How to Compare the Frequency Dependent Adiabatic Compressibility with Other Thermoviscoelastic Response Functions at the Glass Transition

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The relation between thermal and mechanical relaxation is considered in general and in a model. In the model the thermal relaxation has a mechanical origin and the relaxation spectra of the adiabatic compressibility and the reciprocal isobaric specific heat are identical. The solutions to 1-dimensional thermoviscoelastic problems indicate that actual specific heat measurements at the glass transition are not isobaric. This renders a comparison problematic.

§1. Introduction

One of the main problems of the glass transition is to explain the linear thermal and mechanical response in terms of microscopic properties. There has been a tremendous development in microscopic probing techniques whereas proper methods for measuring some of the macroscopic properties are still missing. The scalar parts of the thermomechanical relaxation are completely described by three independent complex functions,[1] which can be chosen as the isobaric specific heat $c_p(\omega)$(per volume), the thermal expansion coefficient $\alpha_p(\omega)$ and the adiabatic compressibility $\kappa_s(\omega)$. The response functions are complex and frequency dependent describing linear relaxation. Classical thermodynamic relations hold for these complex functions. Thus the isothermal compressibility becomes

$$\kappa_T(\omega) = \kappa_s(\omega) + T_0 \frac{\alpha_p^2(\omega)}{c_p(\omega)} , \tag{1}$$

which goes into the thermoviscoelastic compliance matrix

$$\begin{pmatrix} ds \\ d\epsilon \end{pmatrix} = \begin{pmatrix} \frac{1}{T_0}c_p(\omega) & \alpha_p(\omega) \\ \alpha_p(\omega) & \kappa_T(\omega) \end{pmatrix} \begin{pmatrix} dT \\ -dp \end{pmatrix} = J \begin{pmatrix} dT \\ -dp \end{pmatrix} . \tag{2}$$

Here ds, $d\epsilon$, dT, dp are the amplitudes of harmonically varying small perturbations $\propto e^{-i\omega t}$ of entropy density, relative volume change, temperature and pressure. The symmetry of the matrix is an expression of the Onsager relations. A characterization by a complete set of such 3 independent thermoviscoelastic response functions has not been given for any supercooled liquid yet.

Measurements on $\alpha_p(\omega)$ are scarcely existing! Techniques for $c_p(\omega)$ have been developed.[2],[3] However it can be questioned as we shall see whether these measurements are really isobaric! This is due to the fact that near the glass transition non-hydrostatic stresses emerges as the shear modulus increases. Recently a method

for obtaining $\kappa_s(\omega)$ was developed.[1] The liquid is put into a piezoceramic spherical shell, that acts as a transducer converting the mechanical impedance into an electrical impedance. Results have been published on glycerol,[1] 1,2,6-hexantriol[4] and 2,5-hexandiol.[5] Here the possibility of a proper comparison of $\kappa_s(\omega)$ with other thermoviscoelastic response functions will be discussed.

§2. A model of pure mechanical relaxation

Let us consider a model in which the relaxation process is of mechanical nature only. In such a model the isochoric specific heat c_V is frequency independent. Such a model has earlier been proposed[6] and it does not come from first principles.[8] An input of thermal energy dq per volume to the phonon bath increases the temperature by $dT = dq/c_{\text{phonon}}$. If volume is kept constant no relaxation takes place and $c_V = c_{\text{phonon}}$. The increase of temperature gives an increase of pressure, $dp = \left(\frac{\partial p}{\partial T}\right)_V dT$ due to the anharmonicity of the potential. However if pressure is kept constant $\left(\frac{\partial p}{\partial T}\right)_V dT$ must be thought of as an internal pressure dp_i that slowly relaxes mechanically while temperature decreases accordingly. Denote the frequency independent coefficient $\left(\frac{\partial p}{\partial T}\right)_V$ by β. We can then write

$$
\begin{pmatrix} ds \\ -dp_i \end{pmatrix} = \begin{pmatrix} \frac{1}{T_0}c_v & \beta \\ -\beta & 0 \end{pmatrix} \begin{pmatrix} dT \\ d\epsilon \end{pmatrix} , \tag{3}
$$

where the antisymmetry of the matrix follows from energy considerations. In the model all frequency dependence is ascribed to the relaxation of the internal pressure p_i to the pressure,

$$
dp - dp_i = -K(\omega)d\epsilon \tag{4}
$$

and thereby

$$
\begin{pmatrix} ds \\ -dp \end{pmatrix} = \begin{pmatrix} \frac{1}{T_0}c_v & \beta \\ -\beta & K_T(\omega) \end{pmatrix} \begin{pmatrix} dT \\ d\epsilon \end{pmatrix} , \tag{5}
$$

since $K(\omega)$ must be the isothermal bulk modulus $K_T(\omega) = 1/\kappa_T(\omega)$. From (5) one can find all implications of the model. Thus

$$
c_p(\omega) = c_V + \beta^2 \frac{1}{K_T(\omega)} , \tag{6}
$$

telling that the normalized isobaric specific heat and isothermal compressibility are identical. This is not very useful since $K_T(\omega)$ is difficult to obtain experimentally. More interesting is the isobaric thermal modulus $\Gamma_p(\omega) = \frac{1}{c_p(\omega)}$. Defining the normalized functions $\Gamma_n(\omega) = (\Gamma_p(\omega) - \Gamma_p(0))/(\Gamma_p(\infty) - \Gamma_p(0))$ and $\kappa_n(\omega) = (\kappa_s(\omega) - \kappa_s(\infty))/(\kappa_s(0) - \kappa_s(\infty))$ one finds $\Gamma_n = 1 - \kappa_n$. If both functions are believed to have been found experimentally the model can be validated. However one can certainly question whether the specific heat derived from actual experiments really is measured at isobaric conditions. The last part of the article is devoted to this problem.

§3. The influence of the mechanical boundary conditions on the measured specific heat

Since mechanical and thermal relaxation are inseparable let us examine methods of measuring $c_p(\omega)$. In this section we introduce the shear modulus G and heat conductivity λ. All of the constitutive parameters could be frequency dependent but we suppress this in the notation.

In experimental AC-calorimetry the direct obtainable quantity is the thermal admittance $Y = j_\omega/T_\omega$ which is the ratio of the amplitude j_ω of the total thermal heat current to the complex temperature amplitude T_ω. The thermal admittance can be related to the specific heat. One can recognize two different experimental situations in AC-calorimetry depending on the (complex) thermal diffusion length $l_D(\omega) = \sqrt{D/(-i\omega)}$ where $D = \lambda/c_p$.

For the homogeneous method[3] all parts of the sample are at the same temperature (quasistatic limit), $|l_D(\omega)| \gg l_{\text{sample}}$. The thermal admittance becomes $Y = \Lambda - i\omega(C_{\text{calorimeter}} + C_{\text{liquid}}(\omega))$, where Λ is the thermal leak between calorimeter and cryostat.

For the inhomogeneous method[2] (thermal wave limit), $|l_D(\omega)| \ll l_{\text{sample}}$, thermal diffusive waves are sent into the liquid by a thin plane heater on a plate. The thermal admittance per area seen at the heater becomes $Y = \sqrt{-i\omega c_{\text{liquid}}(\omega)\lambda_{\text{liquid}}} + \sqrt{-i\omega c_{\text{plate}}\lambda_{\text{plate}}}$.

We claim that both expressions for the thermal admittance describe the experimental situations inadequately. This is because the ordinary heat diffusion equation $-i\omega T_\omega = D\Delta T_\omega$ is inadequate. A thermoviscoelastic theory is necessary due to two conditions prevailing at the glass transition:

i) $\frac{c_p - c_V}{c_V} = T_0\frac{\alpha_p^2 K_T}{c_v}$ is significant in the liquid state and at the glass transition.

ii) $\frac{G}{K_T}$ is significant in the glassy state and at the glass transition.

We have thus to consider instead the coupled equations[7] of temperature T and displacement field $\boldsymbol{u}$ in the frequency domain:

$$\left(\frac{4}{3}G + K_T\right)\text{grad}(\text{div}(\boldsymbol{u})) - K_T\alpha_p\,\text{grad}(T_\omega) - G\,\text{curl}(\text{curl}(\boldsymbol{u})) = -\rho\omega^2\boldsymbol{u}\ , \quad (7)$$

$$-i\omega c_V T_\omega - i\omega T_0 K_T\alpha_p\,\text{div}(\boldsymbol{u}) = \lambda\,\text{div}(\text{grad}(T_\omega))\ . \quad (8)$$

What kind of specific heat is then measured? Is it isobaric, isochoric or is it another quantity? It is certainly complicated to apply these equations to the real experimental situations taking the boundary conditions in three dimensions into account. They are however tractable if inertia is neglected, i.e., $l_{\text{sample}} \ll \lambda_{\text{sound}}$ and if the displacement field is curl-free.

The simplest special example that can be given is the 1-dimensional case. It is illustrative although the boundary conditions are somewhat unrealistic.

Consider a rectangular box with end faces A and B. We want the thermal admittance on the clamped end face (A) with adiabatic and sliding boundary conditions on the side faces. The side faces experience no tangential stress but are vertically

clamped. Two cases of boundary conditions on the other end face (B) is considered:
i) adiabatic and free ii) adiabatic and clamped
One finds in the solution to these problems that the longitudinal heat capacity
$c_l = c_V(K_s + 4/3G)/(K_T + 4/3G)$ goes into the diffusion constant: $D = \sqrt{\lambda/c_l}$
and the thermal admittance per area becomes:

i) $$Y_{\text{free}} = \sqrt{-i\omega c_l \lambda} \tanh\left(\frac{l_{\text{sample}}}{l_D}\right)$$

$$\rightarrow -i\omega l_{\text{sample}} c_l \quad \text{for} \quad \left|\frac{l_{\text{sample}}}{l_D}\right| \rightarrow 0 \text{ (homogeneous limit)}$$

$$\rightarrow \sqrt{-i\omega c_l \lambda} \quad \text{for} \quad \left|\frac{l_{\text{sample}}}{l_D}\right| \rightarrow \infty \text{ (inhomogeneous limit)},$$

ii) $$Y_{\text{clamp}} = \sqrt{-i\omega c_l \lambda} \left[\coth\left(\frac{l_{\text{sample}}}{l_D}\right) + \frac{l_D}{l_{\text{sample}}}\frac{c_l}{c_V}\right]^{-1}$$

$$\rightarrow -i\omega l_{\text{sample}} c_V \quad \text{for} \quad \left|\frac{l_{\text{sample}}}{l_D}\right| \rightarrow 0 \text{ (homogeneous limit)}$$

$$\rightarrow \sqrt{-i\omega c_l \lambda} \quad \text{for} \quad \left|\frac{l_{\text{sample}}}{l_D}\right| \rightarrow \infty \text{ (inhomogeneous limit)}.$$

These results suggest that c_p at the glass transition has probably never been measured, only a quantity between c_V and c_p. If the above mentioned boundary conditions approximate those of the plate experiments then it is the longitudinal specific heat one gets. The frequency dependence of the other relaxing properties will affect the frequency dependence of this quantity. Furthermore the examples show that the mechanical boundary conditions are as important as the thermal ones in determining what is actually measured. The significance of the longitudinal specific heat in the thermoviscoelastic case was also recognized by Jäckle [8] although the consequences for the interpretation of actual measurements were not drawn.

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