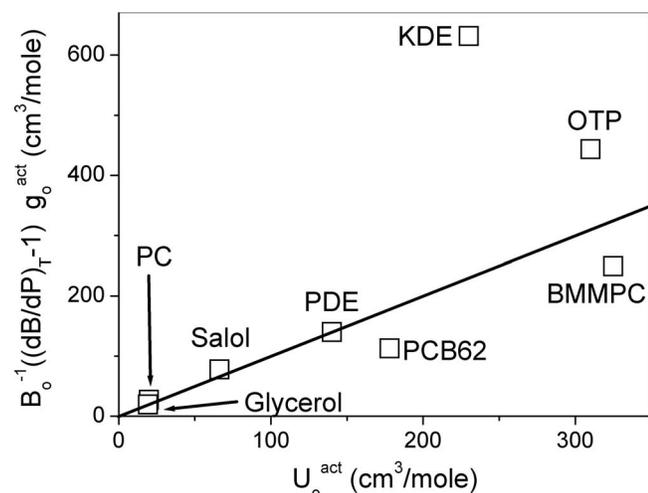


FIG. 1. The quantity $B_0^{-1} [(\partial B/\partial P)_T - 1] g_0^{\text{act}}$ vs U_0^{act} for various viscous liquids. The line is the prediction of the $cB\Omega$ model (Eq. (2)), which implies that relaxation is controlled by the isothermal bulk modulus.

terest, provided precise data were available for a sufficient number of materials and a broad range of temperature. We illustrate with results for OTP: For a different temperature ($T = 275$ K) than that appearing at Table I, using the data found in the reference cited therein, the experimental activation volume is 293 cm³/mole, while the predicted value (i.e., $B_0^{-1} [(\partial B/\partial P)_T - 1] g_0^{\text{act}}$) is 422.9 cm³/mole. A comparison with the corresponding values enlisted in Table I at $T = 275$ K, implies that the experimental activation volume decreases with temperature by about 5%, while that predicted by the $cB\Omega$ model is roughly by 4.5%. This is a very satisfactory agreement although analysis of other materials is necessary. The required isochronal data for the activation volume are not available and their estimation entails large errors. Thus, the temperature evolution of the activation volume and activation enthalpy as predicted by the $cB\Omega$ model remains for future investigation.

III. CONCLUSIONS

Relaxation results and elastic data for various supercooled liquids were used to assess the validity of Eq. (2); i.e., whether the isothermal bulk modulus is a control parameter for relaxation. In the ambient pressure limit and within the assumptions made to estimate the activation entropy and Gibbs free energy, bulk compression is shown to play a significant role in the relaxation of materials exhibiting small activation volumes. However, for materials whose relaxation dynamics involves disruption of substantial volume locally, additional

mechanisms evidently contribute and further investigation is required. It is an open question whether the bulk compression transmitting in the immediate environment of the relaxing species evolves (as speculated and discussed by Dyre⁸) to shear displacements in the far field. Such a process would produce local density fluctuations (bulk dominance) in the vicinity of the relaxing entity, but shear dominance (without density changes) far from it. An interpretation of our present finding, that the bulk modulus governs relaxation in viscous liquids with small activation volumes, is that relaxation experiments trace short-scale phenomena, sensing the neighboring (local) landscape, and consequently the relaxation can be directly related to the bulk modulus. This conclusion is based on representative super-cooled liquids, mainly van der Waals ones, and further tests on more diverse materials are desirable.

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