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## LETTER TO THE EDITOR

**Two-order-parameter description of liquids: critical phenomena and phase separation of supercooled liquids**

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**Abstract.** Because of the isotropic and disordered nature of liquids, anisotropy hidden in many-body intermolecular interactions is usually neglected. Thus, it has been believed so far that the only order parameter required to describe a simple liquid is the density. Not accepting this common-sense view, we argue that a new additional order parameter, which represents the spontaneous formation of locally favoured structures, is necessary for the physical description of liquids near the lower stability limit. This model explains well two mysterious phenomena of supercooled liquids: (i) the large-scale density fluctuations known as ‘Fischer clusters’ and (ii) the phase separation of a one-component liquid into two phases.

Generally, a liquid phase is bound by a gas phase and a solid phase, although some anisotropic molecules exhibit an additional phase known as a liquid-crystalline phase above their solid phases [1]. On lowering the temperature of the gas phase, the potential energy becomes more important than the kinetic energy, and intermolecular interactions come into play. At the gas–liquid phase transition point, attractive interactions prevail, and lead to the formation of a ‘liquid’ phase. The principal physical quantity distinguishing the liquid phase from the gas phase is the density. Both phases have complete translational and rotational symmetry, and they are isotropic and homogeneous. Because of these features, a liquid state is usually assumed to be describable by just one order parameter, density.

The physical properties of liquid in the equilibrium state are rather well understood, while for liquid in the metastable state they are very poorly understood, especially near the liquid–glass transition [2–4]. Here we mention three relevant examples:

- (i) the liquid–glass transition phenomenon itself [2–4],
- (ii) large-scale density fluctuations in supercooled liquids [5–7], and
- (iii) an unusual phenomenon of phase separation of a simple one-component liquid into two liquid phases [8, 9].

Since phenomenon (i) is well known, we here explain phenomena (ii) and (iii).

**Phenomenon (ii).** According to the standard theory of pure liquids, the structure factor at wavenumber  $q = 0$ ,  $F(0)$ , is determined by the isothermal compressibility  $K_T$  as  $F(0) = \rho k_B T K_T$  ( $\rho$ : density;  $k_B$ : the Boltzmann constant;  $T$ : temperature) [10]. If density is the only order parameter required, the light scattering intensity at  $q = 0$  should be given by  $I_\rho(0) = (\partial n / \partial \rho)^2 F(0)$ . This is actually the case for most pure liquids. Contrary to

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this common-sense expectation, however, Debye and Bueche found excess light scattering far beyond this prediction and the existence of long-range density fluctuations with a correlation length  $\xi_{cl}$  of 200 nm in a glassy polymer [5]. Furthermore, Fischer *et al* [6] recently found that large-scale density fluctuations commonly exist near the glass-transition temperature  $T_g$  both in molecular liquids such as ortho-terphenyl (OTP), bis-methyl-phenyl-cyclohexane (BMPC), and bis-methyl-methoxy-phenyl-cyclohexane (BMMPC), and in polymeric liquids such as poly(methyl methacrylate) and polysiloxane. These surprising results strongly suggest that large-scale fluctuations, which are called ‘Fischer clusters’, commonly exist in various fragile liquids. Their findings [6] are summarized as follows:

- (A) Excess isotropic light scattering intensity beyond  $I_\rho(0)$  [11].
- (B) The Ornstein–Zernike form for the light scattering function,  $I(q) \sim 1/[1 + \xi_{cl}^2 q^2]$ .
- (C) A divergent increase in  $\xi_{cl}$  near a glass-transition temperature  $T_g$ , which is suggestive of the existence of a hidden critical point  $T_c$  or spinodal temperature  $T_{sp}$  [12].
- (D) A  $q^2$ -dependence of the decay rate,  $\Gamma_q \propto q^2$ , and  $\Gamma_q \rightarrow 0$  with  $T \rightarrow T_c$  (a diffusional ultraslow mode).
- (E) The annealing behaviour after a temperature quench to  $T_f (>T_g)$  can be described by  $I(q, t) = I(q, 0) + \Delta I[1 - \exp(-t/\tau_e)]$ , where  $\Delta I = I(q, \infty) - I(q, 0)$ . It is found that  $\tau_e$  is almost independent of  $q$ .
- (F) Cluster formation can be avoided by a rapid quench from far above a melting point to near or below  $T_g$ .
- (G) Vacuum distillation of OTP avoids clusters being produced; however, after melting they appear again.

None of these phenomena can be understood in the framework of the conventional theories of liquids [6]. Furthermore, their connection to glass transitions has so far been largely unexplored.

**Phenomenon (iii).** Aasland and McMillan [8] recently reported a striking experimental finding: for the supercooled state of  $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3$ , they directly observed, by means of microscopy, the coexistence of two glassy liquids, which have the same composition but different densities. This surprising finding indicates that even a single-component liquid can phase separate into two liquid phases [2]. Similar phenomena have been reported by a number of researchers for various liquids (see the references in [2, 8]). Numerical simulations of water also indicate the possibilities of a second critical point and the coexistence of two distinct forms of amorphous water [9]. Thus, the phenomena may be universal for supercooled liquids.

The key to understanding vitrification phenomena and these unusual (even mysterious) phenomena is, we believe, to realize that the above-mentioned common-sense view that a liquid state can be described by just one order parameter (density) may be basically ‘wrong’. There are a number of studies that have tried to improve the theory of liquids by including many-body effects, or higher-order density correlations. Most important is the concept of local bond-orientational order (LORO) [13, 14], which is based on the fact that even spherical molecules locally favour a tetrahedral configuration in a liquid phase. For example, Frank [13] pointed out that icosahedral clusters composed of 13 particles have a significantly lower energy than the more obvious ‘crystallographic’ arrangements of the corresponding fcc or hcp structures. On the basis of this idea, he explained why a simple liquid metal can be so deeply supercooled. This concept of LORO led to the recent developments along these lines [13–18]. However, we also need to consider specific anisotropic interactions that commonly occur in molecules having no spherical symmetry [19, 20]. The most extreme case is the formation of a local tetrahedral network due to covalent or hydrogen bonding as observed in  $\text{SiO}_2$ , glycerol, and

water [20]. In general, thus, a liquid at least ‘locally’ favours two different types of symmetry: one maximizes density, while another maximizes the quality of local bonds. The symmetry of the latter is generally not consistent with the crystallographic symmetry of the former. This causes energetic frustration, which we propose plays key roles in the stabilization of a supercooled liquid and the resulting vitrification [19]. It should be stressed that *the formation of locally favoured structures mentioned above always accompanies a decrease in local density.*

Here we explain our ‘new physical picture of liquid’ intuitively. We argue that

- (a) there exist rather well-defined, unique, locally favoured structures in any liquid and
- (b) such structures are created in a sea of normal-liquid structures and their number density increases upon cooling since they are energetically more favourable than normal-liquid structures.

We define a new ‘bond order parameter’  $S(\mathbf{r})$  as the ‘local fraction of locally favoured structures’ [21]. A simple two-state model tells us that

$$\bar{S} = \frac{g_S \exp(-\beta E_S)}{g_\rho \exp(-\beta E_\rho) + g_S \exp(-\beta E_S)} \sim \frac{g_S}{g_\rho} \exp[\beta(\Delta E - P \Delta v_S)]. \quad (1)$$

Here  $\bar{S}$  is the average of  $S(\mathbf{r})$ ,  $E_i$  and  $g_i$  are the energy and the degeneracy of the  $i$ -state,  $\beta = 1/k_B T$ ,  $P$  is the pressure, and  $\Delta E$  and  $\Delta v_S$  are the energy gain and volume increase upon the formation of locally favoured structures, respectively, and, thus,

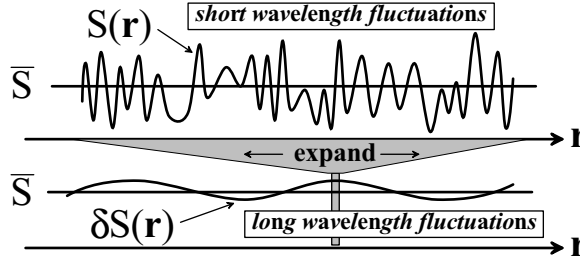
$$E_\rho - E_S \simeq \Delta E - \Delta v_S P.$$

In the derivation of the final relation of equation (1), we use the fact that  $g_\rho \gg g_S$ , which is a direct consequence of the uniqueness of locally favoured structures and the existence of many possible configurations of normal-liquid structures. This picture is supported by the validity of our two-order-parameter model of water [20]. At high temperatures, locally favoured structures are created ‘randomly’ in space and time. At low temperatures, on the other hand, locally favoured structures are created at higher probability near to other locally favoured structures (*cooperative creation*): *there is a possibility that this cooperative effect leads to a gas–liquid-like phase transition of locally favoured structures, or a liquid–liquid phase transition, upon cooling.*

On the basis of this picture, we propose that the behaviour of supercooled liquids can be described by a two-order-parameter Landau-type theory [22–24], which includes couplings between the density  $\rho$  and bond order  $S$ . Our theory can explain well the following unusual phenomena exhibited by supercooled liquids within the same framework:

- (i) vitrification (slow dynamics near a glass transition) [19],
- (ii) critical-like large-scale density fluctuations, and
- (iii) phase separation of a supercooled liquid into two liquid (glassy) phases.

As regards phenomenon (i), we argued [19] that the random nature of  $S(\mathbf{r})$  on a short length scale (see figure 1) produces the random-transition-temperature and random-field effects on the ordering of  $\rho$  at  $q_{cry}$  ( $q_{cry}$ : the characteristic wavenumber of a crystalline lattice)—namely, crystallization—in much the same way as in spin systems, and that these spin-glass-like effects are the origin of the vitrification and slow  $\alpha$ -relaxation. Thus, the strength of frustration between  $\rho$  and  $S$  is a physical factor controlling ‘fragility’: stronger frustration causes a stronger liquid [19]. We propose that phenomena (ii) and (iii) are caused by a gas–liquid-like phase transition of locally favoured structures, and that the coupling between *long-wavelength* (small- $q$ ) spatial fluctuations of  $\rho$  and  $S$ ,  $\delta\rho$  and  $\delta S$  (see figure 1), plays a major role. In



**Figure 1.** A schematic diagram of spatial fluctuations of  $S$ . Short-wavelength fluctuations are responsible for vitrification, while long-wavelength ones are responsible for Fischer clusters.

this letter, we focus just on phenomena (ii) and (iii), since phenomenon (i) has already been discussed elsewhere [19].

First we construct a phenomenological Landau-type theory, which describes gas–liquid-like critical phenomena of locally favoured structures. Since we assume in this letter that a system is in a liquid state and does not crystallize, we take the coarse-grained Hamiltonian of liquids [25], which governs long-wavelength density fluctuations, as

$$\beta H_\rho = \int \mathrm{d}\mathbf{r} \left[ \frac{\tau}{2} \delta\rho^2 + \frac{a_3}{3} \delta\rho^3 + \frac{a_4}{4} \delta\rho^4 \right] = \int \mathrm{d}\mathbf{r} f(\delta\rho)$$

where  $\tau$  and  $a_4$  are positive and  $\tau = \beta(\bar{\rho}^2 K_T)^{-2}$ . Here  $\bar{\rho}$  is the average density and is a decreasing function of  $T$  (note that  $\rho = \bar{\rho} + \delta\rho$ ).  $a_3$  may be positive or negative. For a real liquid, however, the bond order parameter plays essential roles, as explained above. Using  $\delta S = S - \bar{S}$ , we introduce the following minimal Hamiltonian, which governs  $S$ -fluctuations near a gas–liquid-like critical point or mean-field spinodal lines of bond ordering:

$$\beta H_S = \int \mathrm{d}\mathbf{r} \left[ \frac{\kappa}{2} \delta S^2 + \frac{b_4}{4} \delta S^4 \right] = \int \mathrm{d}\mathbf{r} g(\delta S)$$

where  $\kappa = b_2(T - T_S^*)$  ( $T_S^*$ : a critical or spinodal temperature of bond ordering without the coupling to  $\rho$ ), and  $b_2$  and  $b_4$  are positive constants. By further including the gradient terms and the lowest-order (up to second order) couplings between  $\delta\rho$  and  $\delta S$ , we obtain the following Hamiltonian that we believe is relevant to the physical description of liquid near a gas–liquid-like transition of locally favoured structures:

$$\beta H_{\rho S} = \int \mathrm{d}\mathbf{r} \left[ h(\delta\rho, \delta S) + \frac{K_\rho}{2} |\nabla \delta\rho|^2 + \frac{K_S}{2} |\nabla \delta S|^2 \right] \quad (2)$$

$$h(\delta\rho, \delta S) = f(\delta\rho) + g(\delta S) - c_{1\rho} \delta\rho (\bar{S} + \delta S) - c_{1S} (\bar{\rho} + \delta\rho) \delta S - \frac{c_{2\rho}}{2} \delta\rho^2 \bar{S} - \frac{c_{2S}}{2} \bar{\rho} \delta S^2. \quad (3)$$

Note that  $f$ ,  $g$ , and  $h$  are dimensionless free-energy densities. As explained before, an increase in  $S$  leads to a decrease in  $\rho$  and an increase in  $\tau$ , while an increase in  $\rho$  leads to a decrease in  $S$  and  $T_S^*$ . Hence, all of the coupling constants  $c_i$  in equation (3) should be negative.

Here we consider how the ultraslow dynamics [26] of  $\delta\rho$  and  $\delta S$  should be described. At a point of liquid instability against density ordering, the supercooled liquid as a whole becomes intrinsically unstable with respect to a density fluctuation of wavenumber  $q_0$  ( $q_0$ : first-scattering-peak wavenumber). This causes the softening of a non-propagating soft mode with  $q \sim q_0$  [27], which leads to the breakdown of the incompressibility assumption. Thus, we should regard a supercooled liquid as being compressible. For such compressible liquids,

it is known [1] that  $\delta\rho_q \propto -\delta Q_q$  ( $Q$ : heat mode), as long as we consider ultraslow dynamics at small  $q$ . Thus,  $\delta\rho$  should be treated as a conserved order parameter obeying a diffusion-type equation. This conclusion can also be derived from a more microscopic basis [29]. On the other hand,  $\delta S$  should be treated as a non-conserved order parameter. Thus, we have the following dynamic equations:

$$\frac{\partial \delta\rho(\mathbf{r}, t)}{\partial t} = L_\rho \nabla^2 \left[ -K_\rho \nabla^2 \delta\rho + \frac{\partial h(\delta\rho, \delta S)}{\partial \delta\rho(\mathbf{r}, t)} \right] \quad (4)$$

$$\frac{\partial \delta S(\mathbf{r}, t)}{\partial t} = -L_S \left[ -K_S \nabla^2 \delta S + \frac{\partial h(\delta\rho, \delta S)}{\partial \delta S(\mathbf{r}, t)} \right] \quad (5)$$

where  $L_\rho$  and  $L_S$  are kinetic coefficients. Here the Gaussian noise terms are not written out explicitly. We propose that equations (2)–(5) are the fundamental equations universally describing the ultraslow dynamics [26] of supercooled liquids. These dynamic equations are basically the same as those of the so-called ‘model C’ [22–24].

Within the framework of a linearized theory [23, 24], we study the slow dynamics of large-scale fluctuations. First we introduce a vector notation:

$$\mathbf{x} = \begin{bmatrix} \delta\rho \\ \delta S \end{bmatrix} \quad \text{and} \quad \mathbf{x}_0 = \begin{bmatrix} \langle \delta\rho \rangle \\ \langle \delta S \rangle \end{bmatrix}.$$

The average values of the order parameters,  $\bar{\rho}^r$  and  $\bar{S}^r$ , are shifted due to their bilinear coupling compared to those without the coupling,  $\bar{\rho}$  and  $\bar{S}$ , respectively, by

$$\langle \delta\rho \rangle \sim \frac{c_{1\rho} \bar{S}}{\tau^*} \quad \text{and} \quad \langle \delta S \rangle \sim \frac{c_{1S} \bar{\rho}}{\kappa^*}$$

where  $\tau^* = \tau - c_{2\rho} \bar{S}$  and  $\kappa^* = \kappa - c_{2S} \bar{\rho}$ . After linearization with respect to small deviations

$$\mathbf{x}^* = \begin{bmatrix} \delta\rho^* \\ \delta S^* \end{bmatrix}$$

from  $\mathbf{x}_0$ , equations (4) and (5) reduce to the following eigenvalue problem on using

$$\mathbf{x} = \mathbf{x}_0 + \mathbf{x}^* \exp(i\mathbf{q} \cdot \mathbf{r} + \omega t)$$

( $\mathbf{q}$ : wave vector):  $\mathbf{A}\mathbf{x}^* = -\omega\mathbf{x}^*$ , where  $\mathbf{A} = \mathbf{T}(\mathbf{H} + q^2\mathbf{K})$  with

$$\mathbf{T} = \begin{bmatrix} L_\rho q^2 & 0 \\ 0 & L_S \end{bmatrix} \quad \mathbf{K} = \begin{bmatrix} K_\rho & 0 \\ 0 & K_S \end{bmatrix} \quad (6)$$

and

$$\mathbf{H} = \begin{bmatrix} h_{\delta\rho\delta\rho} & h_{\delta\rho\delta S} \\ h_{\delta S\delta\rho} & h_{\delta S\delta S} \end{bmatrix} = \begin{bmatrix} \tau^* & c_{1\rho} + c_{1S} \\ c_{1\rho} + c_{1S} & \kappa^* \end{bmatrix} \quad (7)$$

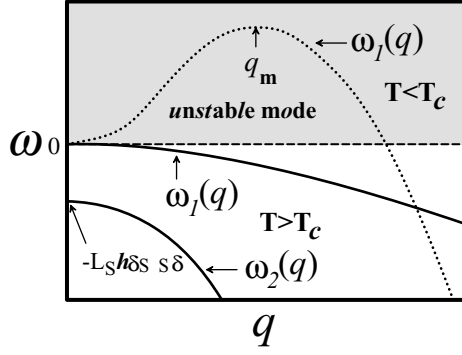
where  $\mathbf{H}$  is the so-called Hesse matrix and the derivatives  $h_{xy} = \partial^2 h / \partial x \partial y$  are taken at  $\mathbf{x}_0$ . In the limit of small  $q$ , the two dispersion branches (see figure 2) are given by

$$\omega_1 \sim -L_\rho \left[ \frac{\det \mathbf{H}}{h_{\delta S\delta S}} \right] q^2 + \text{O}(q^4) \quad (8)$$

$$\omega_2 \sim -L_S \left[ h_{\delta S\delta S} + \left( K_S + \frac{L_\rho h_{\delta\rho\delta S}^2}{L_S h_{\delta S\delta S}} \right) q^2 \right] + \text{O}(q^4). \quad (9)$$

In the limit of large  $q$ , on the other hand,  $\omega_1 \sim -L_\rho q^4$  and  $\omega_2 \sim -L_S K_S q^2$ .

Before discussing critical-like phenomena on the basis of the above general results for a two-order-parameter model, we consider the mechanism of the avoidance of crystallization in glass-forming material. Crystallization requires the break-up of locally favoured structures,



**Figure 2.** Dispersion branches of a supercooled liquid in a small- $q$  region.  $\omega_1(q)$  is the critical mode, and it becomes unstable below  $T_c$ . In an unstable region, the mode with wavenumber  $q_m$  has the maximum growth rate.

since their symmetry is not consistent with the crystallographic symmetry. In addition to the interface energy, thus, a system has to overcome a large energy barrier corresponding to the break-up or deformation of all locally favoured structures in a critical nucleus of crystal, which costs an energy of the order of  $\sim \Delta E \bar{S} v_c$  ( $v_c$  is the volume of a critical nucleus). This gives an extra mechanism preventing crystallization in addition to the classical one [4]. Crystallization can thus be kinetically prevented by this extra energetic barrier to nucleation being present for a sufficient cooling rate, and, therefore, a supercooled state is kinetically stabilized. Hence we can regard a supercooled state as a quasi-equilibrium thermodynamic state.

Here we consider critical fluctuations caused by the existence of a hidden critical point in a supercooled liquid. The avoidance of crystallization due to local bond ordering reveals a critical point  $T_c$  or a spinodal line usually hidden by crystallization. In general, thus, the mode having the eigenvalue  $\omega_1$  can become unstable first when  $\det \mathbf{H} = \tau^* \kappa^* - (c_{1\rho} + c_{1S})^2 < 0$ , as shown in figure 2. Hence critical-like fluctuations enhance with approach to a temperature  $T_c$  where  $\det \mathbf{H} = 0$ . Thus,  $T_c = T_S^{**} + (c_{1\rho} + c_{1S})^2 / \tau b_2$ , where  $T_S^{**} = T_S^* + c_{2S} \bar{\rho} / b_2$ .

Here we consider light-scattering phenomena on the basis of the above model. The refractive index  $n$  is a function of not only  $\rho$ , but also  $S$ , since  $n$  for locally favoured structures is smaller than that for normal structures. In our model, thus,  $I(q)$  is given by [28]

$$I(q) \propto \left( \frac{\partial n}{\partial \rho} \right)^2 \langle |\delta \rho_q^*|^2 \rangle + 2 \left( \frac{\partial n}{\partial \rho} \right) \left( \frac{\partial n}{\partial S} \right) \langle \delta \rho_q^* \delta S_{-q}^* \rangle + \left( \frac{\partial n}{\partial S} \right)^2 \langle |\delta S_q^*|^2 \rangle \quad (10)$$

where  $n$  is the refractive index. These correlation functions at small  $q$  can be straightforwardly obtained as

$$\langle |\delta \rho_q^*|^2 \rangle = (\kappa^* + K_S q^2) / A(q) \quad (11)$$

$$\langle \delta \rho_q^* \delta S_{-q}^* \rangle = (c_{1\rho} + c_{1S}) / A(q) \quad (12)$$

$$\langle |\delta S_q^*|^2 \rangle = (\tau^* + K_\rho q^2) / A(q) \quad (13)$$

where

$$A(q) = (\tau^* + K_\rho q^2)(\kappa^* + K_S q^2) - (c_{1\rho} + c_{1S})^2 \sim \det \mathbf{H} + [\tau^* K_S + \kappa^* K_\rho] q^2. \quad (14)$$

On the basis of the above two-order-parameter description of liquids, we now explain the experimental findings of Fischer *et al*, which are summarized in the introduction as facts (A)–(F). In our model, fact (A) can be explained by  $\kappa^* \ll c_{1\rho} + c_{1S}$ ,  $\tau^*$ , which guarantees the dominance of equation (12) and equation (13) over equation (11) near the spinodal lines. This

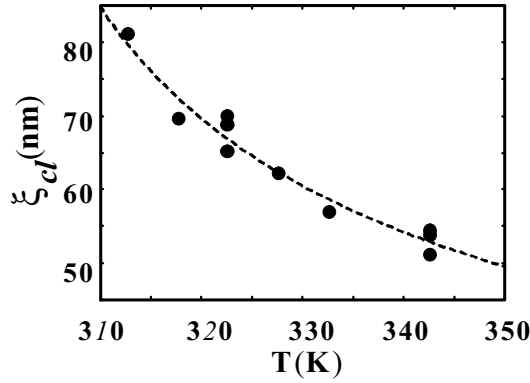
is a direct consequence of the fact that there is instability for bond fluctuations (a gas–liquid-like transition of locally favoured structures) but not for density fluctuations in a liquid state. The reason for the apparent violation of the compressibility sum rule [10] can be understood by comparing equation (10) [28] with

$$K_T = \frac{1}{k_B T \rho^2} \int d\mathbf{r} \langle \rho^r(\mathbf{r}) \rho^r(\mathbf{0}) \rangle$$

where  $\delta\rho^r = \delta\rho^* + c_{1\rho}/\tau^* \delta S^*$  is the fluctuation of real density, on noting the smallness of  $|c_{1\rho}/\tau^*|$ . Fact (B) is also consistent with the  $q$ -dependence of equations (12) and (13). In our model,  $\xi_{cl}$  is given by

$$\xi_{cl}^2 \sim (\tau^* K_S + \kappa^* K_\rho) / \det \mathbf{H}$$

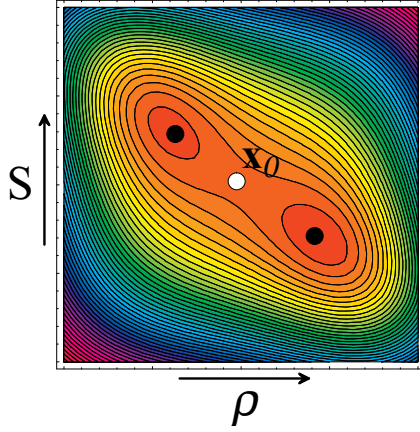
which diverges as  $T \rightarrow T_c$  near  $T_c$ . Within the mean-field approximation,  $\xi_{cl} \sim (T - T_c)^{-1/2}$ . This relation is consistent with fact (C), as shown in figure 3. Fact (D), which is suggestive of simple diffusion [6], can be explained as follows. In our model, both  $\delta\rho_q^*$  and  $\delta S_q^*$  can be expressed as linear combinations of two eigenmodes characterized by  $\omega_1$  and  $\omega_2$ . In particular, the ‘slow’ critical mode decays as  $\exp(\omega_1 t)$ , and the decay rate of this mode,  $\Gamma_q = -\omega_1$ , is proportional to  $q^2$  (see equation (8)). Furthermore,  $\Gamma_q \propto \det \mathbf{H} \propto (T - T_c) \rightarrow 0$  with  $T \rightarrow T_c$ . Thus, our model can well explain all essential features (facts (A)–(D)) of the anomalous excess light scattering observed in supercooled liquids (‘Fischer clusters’) [6] at least qualitatively.



**Figure 3.** Fitting of our prediction  $\xi_{cl} = \xi_0((T - T_c)/T_c)^{-1/2}$  to the  $T$ -dependence of  $\xi_{cl}$  experimentally observed for BMMPC [6]. The adjustable parameters are determined as  $\xi_0 = 22$  nm and  $T_c = 289$  K, although they may have large errors. This long bare correlation length is consistent with the assumption of the mean-field spinodal, according to the Ginzburg criterion.

Next we speculate as regards facts (E)–(G). Fact (E) is apparently inconsistent with the diffusional dynamics of density fluctuations, and has been considered to be quite puzzling [6]. However, it can be explained reasonably as follows. The equilibrium dynamics is dominated by a slow diffusional mode, while the non-equilibrium dynamics is dominated by a non-diffusional mode. Note that, in the latter,  $\rho$  can be ‘locally’ (not diffusively) changed. This is because during this non-equilibrium process, after a temperature quench, the average density  $\bar{\rho}$  itself increases, and thus the density is ‘not’ conserved, contrary to the equilibrium case. Because of this local nature of the change in  $\rho$ ,  $\tau_e$  can be  $q$ -independent for this non-equilibrium process. Next, fact (F) is due to the feature that the time required for cluster formation,  $\tau_e$ , becomes extremely long for  $T_f$  near to or below  $T_g$ , reflecting the increase in  $\eta$ . The divergence of  $\tau_e$  with decreasing  $T$  means that a sample inevitably becomes out of equilibrium before reaching  $T_c$ , and thus  $T_c$  is kinetically hidden in real experiments ( $\tau_e$  readily becomes longer than the





**Figure 4.** A contour plot of the free energy of a supercooled liquid below  $T_c$  on the  $(\rho, S)$  plane. The region of  $(\rho, S)$  near a normal-liquid state at  $x_0$  is shown. The crystalline state ( $S \sim 0$ ) is located outside this region. Crystallization is kinetically prevented by the presence of a large energy barrier (see the text). A homogeneous one-component liquid can demix into two phases, indicated by the filled circles on the  $(\rho, S)$  plane.

$\alpha$ -relaxation time at  $T_g$ , even at a temperature far above  $T_g$ ). Finally, we speculate concerning fact (G). Vacuum distillation may realize the homogeneous situation ( $\delta\rho \sim 0$ ,  $\delta S \sim 0$ ), which is marginally stable and lasts for a long time. However, crystallization destroys this metastable state easily.

Finally we consider phase separation below  $T_c$ . Because of the existence of a new order parameter  $S$  and the resulting coupling between  $\rho$  and  $S$ , phase separation can proceed on the  $(\rho, S)$  plane even for a one-component liquid [30], as shown schematically in figure 4. For the case where  $h_{\delta S \delta S} > 0$  and  $\det \mathbf{H} < 0$  [31], the eigenvector of the unstable branch shown in figure 2 is of mixed character for all  $q$  (see equation (8)), and, thus, fluctuations of both  $\delta\rho$  and  $\delta S$  grow simultaneously. At  $q = 0$  the components  $\delta\rho^*$  and  $\delta S^*$  of the eigenvector  $\mathbf{x}^*$  satisfy  $\delta\rho^*/\delta S^* = -h_{\delta S \delta S}/h_{\delta\rho \delta S}$ . This is quite consistent with the phase-separation behaviour of water demonstrated by Stanley *et al* [9] with numerical simulations near a so-called ‘second critical point’, which may correspond to our gas–liquid-like critical point of locally favoured structures: according to their simulation, density fluctuations ( $\delta\rho$ ) have a phase difference of  $\sim 180^\circ$  from fluctuations of the number density of hydrogen bonding ( $\delta S$ ). Our model naturally predicts this negative correlation between two order parameters [32]: a high-density region has less bond order, while a low-density region has more bond order (see figure 4). It can, thus, naturally explain why phase coexistence is possible in a single-component liquid [2, 8, 9]. Our model gives an intuitive physical explanation for a second critical point proposed by Stanley *et al* [9] and demonstrates that it may generally exist in any liquid. Glass-forming liquids automatically satisfy the condition necessary for the existence of such a gas–liquid-like transition, since vitrification is itself caused by the existence of *locally favoured structures* in our picture [19].

In conclusion, we propose that the viscous slowdown near  $T_g$  [2, 3, 19], the ‘Fischer clusters’ [6], and eventually the liquid–liquid phase transition [2, 8, 9, 30] are all related, and appear as successive consequences of the competition (negative couplings) between the density and bond ordering. In particular, the latter two phenomena are caused by a gas–liquid-like

phase transition of locally favoured structures—in other words, the *collective creation* of locally favoured structures. We stress that a new additional order parameter (the bond order parameter) is necessary for the physical description of (supercooled) liquids, contrary to the common-sense view that liquids can be described using just one order parameter, density. This two-order-parameter model can also describe the thermodynamic and dynamic anomalies of liquid water [20]. Further studies are highly desirable, to check the relevance of our new picture of liquid and its universality.

Finally, we mention some predictions of our model:

- (a) There should exist neither clusters nor anomalous excess scattering for a liquid, which does not form glass easily ( $c_{1\rho}, c_{1S} \sim 0$ ).
- (b) The scattering intensity should decrease with increase in pressure for ordinary liquids.
- (c) A larger  $\Delta v_S$  leads to larger  $\partial n/\partial S$  [28].
- (d) Liquids with excess scattering should exhibit ‘polyamorphism’ at lower temperatures.
- (e) Critical-like phenomena should be observed only in a mean-field-type system having long-range interactions between locally favoured structures. This may explain why ‘Fischer clusters’ are often observed in polymers.

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