The relation between the positional specific heat and the static relaxation length: application to supercooled liquids

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Abstract
A general identification of the *positional specific heat* as the thermodynamic
response function associated with the *static relaxation length* is proposed,
and a phenomenological description for the thermal dependence of the static
relaxation length in supercooled liquids is presented. Accordingly, through a
phenomenological determination of the positional specific heat of supercooled
liquids, we arrive at the thermal variation of the static relaxation length ξ, which
is found to vary in accordance with $\xi \sim (T - T_0)^{-\nu}$ in the quasi-equilibrium
supercooled temperature regime, where T_0 is the Vogel–Fulcher temperature
and exponent ν equals unity. This result to a certain degree agrees with that
obtained from mean field theory of the random-first-order transition, which
suggests a power law temperature variation for ξ with an apparent divergence
at T_0. However, the phenomenological exponent $\nu = 1$ is higher than the
corresponding mean field estimate (becoming exact in infinite dimensions),
and in perfect agreement with the relaxation length exponent as obtained from
numerical simulations of the same models of structural glass in three spatial
dimensions.

1. Introduction

The deepest and most interesting unsolved problem in the theory of solids is probably that of
the theory and the nature of glass and the glass transition [1]. One of the most striking features
of the typical supercooled liquid is that its relaxation time or viscosity η changes by several
decades on changing the temperature by a few tens of degrees. All available data for viscosity
fall between Arrhenius and highly non-Arrhenius extremes, designated as 'strong' and 'fragile',
respectively [2]. The latter is characterized by a highly temperature-dependent effective energy
barrier against the viscous flow; i.e., a temperature-dependent energy barrier E_{eff} appears in
$\eta = \eta_0 \exp(\beta E_{\text{eff}})$, where η_0 is a temperature-independent but species-dependent parameter
of the order of 10^{-2}–10^3 P, $\beta = 1/k_B T$, and k_B is the Boltzmann constant. The temperature

variation of the viscosity for fragile supercooled liquids is described accurately over a wide range of temperatures by the Vogel–Fulcher empirical equation [3]:

$$\eta = \eta_0 \exp\left(\frac{A}{T - T_0}\right). \tag{1}$$

The apparent divergence temperature T_0 appearing in equation (1) is called the Vogel–Fulcher temperature and is often found to be very close to the Kauzmann temperature T_K [4], where the configurational entropy of the liquid extrapolates to zero [5]. This well known experimental fact, $T_0 \approx T_K$, is indeed a matter of considerable interest as it seems to suggest that the ideal glass transition temperatures observed dynamically and thermodynamically must have a common physical origin [6]. It should also be pointed out that in addition to non-Arrhenius variation of the viscosity with the temperature in the supercooled temperature regime, fragile liquids are also characterized by a distinct jump in the second-order thermodynamic functions such as the specific heat C_p, the isothermal compressibility κ_T, and the thermal expansion coefficient α at the laboratory or calorimetric glass temperature T_g, where $T_g > T_0$.

Furthermore, fragile supercooled liquids are also distinguished by a highly non-exponential relaxation response as they approach equilibrium when perturbed. Often the Kohlrausch–Williams–Watts (KWW) [7] or stretched exponential function is used to characterize the relaxation response of fragile liquids $\phi(t) = \exp[-(t/\tau)^\beta]$, where β is the non-exponentiality parameter such that $0 < \beta < 1$, τ is a relaxation time, and both are found to be temperature dependent. The above relaxation response typical of fragile liquids is well explained in terms of the existence of dynamically heterogeneous regions in the supercooled liquid such that the relaxation in a given region is exponential but the average relaxation time τ varies with a broad distribution among regions [8]. This dynamical heterogeneity of the supercooled liquids has been further confirmed by recent numerical [9] and experimental research [10], which confirmed the presence of such regions with characteristic lengths spanning hundreds of molecules. The above numerical and experimental confirmations of the dynamical heterogeneity of the supercooled glass forming liquids lend further support to the notion of cooperatively rearranging regions (CRRs) in a supercooled liquid [11].

There are several indications that the viscosity, and the various other structural relaxation times of a supercooled liquid, must be correlated with the average size of a CRR, which is a concept dating back to the considerations of cooperative relaxation by the Adam and Gibbs [12]. In their approach the increase of the effective potential energy barrier $E_{\text{eff}} = z\Delta\mu$, with $\Delta\mu$ being largely the potential energy barrier against rearranging a single molecule in a cluster composed of z molecules, is due to an increase in the cluster size z as the temperature is lowered. This cooperativity concept requires a characteristic static length ξ characterizing the average linear size of a CRR. Evidently, an incremental increase in ξ of the order of a few nanometres is magnified in an exponentially large (macroscopic) relaxation time as a consequence of which the supercooled liquid falls out of equilibrium on experimental timescales, hence making any underlying static thermodynamic phase transition unreachable under laboratory conditions. From a theoretical point of view, the mean field theory of the random-first-order transition (or discontinuous spin glass) that exhibits qualitative features in tandem with the structural glass phenomenology suggests an approximate power law temperature dependence for the static relaxation length such that $\xi \sim (T - T_0)^{-\nu}$, where the apparent divergence temperature T_0 is the Vogel–Fulcher temperature, and the exponent $\nu = 2/d$ or $\nu = 2/3$ in $d = 3$ dimensions [13, 14]. There has been an empirical attempt to investigate the temperature variation of ξ, the results of which are more or less consistent with the above-proposed power law [15]. The results reported for the fragile liquid o-terphenyl are $\nu = 0.69 \pm 0.06$ with $T_0 = 203 \pm 6$ K. But the relevance to the static relaxation length of the experimental procedure

adopted by [15], and the various interpretations of the experimental data, have been called into question by the subsequent experimental investigations [16]. More recently, numerical simulations in three dimensions of the microscopic models that exhibit a random-first-order transition in the mean field, such as the p-spin glasses [17] and the frustrated Ising lattice gas model [18], have been found to favour a static relaxation length exponent $\nu = 1$.

In an attempt to clarify some of the discrepancies concerning the precise nature of the thermal dependence of the static relaxation length ξ of the fragile supercooled liquids, as alluded to in the above discussion, we adopt a phenomenological approach to obtain the temperature variation of ξ. The main ingredients in this semi-empirical approach are:

(i) The temperature-dependent potential energy barrier E_{eff} against the viscous flow that is embodied in the Vogel–Fulcher equation for the viscosity.
(ii) The thermodynamic response function bond susceptibility χ_b as applied here in the case of liquids, which is to be regarded as the response function measure of the tendency for bond ordering or correlated relaxation of bonds into their low-lying energy states, brought about by the rearrangement of a CRR.

Bond susceptibility was introduced earlier in the context of a diluted-bond model system relevant to the problem of the glass transition, the thermodynamic properties of which were investigated by means of Monte Carlo simulation [19]. Here, the very concept underlying bond susceptibility, i.e., correlated ordering or relaxation of bonds where intermolecular bonds are treated as distinct objects possessing internal degrees of freedom or energy states, is generalized and applied to the case of laboratory liquids. This approach paves the way for identification of the interaction or positional specific heat C_i as the thermodynamic response function associated with the characteristic length of relaxation ξ. Subsequently, a semi-empirical determination of the positional specific heat C_i for the general class of fragile liquids is used to arrive at the thermal variation of the static relaxation length ξ that, by definition, gives the average linear size of a CRR in the liquid.

The rest of this paper is organized as follows. In section 2 we describe the relevant conceptual and theoretical background concerning the various competing ordering processes in a liquid, and give a definition for the bond susceptibility χ_b as a response function measure of the tendency for correlated bond ordering. Section 3 contains the derivations of the various relationships among thermodynamic and correlation functions relevant to the present discussion. As will become evident in section 3.1, there exists a relationship of the form $\chi_b = TC_i$ relating the bond susceptibility of a liquid in the canonical ensemble with the interaction or positional part of the specific heat. Furthermore, in section 3.2 bond susceptibility is shown to be intimately related to the static relaxation length such that essentially $\chi_b \sim \beta \xi^2$. These results essentially indicate an association of the positional specific heat C_i as a thermodynamic response function with the characteristic length of relaxation ξ, which is a novel concept brought to light in section 3.3. This association of C_i and ξ is then applied in section 4 to develop a phenomenological description for the temperature variation of the static relaxation length in fragile supercooled liquids. Concluding remarks and a summary of the main results are presented in section 5.

2. Relevant background

2.1. Two-order-parameter description of liquids

Attempts have been made to incorporate frustration arising from the local ordering of bonds in a supercooled liquid through the introduction of a local order parameter characterizing the

energetically favoured local arrangements of the liquid molecules, which are not consistent with the crystallographic symmetry favoured by the density ordering or crystallization. In this two-order-parameter description of the liquids due to Tanaka [20, 21], the frustration arises from competition between density ordering and local bond ordering, explaining why some molecules crystallize easily without vitrification, while others easily form glasses without crystallization. The effect of density ordering is to maximize the density of molecules favouring a close-packed crystallographic symmetry, while local bond ordering tends to improve the quality of bonds by reducing the bond energies at the local level. This model therefore emphasizes that introduction of a bond order parameter, in addition to the density $\rho(r)$, is necessary in order to have a complete thermodynamic description of the liquid state, and, in particular, of the supercooled glass forming liquids. The energetically favoured local structures, such as the icosahedral arrangements favoured by the spherical molecules [22], are taken to be randomly distributed in a sea of normal liquid. It is further argued that the local structures with finite but long lifetimes act as impurities and produce the effects of fluctuating interactions and *symmetry-breaking random fields* against the density ordering in a liquid, in much the same way as magnetic impurities frustrate magnetic ordering in a spin glass system [23]. In this two-order-parameter description of the liquids the 'bond order parameter' $S(r)$ is taken to be defined by the local concentration of the energetically favoured structures, and the average concentration of local structures $\bar{S}$ is estimated to be given by $\bar{S} \sim g_S/g_\rho \exp[\beta(E_\rho - E_S)]$, where E_i and g_i are the energy level and the number of degenerate states of the i-type structure. ($i = \rho$ corresponds to the normal liquid while $i = S$ corresponds to the energetically favoured local structures.) Thus, the active bond concentration $S(r)$ is taken to have a frustrating influence on crystallization at the local level, and each molecule intrinsically has the cause of disorder and random fields against the density ordering.

2.2. Bond susceptibility

Bond susceptibility is defined as a response function measure of the tendency for bond ordering or correlated relaxation of bonds into their low-lying energy states, brought about by the rearrangement of a molecular group/CRR. Bond susceptibility, apart from normalization, is defined by

$$\chi_b = \left(\frac{\partial \langle M_b \rangle}{\partial H_b} \right)_{T, H_b=0} \tag{2}$$

where $\langle M_b \rangle$ denotes the thermally averaged bond energy order parameter characterizing the configurational energy of the system (more of which in section 3), and the average field H_b that is referred to as the bond ordering field is a *self-generated* molecular field favouring the local ordering of bonds and against the density ordering or crystallization [19]. The above physical quantities are introduced in order to be consistent with the above two-order-parameter description of the liquids that recognizes two competing ordering processes in a liquid, namely, global density ordering that results in crystallization, and local bond ordering that is responsible for the glass transition. Bond susceptibility is further expressed in terms of the equilibrium fluctuations of the bond energy order parameter

$$\chi_b = N\beta \langle \delta m_b^2 \rangle, \tag{3}$$

where $\langle m_b \rangle = \langle M_b \rangle / N$ is the normalized bond energy order parameter characterizing the configurational energy, $\delta m_b = (m_b - \langle m_b \rangle)$ is the corresponding fluctuation, N is the system size, and angular braces denote the usual thermal average. Equations (2) and (3) for bond susceptibility can be readily derived from the thermodynamic relation $dG = -S\,dT - \langle M_b \rangle\,dH_b$, which gives the change in free energy $G(T, H_b)$ of a system undergoing

bond ordering as opposed to density ordering or crystallization [19]. Evidently, the bond ordering field H_b is the thermodynamic conjugate field that couples to the bond energy order parameter $\langle M_b \rangle$ (which characterizes the configurational energy), and can be regarded as the average concentration of energetically favoured local structures $\bar{S}$.

3. Relations among thermodynamic and correlation functions

In this section the very concept underlying bond susceptibility, i.e., bond ordering or correlated relaxation of bonds, is generalized and applied to the case of laboratory liquids where we treat intermolecular bonds as distinct objects possessing internal degrees of freedom or energy states. The line of reasoning presented culminates in the identification of positional specific heat as the thermodynamic response function associated with the static relaxation length.

3.1. Bond susceptibility and positional specific heat

The bond energy order parameter $\langle m_b \rangle$ is defined as a measure of the bond order prevailing in a system, and characterizes the configurational energy [19]. By definition, it assumes large values when intermolecular bonds are in their low-lying energy states, as for a bond ordered low-temperature phase such as the glass, and is negligible when bonds are distributed uniformly among all possible energy states, which is indeed the case when the thermal energy is far in excess of the typical intermolecular binding energy. As a result, the bond energy order parameter of a liquid in the canonical (NVT) ensemble can be simply defined in terms of the configurational energy of the liquid. With $\Phi(r_1, r_2, \ldots, r_N)$ denoting the potential energy function of a liquid composed of N molecules, the bond energy order parameter for this system is defined by

$$\langle m_b \rangle = -\langle \Phi \rangle / N. \tag{4}$$

Equation (4) satisfies all that is required of a bond energy order parameter. On substituting this expression into the fluctuation-dissipation equation (3), for the liquid in question we have

$$\chi_b = \beta \langle \delta \Phi^2 \rangle / N \tag{5}$$

where $\delta \Phi = (\Phi - \langle \Phi \rangle)$. Another response function of interest and of immense relevance to the problem of the glass transition is the specific heat. For a liquid in a canonical ensemble it may be expressed as a sum of two terms: a kinetic part C_k; and an interaction or positional part C_i. The above distinction follows from the fact that the liquid Hamiltonian consists of two distinct parts: a kinetic energy part $\sum_{i=1}^{N} p_i^2 / 2m_i$ covering the degrees of freedom associated with the molecular momenta; and a potential energy part $\Phi(r_1, r_2, \ldots, r_N)$ containing the contributions to internal energy from interactions or positional degrees of freedom. The positional part of the specific heat is in fact the temperature rate of change of configurational energy:

$$C_i = \frac{1}{N} \frac{\partial \langle \Phi \rangle}{\partial T}. \tag{6}$$

It can be readily shown that an expression for the positional specific heat in terms of the equilibrium fluctuations of the configurational energy is given by

$$C_i / k_B = \beta^2 \langle \delta \Phi^2 \rangle / N. \tag{7}$$

On comparing equation (5) for the bond susceptibility of a liquid in the canonical ensemble with equation (7) for the positional part of the specific heat, we arrive at the following simple result:

$$\chi_b = T C_i. \tag{8}$$

It becomes evident from equation (8) that the bond susceptibility of a liquid in the canonical ensemble, characterizing the tendency for bond ordering or correlated relaxation of bonds, can be simply interpreted as the response function *positional specific heat*.

It is noteworthy that the result expressed by equation (8) is readily verifiable for certain lattice models such as the two-dimensional Ising model [24], and some impurity variants thereof [25], where analytic solutions are available. In particular, the four-spin correlation functions $w(r) = \langle \sigma_1 \sigma_2 \sigma_r \sigma_{r+1} \rangle - \langle \sigma_1 \sigma_2 \rangle \langle \sigma_r \sigma_{r+1} \rangle$ that can also be interpreted as *two-bond energy correlation functions*, with $\sigma_1 \sigma_2$ characterizing the energy of a reference bond while $\sigma_r \sigma_{r+1}$ characterizes that of a bond in a different location in the system, when summed over r or all distinct pairs of bonds, essentially produce the specific heat which is entirely interaction or positional for the aforesaid lattice models: $\sum_r w(r) = \partial \epsilon / \partial \beta - 1 + \epsilon^2$, where $\epsilon = \langle \sigma_1 \sigma_2 \rangle$ [25]. This apparent connection between bond susceptibility and two-bond energy correlation functions will be used extensively next to establish a quantitative relationship between the bond susceptibility and static relaxation length.

3.2. Bond susceptibility and the static relaxation length

In the context of the bond ordering picture, a CRR can be viewed as a correlated region of relaxing bonds. Thus, the correlation length of such a region of bonds can be regarded as the characteristic length of (cooperative) relaxation ξ. Following equation (3), the bond susceptibility of a liquid in the NVT ensemble is expressed as

$$\chi_b = \frac{\beta}{V} \left[\langle M_b^2 \rangle - \langle M_b \rangle^2 \right] \tag{9}$$

where V is the liquid volume and M_b is the extensive bond energy parameter whose thermal average is the bond energy order parameter characterizing the configurational energy. For short-range molecular interactions that is almost always the case; M_b can be expressed in terms of the volume integral of a microscopic bond energy density $m_b(r) = \sum_{i=1}^{N_b} m_{bi} \delta(r - r_i)$, where m_{bi} characterizes the energy of the ith bond and N_b denotes the total number of bonds in the system. Thus, for a d-dimensional system we can write

$$M_b = \int d^d r \, m_b(r) \tag{10}$$

where the integral is evaluated over the liquid volume and $m_b(r)$ characterizes the energy of an intermolecular bond situated at r. On substituting this expression into equation (9) and simplifying, we have

$$\chi_b = \beta \int d^d r \left[\langle m_b(r) \, m_b(0) \rangle - \langle m_b(r) \rangle \langle m_b(0) \rangle \right]. \tag{11}$$

Clearly, the quantity in the square brackets of equation (11) is the two-bond energy correlation function $G_b(r) \equiv \langle \delta m_b(r) \, \delta m_b(0) \rangle$, quantifying the spatial correlation of the fluctuations of the bond energy order parameter. For an isotropic system, $G_b(r) = G_b(r)$. Furthermore, if we take the spatial variation of $G_b(r)$ to be of the form [26, 27]

$$G_b(r) \sim \frac{g(r/\xi)}{r^{d-2}}, \tag{12}$$

where ξ is a characteristic length beyond which the correlation function rapidly vanishes, the bond susceptibility of a liquid and the characteristic length of relaxation are related by

$$\chi_b \sim \beta \int^\xi dr \frac{r^{d-1}}{r^{d-2}} = \beta \xi^2 / 2. \tag{13}$$

We must point out that in a previous work the functional form of equation (12) has been used for a similar spatial correlation function in the context of a defect theory of relaxation to successfully recover the generalized Vogel–Fulcher equation for the viscosity [26]. There the relaxation is considered to be brought about by the movements of mobile defects whose spatial correlation is governed by equation (12). In the context of the bond ordering picture, equation (12) is applied to the two-bond energy correlation function $G_b(r)$ as the structural relaxation is now considered to be a consequence of correlated relaxation of bonds within a region whose average linear size gives the static relaxation length ξ.

We note that, as a corollary of the result expressed by equation (13), a possible diverging bond susceptibility χ_b at some finite temperature T^* must necessarily imply a diverging static relaxation length ξ at the same temperature. That is, if the variation with temperature of the bond susceptibility for a system of interest is found to be a power law of the form $\chi_b \sim (T - T^*)^{-\gamma_b}$, then the temperature variation of the relaxation length must also be governed by a similar power law, $\xi \sim (T - T^*)^{-\nu}$, such that the exponents are related by the scaling relation

$$\gamma_b = 2\nu. \tag{14}$$

We must emphasize that the above result is consistent with a standard result of statistical mechanics, namely, $\alpha = (2 - \eta')\nu$, where α is the specific heat exponent and η' is the power law decay exponent of the energy–energy correlation function [27]. In our treatment leading to equation (14), however, we have taken $\eta' = 0$ for a supercooled liquid system, which is corroborated by the numerical simulations of various models of structural glass in three dimensions [17, 18]. One can further identify γ_b with α, as expected. In an application to disordered systems, the results established here will be used in section 4 in a phenomenological description of the static relaxation length of the fragile liquids.

3.3. Positional specific heat and the static relaxation length

It has now become evident that the bond susceptibility of a liquid can be expressed as $\chi_b = T C_i$, where C_i is that part of the specific heat containing contributions from interactions or positional degrees of freedom. Furthermore, the bond susceptibility χ_b or indeed C_i is shown to be intimately related to the static relaxation length ξ such that essentially $\chi_b \sim C_i \sim \xi^2$. With their thermal behaviours so closely correlated, we therefore propose the identification of the positional specific heat C_i as the thermodynamic response function associated with the static relaxation length ξ. Hence, we must further emphasize the significance of the role played by the specific heat, and, in particular, the interaction or positional part of it, in the problem of the glass transition. Unfortunately not enough is known about the precise behaviour of the specific heat near T_0 and much less about the interaction part of it, from an experimental point of view, as the supercooled liquid falls out of equilibrium on experimental timescales at the kinetic glass temperature T_g for the reasons pointed out in the introduction. It is generally believed that the excess specific heat over the crystal value ΔC_p, which is regarded as being due to a subset of the positional degrees of freedom, involving transitions between inherent structures (metabasins) of the potential energy hypersurface, rises with decreasing temperature in the supercooled temperature regime, and a hyperbolic form $\Delta C_p \propto 1/T$ has been assumed in conjunction with the Adam–Gibbs equation for the viscosity to recover the Vogel–Fulcher equation [28]. However, a drastically different ΔC_p has also been used to accurately account for the viscosity of silicate glasses [29]. Hence, in the forthcoming section where the preceding results will be applied in the case of fragile systems, a semi-empirical approach is adopted to estimate the positional specific heat of fragile supercooled liquids.

4. Application to supercooled liquids

In this section we present a phenomenological description for the thermal dependence of the static relaxation length for the general class of fragile liquids, in an attempt to clarify some of the discrepancies that were referred to in the introduction. As it turns out, the result obtained via this phenomenological approach to a certain degree agrees with that obtained from mean field theory of random-first-order transitions, also referred to in section 1, which suggests a power law temperature variation for the static relaxation length in the quasi-equilibrium supercooled temperature regime with an apparent divergence at the Vogel–Fulcher temperature T_0 [13].

The positional specific heat C_i is the temperature rate of change of the configurational energy (equation (6)). For the case of fragile supercooled liquids where the E_{eff} of equation (1) is to be largely interpreted as a temperature-dependent 'potential energy barrier' against the viscous flow [12, 30], one can consider a relationship of the form

$$\langle \phi \rangle (T) \sim -E_{\text{eff}}(T) \tag{15}$$

where $\langle \phi \rangle = \langle \Phi \rangle / N$ is the normalized configurational energy. Equation (15) expresses the average depths or minima of the potential energy hypersurface explored by the liquid at each temperature in terms of the height of the effective potential energy barrier against the viscous flow. It should also be mentioned that in the present analysis it is only the temperature rate of change of the above quantities that is of interest. The above equation simply indicates that the higher the energy barrier E_{eff}, the lower the minima and consequently the configurational energy $\langle \phi \rangle$. Equation (15) is also consistent with a representation in the potential energy landscape of a supercooled liquid, according to which a liquid is progressively confined to the deeper minima of the potential energy hypersurface with decreasing temperature, whereby it becomes more viscous due to an increased potential energy barrier E_{eff} against the viscous flow [30], or, alternatively, a reduction in the configurational entropy [31]. Although clearly this interpretation of the dynamics of supercooled liquids in terms of increasing barrier heights with decreasing temperature is not the only one found in the current literature [32], it is the one that we deem appropriate for the purposes of the present discussion. Hence, the interaction or positional part of the specific heat of the fragile liquids can be approximated by

$$C_i = -\frac{\partial E_{\text{eff}}}{\partial T}. \tag{16}$$

Using the effective potential energy barrier implied by the Vogel–Fulcher equation (1), i.e., $E_{\text{eff}} = Ak_B T / (T - T_0)$, we obtain

$$\chi_b = T C_i = \frac{Ak_B T T_0}{(T - T_0)^2}. \tag{17}$$

Equation (17) implies a power law temperature variation of the form $\chi_b \sim C_i \sim (T - T_0)^{-2}$ for the bond susceptibility as well as positional specific heat of the fragile supercooled liquids with an exponent $\gamma_b = 2$. From the scaling relation equation (14), the exponent ν governing the thermal variation of the static relaxation length of the fragile supercooled liquids is thus given by $\nu = \gamma_b / 2 = 1$. Hence, with the effective potential energy barrier embodied in the standard form of the Vogel–Fulcher equation, we obtain

$$\xi \sim (T - T_0)^{-1} \tag{18}$$

where T_0 is the Vogel–Fulcher temperature and exponent ν is equal to unity.

One may repeat the same analysis, this time using the generalized form of the Vogel–Fulcher equation:

$$\eta = \eta_0 \, \exp\left(\frac{B}{(T - T_0)^\gamma} \right), \tag{19}$$

with the identification $E_{eff} = Bk_BT/(T - T_0)^\gamma$, where B and γ are constant parameters. The special case of $\gamma = 1$ results in the standard form of the Vogel–Fulcher equation being recovered; however, different values for parameter γ can also be found in the literature [26]. The following is the result obtained with this rather generalized form of E_{eff} that includes γ as an extra parameter:

$$\chi_b = TC_i = \frac{Bk_BT}{(T - T_0)^{\gamma+1}} \left[\gamma T - (T - T_0)\right]. \tag{20}$$

In the limit $T \to T_0$, equation (20) gives

$$\chi_b(T \to T_0) \sim \frac{\gamma Bk_BT_0^2}{(T - T_0)^{\gamma+1}}. \tag{21}$$

Equation (21) implies $\chi_b \sim C_i \sim (T - T_0)^{-(\gamma+1)}$, and from equation (14), the characteristic length exponent is now given by $\nu = (1 + \gamma)/2$. Evidently an accurate experimental measurement of the parameter γ appearing in the generalized Vogel–Fulcher equation is essential for a precise determination of the exponent ν through the phenomenological procedure presented here.

A discussion of the observed difference between the phenomenological ($\nu = 1$) and mean field value ($\nu = 2/3$) of the static relaxation length exponent of the fragile liquids appears to be in order at this stage. This difference can be attributed to the mean field nature of the theory of the random-first-order transition that becomes exact in infinite dimensions, and is believed to have an associated upper critical dimension $d_u = 6$, which is significantly higher than the $d = 3$ space dimensions of supercooled systems. One therefore expects the mean field estimate of the relaxation length exponent to become increasingly accurate as the number of space dimensions approaches the upper critical value of six. Thus, it appears that the mean field theory of the random-first-order transition, which presents qualitative features analogous with the structural glass phenomenology, provides a lower-bound estimate of the static relaxation length exponent of a supercooled liquid. Indeed, there are other instances where mean field theories return lower estimates of correlation length exponents. A prominent example is the mean field theory of the continuous phase transitions (including the Ising model) that, by hyperscaling, has an associated upper critical dimension of four, which returns one half for the correlation length exponent, which is again exceeded by the exact two-dimensional value (unity), and reliable numerical estimates (0.63) for the corresponding three-dimensional system. Nevertheless, it is a matter of considerable interest that the phenomenological value of the static relaxation length exponent, $\nu = 1$, is precisely the value obtained from the three-dimensional numerical simulations of the microscopic models that exhibit a random-first-order transition in the mean field limit, such as the p-spin glasses [17] and the frustrated Ising lattice gas model [18].

In this section, a simple model for configurational energy in terms of increasing barrier heights with decreasing temperature has been used that, despite its simplicity, is applicable to various kinds of fragile liquids with predominantly ionic, Van der Waals, hydrogen, or covalent bonding. It would also be interesting to look at certain specific models such as the Rosenfeld–Tarazona relation for the Lennard-Jones liquid [33], or indeed any model that can be used to distinguish between positional and kinetic contributions to the specific heat in the context of the present work [34]. That effort is deferred to further work to be presented in due course.

5. Summary

For a liquid in the canonical ensemble it is shown that the bond susceptibility and interaction or positional part of the specific heat are related by $\chi_b = TC_i$. Furthermore, the bond

susceptibility and static relaxation length are found to vary as $\chi_b \sim \beta\xi^2$. These relationships essentially indicate the identification of the positional specific heat as the thermodynamic response function associated with the characteristic length of relaxation—a proposition that further emphasizes the significance of the role played by the positional specific heat in the problem of the glass transition, and is likely to find further applications in the theory of disordered systems, as applied here to the case of fragile supercooled liquids in a phenomenological description of the thermal dependence of the static relaxation length in those systems.

Through the phenomenological approach, the temperature variation of the characteristic length of relaxation for fragile supercooled liquids is established to be governed by a power law $\xi \sim (T - T_0)^{-\nu}$, implying an apparent divergence at the Vogel–Fulcher temperature T_0, which to a certain degree agrees with the corresponding result obtained from mean field theory of the random-first-order transition in that the apparent divergence temperature is T_0 in both these cases. However, the phenomenological exponent ν is found to be unity, which is higher than the corresponding mean field estimate, hence favouring a stronger temperature dependence for the static relaxation length in the supercooled temperature regime. This difference can be attributed to the mean field nature of the theory of the random-first-order transition as discussed above. It is indeed a matter of considerable interest that the phenomenological exponent $\nu = 1$ is in perfect agreement with the corresponding value obtained from the three-dimensional numerical simulations of the same models of structural glass that exhibit a random-first-order transition in the mean field limit.

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