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A model for the fragile-to-strong transition in water

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Abstract. A model based on the existence of two different competing local structures in water is described. It is shown that it can explain the transition between fragile and strong behaviour that supercooled water undergoes at around 220 K. The high-temperature behaviour is similar to that observed in standard fragile glass formers. The strong behaviour at low temperatures is associated with the existence of a remanent configurational entropy arising from the possibility of locally choosing between the two possible environments.

1. Introduction

The form of the dependence of viscosity on temperature is among the many properties that make water an anomalous fluid. Water is a fragile fluid when viewed at temperatures close to the melting temperature, indicating that there is an arrest of its degrees of freedom on cooling. This behaviour is typical of many substances known as fragile glass formers [1, 2]. However, close to the glass temperature T_G ($\sim$136 K) supercooled water shows characteristics of a strong liquid [3, 4], in which there is an almost temperature-independent configurational entropy, that manifests itself in an Arrhenius dependence of the viscosity η as a function of T. Thermodynamic constraints limit the transition between these two regimes to occurring rather sharply in a temperature range around $\sim$220 K [5].

There is by now good evidence that many of the anomalous properties of water can be rationalized by the use of an effective, two-particle, spherical interaction potential, of the core-softened type [6–9]. This interaction can be viewed as appearing between clusters of water molecules, rather than between single molecules [10, 11]. The main characteristic of this interaction is that it allows for two different equilibrium distances between clusters, depending on pressure. An appropriate, simplified model that captures many of the anomalies of water is provided by spherical particles interacting through a potential consisting of a hard core plus a soft repulsive shoulder [6, 7]. Here we show—using an analytically solvable version of it—that this kind of interaction can also explain the non-standard behaviour of $\eta(T)$.

2. The hard-sphere model

We will use a model of hard spheres as a starting point (in the next section it will be generalized to describe the properties of water). We will suppose that the pure hard-sphere system has an ideal thermodynamical glass transition at some temperature T_0 if the fluid phase is supercooled preventing crystallization. A possible scenario for this glass transition is the following [12–14]. For glassy systems there is a contribution s_c to the entropy—referred to as configurational entropy—that comes from the many different configurations in which the glass can exist. For the case of spheres it comes from the many ways in which the spheres can be accommodated in stable, non-crystalline arrangements. These configurations differ in the value of the specific volume v. We will suppose that hard spheres have a configurational entropy per particle $s_c^{HS}(v)$ of the form†

$$s_c^{HS}(v) = \alpha(v - v_0) - \beta(v - v_0)^2. \tag{1}$$

According to this formula, s_c^{HS} becomes lower than zero for $v < v_0$ (and for $v > v_0 + \alpha/\beta$), indicating that there are no accessible states in this range, i.e., v_0 is the minimum value that v can take.

To obtain the total entropy s_{tot} of the system we still have to include the contribution coming from small vibrations around each configuration [14]. Notice that v in (1) is the limiting volume of a given glass, whereas the actual volume of the system V is larger, since it includes the vibrational expansion. We will suppose that the vibrational contribution to the entropy s_{vib} depends only on the difference between the actual volume of the system V and the limiting volume of the corresponding glass v. The total entropy for each value of V is then obtained by choosing the appropriate value of v that maximizes s_{tot}, namely

$$s_{\text{tot}}(V) = \max_v (s_c(v) + s_{\text{vib}}(V - v)). \tag{2}$$

The maximum condition can be written in differential form as

$$\frac{\partial s_c(v)}{\partial v} + \frac{\partial s_{\text{vib}}(V - v)}{\partial v} = 0. \tag{3}$$

On the other hand, from thermodynamic relations we get

$$\frac{P}{T} = \frac{\mathrm{d}s_{\text{tot}}}{\mathrm{d}V} = \frac{\partial s_{\text{vib}}(V - v)}{\partial V} + \left(\frac{\partial s_c(v)}{\partial v} + \frac{\partial s_{\text{vib}}(V - v)}{\partial v}\right)\frac{\mathrm{d}v}{\mathrm{d}V} \tag{4}$$

in which, on the right-hand side, v is thought of as a function of V obtained by solving (3). But the second term of (4) is zero because of (3), so from here (using again (3) and the fact that $\partial s_{\text{vib}}/\partial v = -\partial s_{\text{vib}}/\partial V$ due to the dependence on $V - v$ only) we get

$$\frac{P}{T} = \frac{\partial s_c(v)}{\partial v}. \tag{5}$$

This expression coincides with the one that is obtained if the vibrational contribution to the entropy is completely dismissed, but as we see its validity is wider.

Expression (1) for the configurational entropy implies the existence of an ideal thermodynamical glass transition occurring at T_0, where T_0 is obtained from $P/T_0 = \partial s_c^{HS}/\partial v\big|_{v=v_0} = \alpha$. Whereas on microscopic grounds there is no rigorous proof that this transition should occur, the consequences for magnitudes of observables that can be predicted from it are consistent with the known phenomenology of glassy systems [15] and with results of numerical simulations [14,16]. For $T < T_0$ the system is in the fundamental configurational state, and then $s_c^{HS}(T < T_0) = 0$. For $T > T_0$, s_c^{HS} is given by (using (5) and (1))

$$s_c^{HS}(T > T_0) = \frac{\alpha^2}{4\beta T^2}(T^2 - P^2/\alpha^2) = \frac{\alpha^2}{4\beta T^2}(T^2 - T_0^2). \tag{6}$$

This expression for s_c^{HS} can be used to calculate transport properties such as the viscosity η through the use of the Adam–Gibbs formula [17]. This formula states that the value of η is given by

$$\eta(T) = \eta_0 \exp[A/(Ts_c)] \tag{7}$$

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† In reference [14] a parabolic form for s_c as a function of *density* (rather than v) is used. The difference between the two choices is tiny, and both give rise to an ideal glass transition.

where η_0 and A are constants. The presence of s_c in (7) reflects the fact that jumps between different basins of the energy landscape become less probable as the number of these basins diminishes. The Adam–Gibbs formula can be made plausible [17] but it is not rigorous, and should be considered only as an appropriate working hypothesis.

For hard spheres, equation (7) becomes

$$\eta^{HS}(T) = \eta_0 \exp\left[4A\alpha^{-2}\beta T/(T^2 - T_0^2)\right]. \tag{8}$$

This is a behaviour typical of many glass formers, in which η increases more rapidly than in a simple thermally activated process, and it diverges when $T \to T_0$.

3. Core-softened models for water

Properties of water have been studied recently by using models in which particles interact through potentials that allow for two different equilibrium distances between particles, namely d_0 and $d_1 > d_0$ [6–8, 18]. One possibility is, for instance, to take a strict hard core at d_0 and a shoulder that vanishes at d_1 [6, 7]. Here we will use a further simplification of this kind of model in order to be able to extract analytical results [7]. We consider spheres of radius r_1 ($=d_1/2$). Pairs of spheres will be allowed to overlap (more than two overlapping spheres will not be allowed), and each time this happens the system will be charged an energy ε_0. This may be considered as a limiting case for particles with a core-softened potential, in which there is a low-energy hard core at a distance $2r_1$, and a strict hard core at $2r_0$, and we are taking $r_0 = 0$. To make the problem analytically tractable, we will also suppose that each time two spheres overlap, they are constrained to have their centres in exactly the same position. This approximation neglects the entropy associated with small vibrations of the particles in each pair.

We are interested in the configurational entropy s_c of the system, now as a function of the specific enthalpy $h = Pv + e$, that includes the internal energy e coming from the existence of overlapping particles. To calculate $s_c(h)$ we proceed in the following way. Suppose we have a system of N particles, n of them in non-overlapped positions and n' pairs of overlapped particles ($N = n + 2n'$). The configurational entropy will be that of $n + n'$ hard spheres plus the combinatorial entropy for locating the n' pairs in the $n + n'$ possible positions, i.e.,

$$\tilde{s}_c = \frac{n+n'}{N} s_c^{HS} + k_B \ln \binom{n+n'}{n'} \tag{9}$$

(here we use $\tilde{s}_c$ to indicate an entropy functional). Using $x \equiv n'/N$ and $\tilde{v} \equiv V/(n+n') = v/(1-x)$ as independent variables we can write $\tilde{s}_c$ as

$$\tilde{s}_c(x, \tilde{v}) = (1-x)s_c^{HS}(\tilde{v}) + k_B \left[(1-2x)\ln\left(\frac{1-x}{1-2x}\right) + x\ln\left(\frac{1-x}{x}\right)\right]. \tag{10}$$

As in the case of pure hard spheres, in which we supposed that the vibrational contribution to the entropy was a function of $V - v$ only, we will suppose that the vibrational contribution in the present case of soft spheres is a function of $H - h$ only, where H is the actual value of the enthalpy of the system, and h is the enthalpy of the corresponding glass. Under these assumptions the configurational entropy as a function of h is obtained from

$$s_c(h) = \max_{x,\tilde{v}} \Big|_h \tilde{s}_c(x, \tilde{v}) \tag{11}$$

$$h = Pv + e = (1-x)P\tilde{v} + x\varepsilon_0 \tag{12}$$

where the maximum is taken keeping h constant. Also, along the lines of the previous section, we can rewrite the thermodynamic relation $T^{-1} = \partial s_{\text{tot}}/\partial H$ as $T^{-1} = \partial s_c(h)/\partial h$.

4. Results

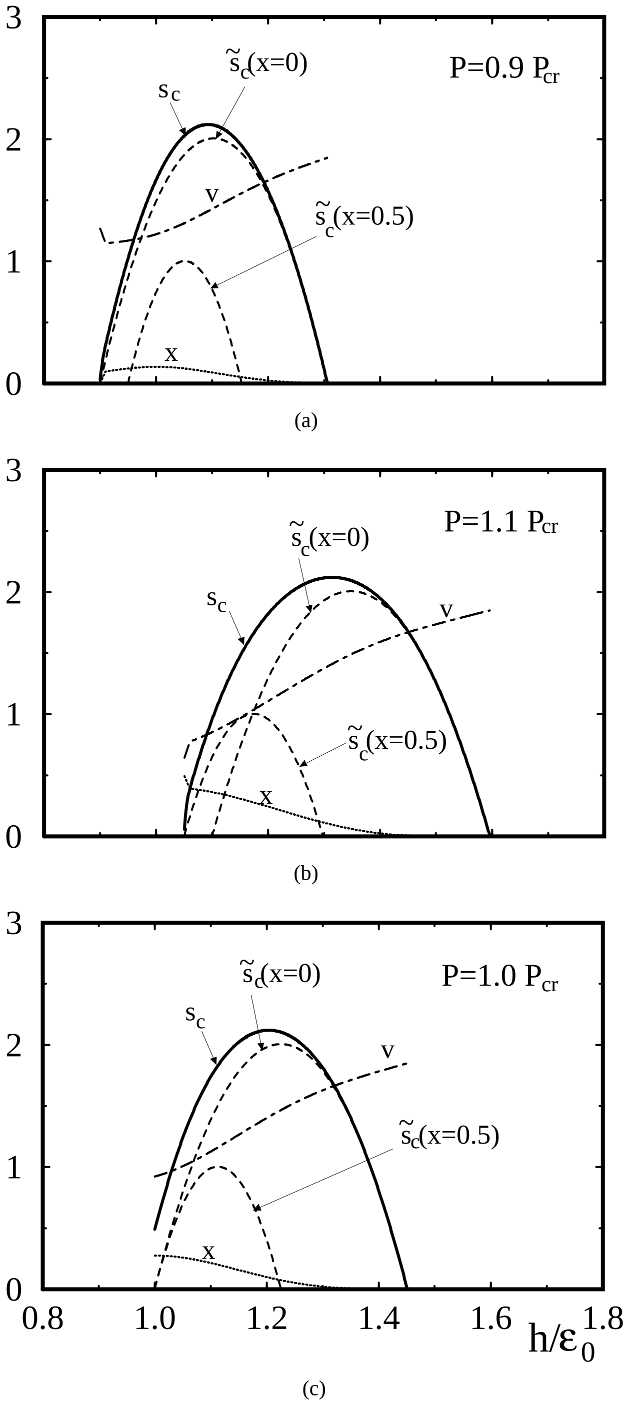
In figure 1 we see s_c, x, and v as functions of h for three different values of P, obtained using expression (6) for $s^{HS}(v)$ with $\alpha = 2.79\ k_B r_1^{-3}$, $\beta = 0.97\ k_B r_1^{-6}$, and $v_0 = 6.37\ r_1^3$ which are values extracted from numerical simulations of hard-sphere systems [14]. We also plot in figure 1 the limiting cases $\tilde{s}_c(x = 0)$ and $\tilde{s}_c(x = 0.5)$, corresponding to all particles in single or overlapped positions, respectively. The thermodynamic value $s_c(h)$ can never be lower than $\tilde{s}_c(x = 0)$ or $\tilde{s}_c(x = 0.5)$. The states with the lowest enthalpy for $x = 0$ and $x = 0.5$ have (from (12)) $h = Pv_0$ and $h = Pv_0/2 + \varepsilon_0/2$, respectively. These values coincide at $P_{\mathrm{cr}} \equiv \varepsilon_0/v_0$. In figure 1(a), for $P = 0.9\ P_{\mathrm{cr}}$, $\tilde{s}_c(x = 0)$ is always greater than $\tilde{s}_c(x = 0.5)$ and for this reason x takes values close to 0, indicating that most particles are in single positions. The $s_c(h)$ function obtained departs from zero with an infinite derivative at $h = 0.9\,\varepsilon_0$ (because of the combinatorial contribution to the entropy) but it still has a singularity (namely a jump in its second derivative) when $\partial s_c/\partial h = \alpha/P$. In (b) the value of $P = 1.1\ P_{\mathrm{cr}}$ is larger, and at low h the contributions with $x = 0.5$ dominate, indicating that the system has almost all particles coupled in pairs. For higher h, x goes down to zero—that is, paired particles become rare. In (c), the value of $P = P_{\mathrm{cr}}$ is exactly that at which the ground state of the system with $x = 0$ and the one with $x = 0.5$ become degenerate. In this case, entropy starts from a finite value $\simeq 0.48\ k_B$ at $h_{\mathrm{min}} = \varepsilon_0$, corresponding to the maximum combinatorial entropy of choosing which particles are single, and which are paired.

To get the values of the thermodynamic variables as a function of T, instead of h, we have to make use of the relation $T^{-1} = \partial s_c/\partial h$. The results for the configurational entropy $s_c(T)$ and the viscosity $\eta(T)$ (calculated using the Adam–Gibbs formula (7)) are shown in figure 2.

5. Discussion and comparison with water

From figure 2(a) we see that for any P, s_c is finite for all $T \neq 0$, i.e., there is no vanishing of s_c at any finite temperature, contrary to what happened in the case of simple hard spheres (see equation (6)). This is due to the possibility for the system having particles single or paired, which always accounts for the existence of a non-zero combinatorial entropy. For $P = P_{\mathrm{cr}}$ the bottoms of the $\tilde{s}_c$-functions corresponding to $x = 0$ and $x = 0.5$ coincide (figure 1(c)), and this combinatorial entropy can be used up to $T = 0$, in such a way that s_c remains finite, even when $T \to 0$. For $P \neq P_{\mathrm{cr}}$, s_c goes to zero as $T \to 0$, as the ground state is unique. There is still a phase transition at finite temperatures, signalled by the kink in the $s_c(T)$ curves in figure 2(a). The position of this kink in the P–T plane is given by $P/T = \alpha$. In the $\log(\eta)$–$1/T$ plot (figure 2(b)), the kinks mark the transition between a fragile and a strong behaviour. At high T, s_c diminishes rapidly with temperature and the system is fragile. This behaviour is equivalent to that of the simple hard-sphere system (see equation (8)). At low T, the dependence of s_c on T is much weaker, indicating a stronger behaviour. In this regime, the available configurational entropy is mainly of combinatorial nature.

For this model there is no ideal glass transition, i.e., η is finite at any finite temperature, and $T_0 = 0$. However, from an experimental point of view, the glass transition temperature T_G is conventionally defined as the value of T at which η takes some large value (this is usually taken to be 10^{13} P). In figure 3 we show curves of constant η extracted from our model. Each of these may be thought of as defining a dynamical glass transition temperature T_G (that depends on pressure), according to different dynamical criteria. The position of the line of the fragile-to-strong transition is also indicated. We see that T_G is systematically lower around the critical pressure $P = P_{\mathrm{cr}}$. This behaviour has been observed in numerical simulations of SiO_2 [19,20], which has a fragile-to-strong transition qualitatively similar to that of water. Notice that the



(a)

(b)

(c)

Figure 1. Configurational entropy s_c, specific volume v, and fraction of pairs of particles relative to the total number of particles x as functions of the enthalpy for three different values of pressure. In order to allow comparison, the limiting cases $\tilde{s}_c(x = 0)$ and $\tilde{s}_c(x = 0.5)$ are also shown (entropies are given in units of k_B, v is in units of $5r_1^3$, where r_1 is the radius of the particles; see the text for details).

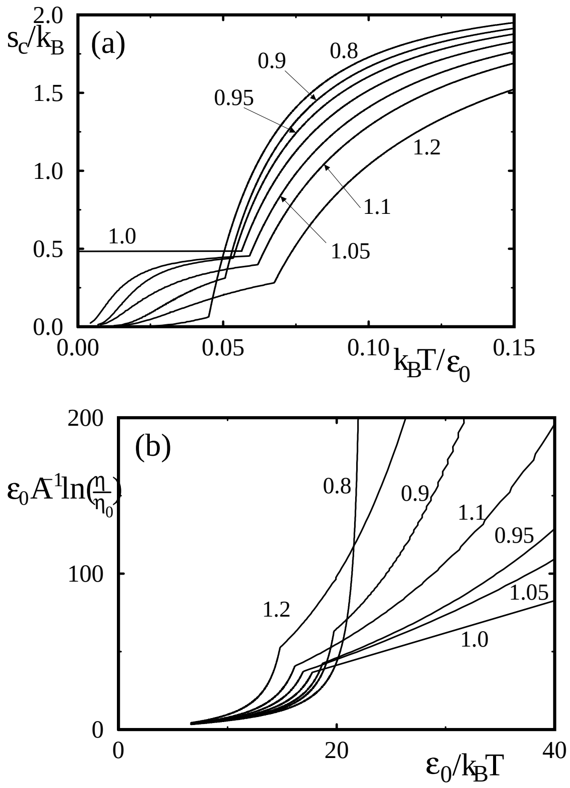


Figure 2. (a) Configurational entropy s_c as a function of T, for different values of P/P_{cr}, as indicated. (b) Viscosity η versus $1/T$, calculated according to the Adam–Gibbs formula (expression (7); η_0 and A are the constants in that expression).

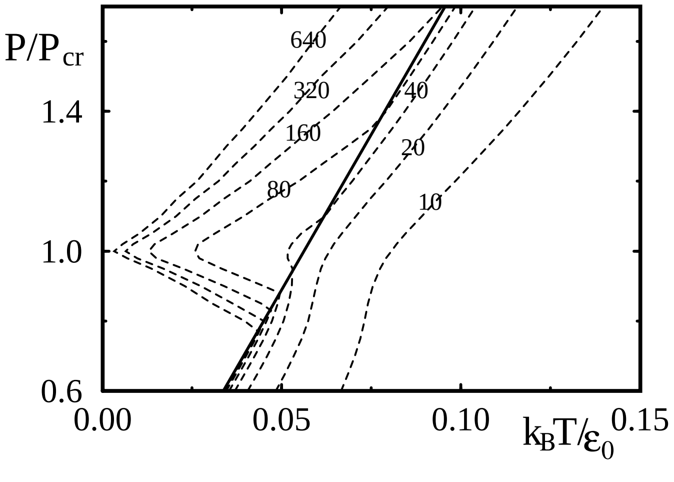


Figure 3. A pressure–temperature plot, indicating the position of the fragile-to-strong transition (solid line) and contour lines of constant viscosity (dashed lines; the corresponding values of $\varepsilon_0 A^{-1} \ln(\eta/\eta_0)$ are indicated).

form of the curves of constant η implies the existence of minima of the viscosity as a function of pressure, at constant temperature. This is a well known fact for simulated water [21].

One important ingredient that we have not included in the model is the existence of an attractive part in the interaction potential. In real water this attraction generates the liquid–vapour first-order coexistence line, and also probably a second first-order line in the supercooled region separating two different amorphous configurations [7]. A simple way of analysing the consequences for our model of an attraction between particles is the following. If the attraction is considered to be long ranged, of van der Waals type, then all of the results that we have obtained remain valid if we replace P by a new effective pressure $P^* \equiv P + \gamma/v^2$ for some constant γ; that is, the attraction acts as an effective pressure (which depends on v) that has to be added to the external pressure P. In the P–T phase diagram, this non-uniform transformation of the P-axis produces (if v decreases rapidly when P increases) a 'folding' that indicates a first-order transition [7]. This is the way in which the liquid–vapour coexistence line appears in the van der Waals equation for a fluid. For our model, since $v(P)$ at $T = 0$ has an abrupt discontinuity at $P = P_{\mathrm{cr}}$, the attraction generates also a new first-order line ending at a critical point. It seems to be [10] that for water this critical point lies at temperatures higher than T_G, so the first-order line determines two different sectors of the glassy phase of water. These two sectors correspond to the experimentally observed high-density amorphous (above the first-order line) and low-density amorphous (below the first-order line) phases [10, 22]. In our model, these two phases differ in the fraction of particles that are paired, and thus they can also be named high-density and low-density amorphous phases.

We have relied in our discussion upon the existence of a thermodynamic phase transition for hard spheres, that is not rigorously proven to occur. However, for slightly different forms for s_c^{HS} (which may imply the absence of an ideal glass transition) to that given by equation (6), our results still remain valid, except for the fact that the sharp fragile-to-strong transition (the kinks in the curves of figure 2) becomes a crossover.

The model that we have presented explains the transition between fragile and strong behaviour of water as arising from the competition between two different local structures. To be able to solve the problem analytically, we had to make the crude approximation that these structures correspond to single and paired particles. In real water it is likely that what plays the role of our particles are the so-called Walrafen pentamers [23], which are clusters of five water molecules. These clusters are naturally expected to be accommodated at one of two possible distances from each other [10]. It is clear that in this more general case the mechanism for a fragile-to-strong transition may remain basically the same. In fact, from the way that we solved the model, it is seen that all that is needed is the existence of two different competing structures, regardless of their details. At high T the fragile behaviour is associated with the configurational entropy of each structure individually. At low T the strong behaviour appears due to the combinatorial entropy of choosing locally between the two structures.

References

[1] Angell C A 1991 *J. Non-Cryst. Solids* **131–133** 13

[2] Angell C A 1995 *Science* **267** 1924

[3] Ito K, Moynihan C T and Angell C A 1999 *Nature* **398** 492

[4] Sastry S 1999 *Nature* **398** 467

[5] Starr F W, Angell C A, Speedy R J and Stanley H E 1999 *LANL Preprint* cond-mat 9903451

[6] Jagla E A 1998 *Phys. Rev.* E **58** 1478

[7] Jagla E A 1999 *J. Chem. Phys.* **111** 8980

[8] Sadr-Lahijany M R, Scala A, Buldyrev S V and Stanley H E 1998 *Phys. Rev. Lett.* **81** 4895

[9] Speedy R J 1997 *J. Chem. Phys.* **107** 3222

[10] Mishima O and Stanley H E 1998 *Nature* **396** 329

[11] Canpolat M, Starr F W, Sadr-Lahijany M R, Scala A, Mishima O and Stanley H E 1998 *Chem. Phys. Lett.* **294** 9

[12] Speedy R J 1993 *Mol. Phys.* **80** 1105

[13] Speedy R J 1994 *Mol. Phys.* **83** 591

[14] Speedy R J 1998 *Mol. Phys.* **95** 169

[15] Young A P (ed) 1998 *Spin Glasses and Random Fields* (Singapore: World Scientific)

[16] Speedy R J and Debenedetti P G 1996 *Mol. Phys.* **88** 1293

[17] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139

[18] Cho C H, Singh S and Robinson G W 1996 *Phys. Rev. Lett.* **76** 1651

[19] Rustad J R, Yuen D and Spera F J 1990 *Phys. Rev.* A **42** 2081

[20] Horbach J and Kob W 1999 *Phys. Rev.* B **60** 3169

[21] Starr F W, Sciortino F, Harrington S and Stanley H E 1999 *Phys. Rev. Lett.* **60** 1084

[22] Mishima O, Calvert L D and Whalley E 1984 *Nature* **310** 393
Mishima O, Takemura K and Aoki K 1991 *Science* **254** 406
Mishima O 1994 *J. Chem. Phys.* **100** 5910

[23] Walrafen G E 1964 *J. Chem. Phys.* **40** 3249
Monosmith W B and Walrafen G E 1984 *J. Chem. Phys.* **81** 669