

Fluctuations, clusters, and phase transitions in liquids, solutions, and glasses: from metastable water to phase change memory materials

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We revisit the relations between clustering, fluctuations and thermodynamics for a range of clustering and disordering phenomena in liquids, seeking commonalities and links to phenomena reported at this meeting.

1. Introduction: clustering, thermodynamics, and scattering

In my concluding remarks I have taken, as my main connecting thread, the phenomenon of clustering of molecules in the liquid state. But since the subject material of the meeting has been broadened to include specifically the matter of crystallization and liquid structure I will also branch into that when it seems appropriate. The two are often interwoven.

As Anisimov has reminded us at this meeting,¹ the presence of large scale clustering usually has consequences in the density or enthalpy and on their intrinsic fluctuations. Fluctuations in these extensive properties are manifested in the familiar response functions, heat capacity, expansivity and compressibility, and the precise relations were written down in the famous Landau–Lifschitz text on Statistical Physics.² These relations are very well known and are reproduced below. They tell us that clustering of molecules, ions *etc.*, in liquids is likely to be associated with anomalies in the response functions.

The isothermal compressibility reflects directly the mean square volume fluctuation, $\langle(\Delta V)^2\rangle$, through the relation,

$$\kappa_T = \langle(\Delta V)^2\rangle/Vk_B T \quad (1)$$

while the heat capacities, C_v and C_p , are related to the corresponding kinetic energy fluctuations

$$C_v = kT^2/\langle(\Delta T)^2\rangle \text{ (at constant volume)} \quad (2)$$

and entropy fluctuations,

$$C_p = kT^2/(\langle \Delta S \rangle)^2 \text{ (at constant volume)} \quad (3)$$

Since the isothermal compressibility is also related to the long wavelength limit of the isobaric structure factor, this scattering quantity is also directly related to the mean square density fluctuation.³ The relation is the well-known

$$S(0) = \langle (\Delta N)^2 \rangle / N = \rho k_B T \kappa_T \quad (4)$$

where N is the number of particles, $\langle (\Delta N)^2 \rangle$ is the mean square fluctuation in N , ρ is the number density, and κ_T is the isothermal compressibility defined above, and by the thermodynamic relation $\kappa_T = (\partial^2 G / \partial p^2)_T / V$.

To these familiar relationships we need to add the relations connecting fluctuations in concentration to thermodynamic functions of *multicomponent* systems. These fluctuations manifest themselves spectacularly in many binary and multicomponent systems where the components mix with positive deviations from ideality, and tend to split into two phases at lower temperatures. As is well known, the concentration–concentration fluctuation lengthscales and times both diverge, in many cases, at the *consolute* temperature, which is a critical point in every sense of the word. To my surprise we have not seen much, if any, mention of the corresponding relation between these fluctuations and the solution thermodynamics, at this meeting though they surely belong at the forefront of our thinking in discussion of clusters in liquid solutions. The thermodynamic equivalent of the compressibility for concentration fluctuations is the activity coefficient, and of course it is this quantity to which the scattering related quantity, S_{cc} , is related.

The relations laid out by Bhatia and Thornton⁴ in a famous paper dealing with metal alloy thermodynamics, are:

$$S_{cc}(0) = N \langle (\Delta c)^2 \rangle,$$

where $\langle (\Delta c)^2 \rangle$ is the mean square fluctuation in the concentration, and is further related to the inverse of the second derivative of the Gibbs free energy with respect to concentration by

$$S_{cc}(0) = N k_B T / [\partial^2 G / \partial c^2]_{T,P,N}$$

which means that the concentration fluctuations, hence the related scattering intensities are giving information on the thermodynamic activity coefficients of the components.

They have been particularly useful in relating excess neutron scattering data to thermodynamic observations for cases of critical demixing, *e.g.*, in metal–ammonia (deuterated) solutions⁵ and metal–molten salt solutions.⁶

Away from the binary solution critical point (consolute temperature) the fluctuations do not occur on all length scales up to the correlation length, but still occur, leading to anomalies in the various measurable quantities, activity coefficients, heat capacities and compressibilities (hence also sound velocities, *etc.*). In this concluding talk of Faraday Discussion 167, I want to range over these signs of anomalous structuring in the liquids in a number of different contexts, relating

them, where I can, to the subjects that have been addressed by our contributors here, and inviting their study where they have not.

2. Structural questions, and the heat capacity as a diagnostic

Of course the question of structure is always a tricky one in liquids. When the same phenomena are seen in solids it is usually possible to decide what, in the way of structural entities, might be responsible. For this reason I will start this contribution by reference to a couple of cases where phenomena similar to those that are seen in liquids, can occur. This meeting, like so many others, has given a lot of attention to the subject of water so I will use water as an example to make my point.

Water is famous for its extraordinary, highly anomalous, heat capacity in the supercooled state, $T \ll 0^\circ\text{C}$. Only liquid silicon and liquid sulfur have anything like it. We show the data below, but first we want to look at a case for which there is much understanding. An excellent example of a system that (i) has a major anomaly in the heat capacity, and also (ii) has a well-defined glass transition at lower temperature, where a state of disorder is frozen in, and (iii) that is well-understood structurally, is the simple ordered alloy Co-Fe.^{7,8} This is one of the simplest of a very broad variety of cooperative transitions falling in the Ising model universality class. The lambda form of the heat capacity is very well known and approximately derivable by Ising model theoretical treatments made famous by Onsager and others. Popularly known as order-disorder transitions, these convert ordered or phase-separated systems at low temperature into infinite clusters at the critical point and then to smaller clusters on the other side of the critical point. At the lambda temperature the order parameter characterizing the state of order of the system, falls to zero.

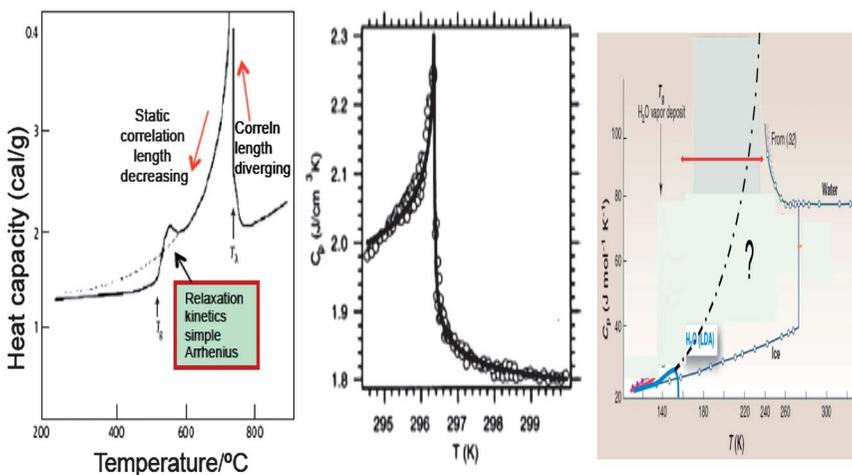


Fig. 1 Heat capacity forms for cooperative disordering systems generating infinite clusters at a critical point. From left, (i) solid Co-Fe ordered alloy (two interpenetrating simple cubic lattices, becoming random BCC above critical temperature T_1) (ii) separate isoctane and perfluoroheptane phases becoming a single phase solution with infinite clusters at the critical temperature (consolute temperature at 296.4 K) and (iii) rationalization of the observed heat capacity behavior of water, on either side of "No-man's land" (indicated by the horizontal red bar) where only very short time scale measurements can be made, see text.

The third of the systems in Fig. 1 is the case of water's heat capacity as published in 2008 (in Science⁹), and elaborated upon more recently in ref. 10, as a way of explaining the weird combination of vanishingly small change in heat capacity at the glass transition at 136 K, and the exponentially increasing heat capacity as the liquid approaches its homogeneous nucleation temperature at 235 K during cooling.¹¹

Our point is, of course, that the strangeness of supercooled water can be understood if it is recognized as the high temperature arm of a critical order–disorder process, just like the well-studied liquid–gas phenomenon at 374 °C but involving the angle disordering of the open hydrogen bond network during heating, or its re-establishment during cooling. Note that this phenomenon lies entirely in the volumetric consequences of the ordering. No unusual heat capacity changes occur, and no excess scattering (due to structural fluctuations) would be seen, if the volume is held constant.¹¹ To continue the discussion, we put aside for the moment the current controversy over whether or not there can be two coexisting liquid phases on time scales short with respect to crystallization, supposing for the sake of argument, that there are (in which case, with the right combination of pressure and composition manipulations,¹² it will prove possible to see them by freeze fracture electron microscopy – and of course their absence would bolster the case for the converse).

Continuing, it would of course be strange indeed if the critical point for this special liquid (and this special disordering process) should lie exactly at ambient pressure. The form of heat capacity would be modified somewhat to a rounded form if the T_c lies at small positive pressure, or alternatively, it would have first order transition character (like that of liquid silicon) if the critical point should lie at negative pressure, as various lines of evidence suggest could be the case.^{9,10} Measurements of heat capacity during rapid scans on thin glassy water films¹³ would support the latter¹⁰ but, for the purposes of this meeting, this question is best left aside.

The controversies in the case of water,¹⁴ particularly the most recent ones,^{15–19} arise from three different sources. There are those where different simulation approaches, hybrid Monte Carlo *vs.* metadynamics, for instance, yield different results for nominally the same state points, there are those involving purely technical discrepancies with the same simulation method (which were detailed in a helpful way at this discussion [by Palmer *et al.* and the pertinent discussion²⁰] and which must be left to the algorithm experts to clarify), and then finally there are those that are a consequence of the high mobility of the molecules near the contested critical temperature. We will comment on the latter with the new observations,¹² in mind.

The problem caused by high mobility is that the exploration of configuration space is so rapid, that structural changes in the liquid become inseparable, on experimentally accessible time scales, from crystal nucleation time scales. *i.e.* before either critical point or first order liquid–liquid transition (if they exist) can be observed, the system has crystallized. Such crystallization is greatly repressed if the cooling is carried out at constant volume, when it would occur closer to –90 °C (since the pressure increases during constant volume cooling) or if it is carried out at temperatures near the glass transition itself, where the outcome of a cooling process can easily be preserved for inspection. This is the case we wish to consider here.

Let us consider the relation between the nucleation and crystallization temperatures for a well studied glassforming system, $\text{Ca}(\text{NO}_3)_2\text{-KNO}_3$ near the limit of its glassforming range.²¹ Fig. 2 shows a relation between internal relaxation time (liquid equilibration time) and crystallization time (the latter being the time needed to crystallize 45% of the liquid and generate a peak in the crystallization exotherm – see ref. 22 for details). The experiments can distinguish the time scale for nucleation from the time scale for the nucleation + growth. The relationship of these to the internal relaxation time (τ_{in}) is very similar to that shown for water (using an inverse temperature axis) by Limmer and Chandler in Fig. 5 of their paper in this Discussion.²³ However, because in the CKN case the data are taken near T_g where everything is slowed down, there is no problem in bypassing the crystallization to obtain the glassy state, just by minor manipulation of the cooling rate (there is no critical point to observe in this case). Structural changes within the liquid state can then be observed at leisure during annealing, the nucleation being greatly delayed by the longer length scale of nucleus-forming fluctuations relative to liquid structure-changing fluctuations.

The same result is obtained by adding salt or other molecular solvents to water, breaking down the network and lowering the temperature, and removing the possibility of large cluster build up, until temperatures near the glass temperature can be reached. One of the early observations of residual clustering in cold aqueous solutions was in the light scattering study of the $\text{LiCl-H}_2\text{O}$ system by Hsich *et al.*,²⁴ recently revisited by the Discussion Chairman Klaas Wynne and his group,²⁵ see also, ref. 26 where an interesting new anomaly arises amongst the hydrate compositions.

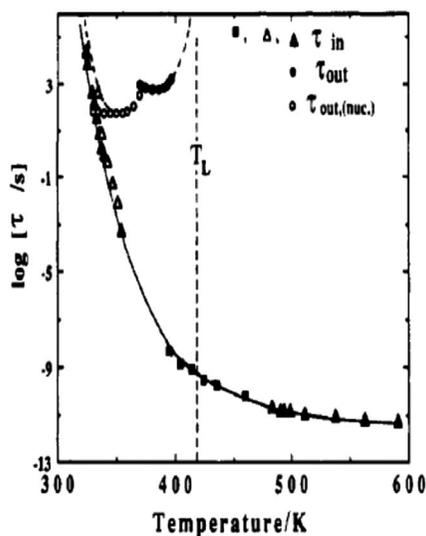


Fig. 2 Relation between internal relaxation time and nucleation time (or crystallization time, which is time for nucleation + growth) obtained near the edge of the glassforming range of the well known model glassformer system, calcium potassium nitrate (4 : 6), by means of one and two-step differential scanning calorimetry techniques (ref. 14). Compare with Fig. 5 in ref. 23. Reproduced from ref. 14 with permission of the American Chemical Society.

The liquid–liquid separation that occurs in the LiCl–H₂O system is of an unusual type which has now been explored rather thoroughly in the laboratory by Mishima,²⁷ and in modelling by Le and Molinero²⁸ (and Bullock and Molinero at this meeting²⁹). We note that the second component can serve as a sort of microscope for the tendencies of the solvent to cluster. Indeed the much less pronounced tendencies of the classical glassformer, SiO₂, to generate network clusters during cooling can be enhanced by addition of second components, and a well-established but puzzling phenomenon of essentially pure SiO₂ micro-droplets forming in silica-rich alkali silicate glasses has been re-interpreted in these terms.³⁰

Rather than pursue this avenue, it is better to turn attention to cases of the more conventional multicomponent systems where there are clustering phenomena that result in critical solution temperatures of both upper and lower types, and then also recognize the existence of “hidden” or “disappearing” types of the same phenomenon which leave behind only a non-critical memory of what has now moved out of reach (rather like the end of the “10 green bottles” song...“There was nothing but a sme-ell, a-hangin’ on the wall”). Anisimov has drawn attention, in one of his discussion comments, to the case of 3-methyl pyridine (3-picoline) in water at 70 °C, and since the water +2-picoline system has a closed loop like those considered next, the thermodynamic spike at disappearance, anticipated below, could be explored systematically.

3. Clustering and its consequences near binary solution critical points

Fig. 3 shows the interesting and well-known system, water + nicotine, which exhibits both upper and lower critical temperatures. We have already seen, in Fig. 1, the lambda-like form of the heat capacity through the familiar upper

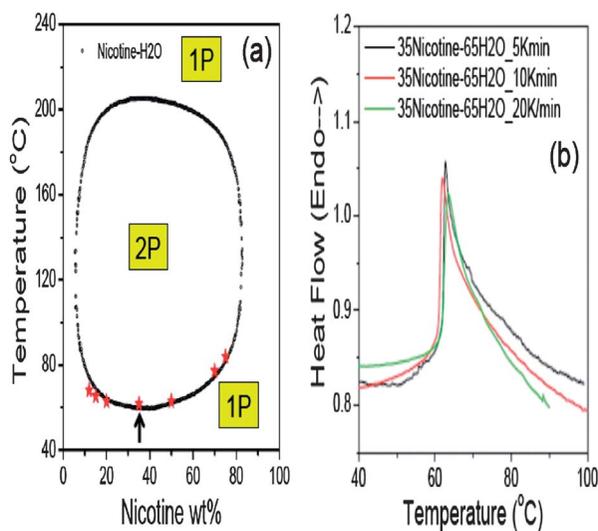


Fig. 3 (LHS) Phase diagram for the water + nicotine system, showing lower consolute point at 35 wt % nicotine (arrow), and (RHS) DSC scans showing the different (mirror image) form of the cooperative excitation profile that distinguishes this case from that seen in Fig. 1 for the upper critical point. Red crosses on LH figure are from DSC endotherms in Fig. 5.

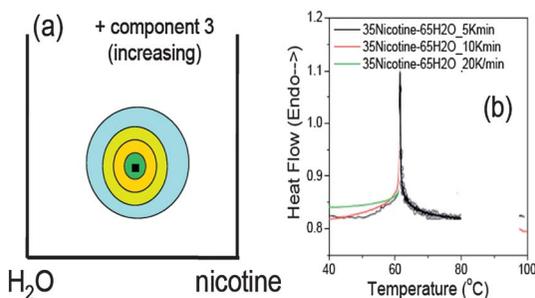


Fig. 4 (a). Phase diagram for a system with a vanishing two-phase loop as a 3rd component is blended in. (b) The heat capacity behavior as temperature is scanned through the composition at which the immiscibility zone disappears.†

critical temperature (UCT) case. Now we show how, as we scan up in temperature from the one phase into the two-phase domain of the (closed loop) water + nicotine system, through the LCT, we obtain just the opposite form of heat capacity with of course some time-dependent effects due to the slow kinetics of two-phase composition equilibration. Precise heat capacity data for this LCT case, were reported by Thoen *et al.*,³¹ for the system triethylamine–D₂O, and are reviewed by Anisimov and Thoen (see Fig. 1.4.10) in Chapter 14 of ref. 32.

The question naturally arises as to what happens when a third component is added to reduce the incompatibility of the two phases at intermediate temperatures such that the two phase region shrinks first to a point and then vanishes altogether.

This scenario is envisaged in Fig. 4 where we can see how an unusual form of heat capacity would appear for the composition where the two phase domain contracts to a point. For a scan at this composition, the form to be seen is illustrated in Fig. 4(b), constructed from the single phase branches of Fig. 3 and its equivalent for an upper critical temperature (obtained from part 2 of Fig. 1 (which we confirmed by scans through the consolute point of the water–propylene carbonate system – $T_{\text{consolute}} = 61.1\text{ }^{\circ}\text{C}$ – see below).

Then, for compositions a little further removed from the two phase domain, only a weak heat capacity anomaly, and weak excess neutron scattering, would be observed. Critical fluctuations die off rather rapidly as the distance from a critical point increases, so the chances of encountering such anomalies, without guidance from systems in which the two phase domain is observable, would be small, but may suffice to explain some unexplained observations, suggesting heterogeneities, in multicomponent systems.

† A practical example of this sort of system was suggested by M. Anisimov in the General Discussion of Professor DeBenedetti's paper. It is the 3-methyl pyridine (3MP) + water system, with a hidden critical point at about 70 °C that can be "brought out" by small additions of salt (*e.g.* 0.4 % NaCl). Confusingly, it is also reported by Jung and Jhon³³ that the β -picoline + water system has a large immiscibility loop. β -Picoline and 3-methylpyridine are the same compound. We observed liquid immiscibility in this binary system ourselves, though had made no special effort to purify the starting materials. The complexity of this system and the need for special attention to equilibration is brought out in the detailed study of the three component system water–3MP–NaBr.³⁴

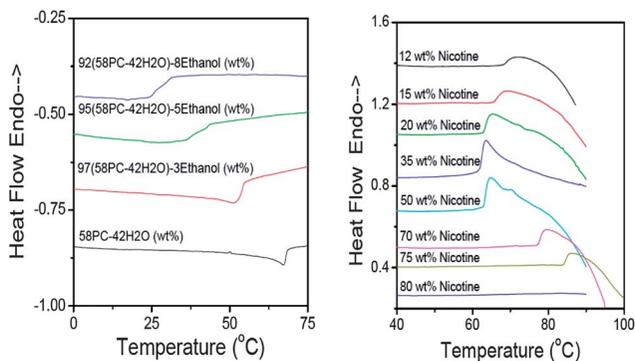


Fig. 5 (a) and (b) effects of composition changes on the heat capacity behavior in systems with binary solution critical points with associated clustering phenomena.

When, instead of diminishing the entire two-phase domain to a point, one merely pushes the probed composition towards the edge of that domain by adding a third component, a different heat capacity effect is seen. Fig. 5(a) takes the case of the system water + propylene carbonate (PC), which has a consolute point at 61.1 °C and 19.3 mol % (57.5 wt %) PC,³⁵ and shows the effect on the DSC *downscans* (from the single phase region into the two-phase region) of adding ethanol as third component. The change in studied composition, away from criticality towards the homogeneous solution domain, systematically eliminates cooperativity from the phenomenon. The conversion of the lambda like-transition into a glass-like transition is probably of significance to the understanding of both types of transition. Of course, in the glass transition, the decrease in heat capacity at low temperatures results from the kinetic elimination of a degree of freedom. (However, see the interesting and anomalous case of LiCl–H₂O at hydrate compositions²⁶). In the case of Fig. 5, it is an ergodic effect that is being observed, where, for structural reasons, the high temperature state has additional degrees of freedom, due to the composition fluctuations that are permitted.

The same effect may be seen in *upscans* in the two-component water + nicotine system for which the phase diagram was shown in Fig. 3. Fig. 5(b) shows DSC *upscans* as composition is changed in each direction from that of the lower consolute point. The most dilute solution (12% nicotine) is still inside the two-phase domain and the composition that is tangent to the 2-phase area, (known as the *plait* point) is unfortunately inaccessible, being well above the boiling point of water. The case referred to in the introduction to this section would provide a better case to characterize the thermodynamic signature of plait point clustering.

Heat capacity measurements are only viable detectors of inhomogeneity (clustering) effects in liquids if the inhomogeneities involve a substantial enthalpy of assembly. For many phenomena, much more sensitive methods of detection of heterogeneities are available. These are the light scattering methods, based on scattering from refractive index fluctuations. Refractive index fluctuations themselves are intimately related to the density fluctuations that determine the response function compressibility as given in eqn (1). The inhomogeneities in focus in the next sections have been revealed by light scattering techniques. We note also the relevance of neutron scattering techniques when the contrast in

neutron scattering lengths of the solution atomic species is favorable,⁶ and Raman scattering techniques using multivariate analysis, as described by Ben-Amotz in his paper presented in the Discussion.³⁶

4. Micelles and mesophases, vesicles

Related to the above-discussed area, are the fields of micelles and mesophases, with their critical micelle concentrations, and critical divergences underlying weak first order phase transitions – for which there exists a huge literature. This is not to be discussed here except for the boundary between the domain of nematic liquid crystals and glassforming liquids, as it relates to molecular aspect ratios, which has a special interest for the present authors.³⁷ This boundary has been studied by the same optical Kerr effect (OKE) spectroscopy used by Torre, in this Discussion,³⁸ to analyze the buildup of inhomogeneities in water as it supercools towards the controversial singularity at 227 K. OKE is a time domain measurement covering the time scale range from ps (below the librational resonance time in the IR) down to ns. It is the *time domain* equivalent of the *frequency domain* depolarized light scattering phenomenon.

Fayer and coworkers^{39,40} have used OKE spectroscopy to study the power law governing orientational fluctuation times in systems undergoing the (weakly first order) isotropic–nematic transition, (for which NMR studies yield the famous Landau–de Gennes singularity slightly below the liquid crystal boundary – *which, like the water 2nd critical point, can only be identified and quantified by theoretical analysis, because of pre-emption by the first order I–N phase transition*). These authors showed that the exponent in the power law describing the reorientation time scale, increases towards unity as the aspect ratio of the molecule under study decreases towards unity. For aspect ratios below 2.5, no liquid crystal phases were found, but the power law describing the OKE scattering continued to describe the single phase liquid

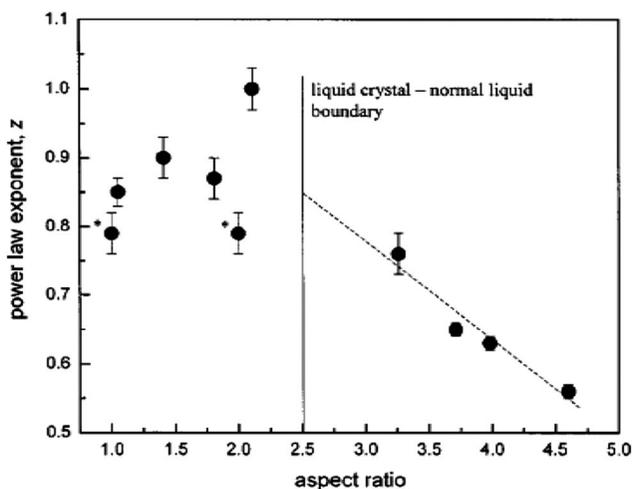


Fig. 6 Exponents of the relaxation time power law deduced from OKE scattering. Compare the cases in which the system approaches an isotropic–nematic first order phase transition temperature, with those for molecules of lower aspect ratio that are merely glassforming.

behavior, with exponents ranging from 0.8 to unity. What sort of clustering does that imply for the smaller aspect ratio liquids? The Fayer group findings are reproduced in Fig. 6. The glassforming ability of the liquids to the left of the vertical line in Fig. 6 is perhaps the reflection of an inability, at lower aspect ratios, to relieve the frustration described by Tanaka, (in the opening lecture⁴¹) by first order liquid–liquid transition. Indeed, for van der Waals ellipsoids at aspect ratio 1.45, it seems that there is no crystal phase more stable than the liquid, down to 0 K – which is the definition of the “ideal glassformer”.³⁷

The relation of the OKE studies to the frequency domain depolarized light scattering (DLS), has been examined in detail Brodin and Rössler⁴² using some of the same liquids studied by Fayer and co-workers. From the comparison, it seems that OKE provides a wider dynamic range than DLS, but probably is not examining anything more cluster-related than that provided by the excess wing absorption of dielectric spectroscopy (about which little is understood).

An alternative light scattering technique, Raleigh–Brillouin scattering, that may be more helpful with respect to giving insight into cluster build-up, is discussed in a final section of this paper, after giving some attention to a fascinating type of inhomogeneity, apparently of very large spatial dimensions (but of minimal thermodynamic significance) that has been introduced to this meeting by Sefcik and coworkers.

5. Feeble clusters

An interesting and provocative type of clustering has been described at the Discussion meeting by Sefcik *et al.*⁴³ The phenomena that Sefcik and co-workers describe might have importance reaching well beyond their particular study of simple binary aminoacids (glycine or alanine) in water. A key feature of their clusters is that they could be easily disrupted by mechanical forces such as stirring and filtering, from which rupture they re-establish themselves on very long time scales. This was also the finding of Fischer, Patkowski and colleagues at the Max Planck Institute for polymer research who conducted a number of investigations into what have since become known, in the field of supercooled liquids, as “Fischer clusters”.

Fischer clusters are the slowest-forming, slowest-relaxing, longest correlation length, inhomogeneities ever discussed in the liquids field – by many orders of magnitude in each case. They are observed in both polymers⁴⁴ and glassforming liquids:⁴⁵ for a short review see ref. 46. While controversial, most workers concede they are real, and the principal authors^{45,47} believe they are to be understood in hierarchical terms with “fluctuons”, of nm dimensions, as the correlated entities.⁴⁷ When the hierarcharchical structure is fully developed, speckle patterns may be observed, *e.g.* in *o*-terphenyl at 293 K, see Fig. 3 of ref. 47. The Fischer clusters are, however, thermodynamically *inconsequential* since the alpha relaxation time (always very sensitive to thermodynamic state because of the inverse exponential dependence on configurational entropy^{48,49}) proves *not* to depend on whether the clusters have developed or not.⁴⁴ It would be of great interest to determine whether or not this is true of the alanine and glycine mesostructures of ref. 43 as well, by determining, for instance, the dielectric relaxation time before

and after a filtration process (or an ultrasonic agitation process) that temporarily removes (or disrupts) the mesostructures.

6. Clustering in single component liquids

The Fischer clusters discussed above, actually belong in this present section as they have been studied most carefully in single component systems. However, we preferred to give a separate section to the “feeble cluster” type of phenomenon.

Light scattering studies of the Rayleigh–Brillouin type have an important role to play in the study of inhomogeneous structure development in single phase liquids as they supercool towards the glass transition. It is known that, in the Rayleigh–Brillouin spectrum of glassforming liquids in their high temperature Arrhenius, the ratio of the central Rayleigh line intensity to the sum of the two Brillouin line intensities (known as the Landau–Placzek (LP) ratio) has a well-defined theoretical value determined by the state variables density and entropy.⁵⁰ It is argued, for instance by Popova and Surovtsev,⁵¹ that any departure from this theoretical behavior implies the need for an additional order parameter, and thus is a direct indication of inhomogeneity onset in the liquid.

An increase in the LP ratio was part of the evidence provided by Fischer and coworkers for the anomalous clustering found, on sufficiently long standing, in the case of the model glassformer orthoterphenyl (see Figure 13 in ref. 46 for the LP ratio in OTP with and without Fischer clusters). A detailed study of this blow-up of the LP ratio on cooling into the super-Arrhenius domain of glassforming liquids, has been provided in ref. 51 for a number of the liquids studied by OKE and DLS that were discussed in a previous section for systems near their isotropic–nematic liquid crystal boundary. Some data illustrating the dramatic

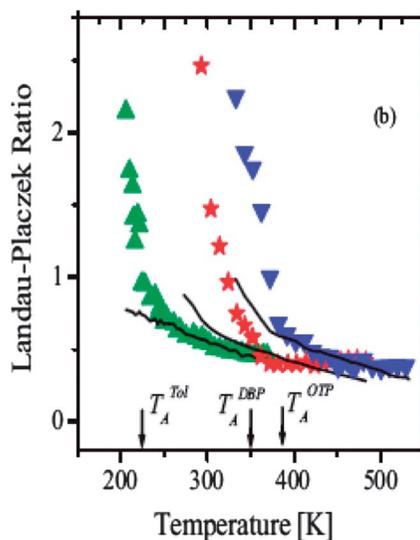


Fig. 7 Temperature dependences of the Landau–Placzek ratio (b) for dibutyl phthalate DBP (red stars), for toluene (Tol) (green up triangles), and for OTP (blue down triangles). Lines correspond to the theoretical estimations for simple (unclustered) liquids. The limits of high temperature Arrhenius behavior are marked T_A in each case.

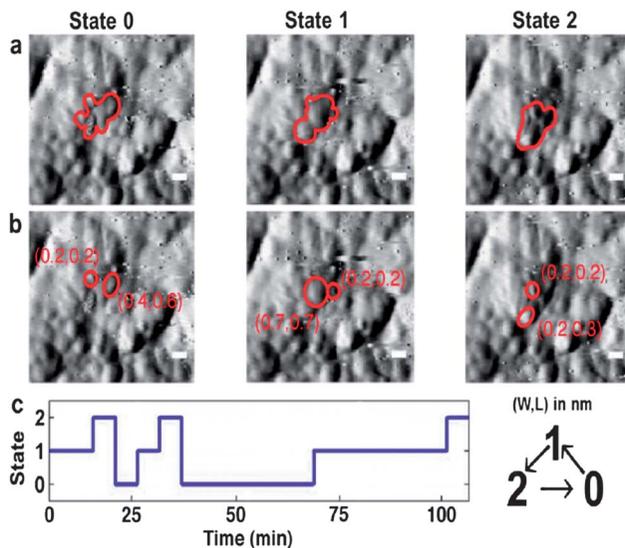


Fig. 8 Visualization using STM images, of two-state rearrangement events, by means of which the glass structure can reorganize (from ref. 53 by permission of Amer. Inst. Phys.).

departure of the LP ratio from the simple two-parameter domain, as the liquid enters the super-Arrhenius state, is shown in Fig. 7. The authors interpret this in terms of scattering from the inhomogeneities that arise, as “locally preferred structures” of the type discussed in Tanaka’s opening lecture,⁴¹ start to form. Clearly they form with rapidly increasing population as the system cools into the low temperature domain. It should be stressed that this is not *in any way* associated with ergodicity-breaking, which only occurs at much lower temperature as the *glass-transformation range* is entered. The glass transformation range is entered when, during cooling at a “standard” 20 K min^{-1} , relaxation times within ~ 2.3 decades of the 100s characteristic of the “standard” glass transition temperature, are reached. Clearly this transformation range (across which the system passes from 99% structurally equilibrated to 1% equilibrated) will depend on the cooling rate. The *temperature range* over which the ergodicity-breaking occurs, depends critically on the liquid “fragility” – and to a lesser extent on the non-exponentiality of the relaxation process⁴⁶ – which will not be discussed here. It is a frequent misconception, (or at least a terminology misuse) particularly among simulationists, that the onset of dynamic heterogeneity is somehow also the onset of “glassy” dynamics. The word “glassy” has always implied broken ergodicity, and therefore time-dependence of physical properties, whereas dynamic heterogeneity, and any related static cluster statistics, are strictly part of the ergodic behavior of supercooled liquids.

The growing-in of such locally preferred structures was nicely illustrated by Royall and co-workers in their paper presented at the meeting,⁵² using simulations to identify the populations of various low-energy packing motifs. An important feature was the observation that the lifetime of clusters of energetically favored topology, can greatly exceed the alpha relaxation time. Furthermore there was no correlation between static and dynamic correlation lengths defined for the

population of anticrystalline-structured clusters. The question of a connection between cluster energetics, correlation lengths (static or dynamic), and overall liquid slowdown (α relaxation time) evidently remains very open.

What cannot be seen in these simulations even with a bias to select the lowest energy trajectories, is the final state, in which a state of vanishing diffusivity ($D = 10^{-22} \text{ m}^2 \text{ s}^{-1}$) is reached at the experimental glass transition temperature. The simulation time scales stop short of those explored in the experiments, by some *eight* orders of magnitude.

However, the type of packings found in experimental glasses, and the manner in which *configurational excitations* can lead to rearrangements of the particles within them (and so to the laboratory glass transition), is now being visualized directly, thanks to high resolution scanning tunnelling microscopy (STM) studies of glass surfaces that are currently being executed by Ashtekar *et al.*⁵³ of the Gruebele group. These workers take advantage of the atomic simplicity of metallic glasses to monitor the surface packings and their two-state reorganizational dynamics (for which movies are available). These workers have also studied cerium-based glasses⁵⁴ and amorphous silicon⁵⁵ at temperatures that they believe lie below the experimental glass transition temperatures for the bulk amorphous phases, though the estimate used for the glass temperature in the latter case is probably rather inaccurate (if we judge by the known diffusivities of *crystalline* silicon⁵⁶).

7. Concluding case. A major change within a single phase, single component, liquid and a connection to technology

This contribution commenced with discussion of the case of water where, despite opinions to the contrary, cooling at one atm. pressure (or decrease in pressure from high pressure low temperature states), appears to be pushing the system into another thermodynamic phase of lower density. It can also be proposed that such changes are pushing the liquid across a supercritical extension of a coexistence line, depending on where one supposes that the second critical point lies. It seems appropriate, then, to conclude our contribution with an example of a liquid in

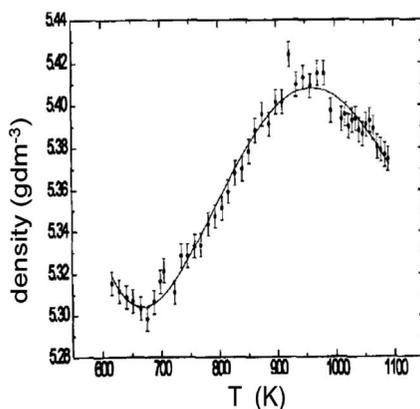


Fig. 9 Anomalous volume vs. temperature relations for liquid As_2Te_3 . The density minimum occurs shortly above the melting point at 640 K.

which both a density maximum and a density minimum exist, and both lie within the stable liquid state, hence beyond the reach of controversy.⁵⁷ The case in question is an interesting liquid, a molten chalcogenide, As_2Te_3 which passes through a semiconductor-to-metal transition at the point of maximum negative expansivity in Fig. 9 – which is also a point of maximum heat capacity. Clearly this is a liquid in which there are major structural adjustments being promoted by change of temperature – but without any first order phase change. Is it a “Widom-line crossing”? Probably not. The high entropy phase in this case is, as in the case of water, a high density phase (Fig. 9). It is noted in ref. 57 that the integral over the heat capacity in the anomalous region is close to the enthalpy of a known phase change in the crystalline state, from monoclinic to rhombohedral, that occurs during heating. The high temperature crystalline phase is also of higher density, and is more metallic in character. Thus one has a good idea of the structural origin of the anomaly in the liquid. In this case, however, the increasing volume during cooling does not seem to be accompanied by any extraordinary viscosity effects as in the case of water. Rather it behaves as a typical fragile liquid, yielding a glassy state if the cooling is fast enough. Pure tellurium is also strikingly water-like, an interesting comparison having been provided by Kanno.⁵⁸ However, like As_2Te_3 , Te is not as cooperative as water, at least not under ambient pressure conditions.

It is interesting that As_2Te_3 is one of three components comprising a technologically exciting ultrafast phase-change switching composition used in the fabrication of light- or heat-activated computer memory devices, pioneered by Ovshinsky and coworkers.⁵⁹ Interestingly enough, a second of the three components in the remarkable phase change switching compositions, is germanium, which has a water-like liquid–liquid phase change – a transition that has been caught in progress by hyperquenching.⁶⁰

One gets the impression from Ovshinsky's writings that the fastest phase change switches occur in systems in which there can be two amorphous phases, and one crystalline phase trapped in the glassy matrix, all separated by only small energy barriers and capable of switching from one to the other by small voltage, or light, pulses. How strange it would be if some clustered aqueous phase, like Tanaka's glycerol–water solution near its T_g ,⁶¹ with triple free energy basins like those seen in the figures of Palmer's paper at this meeting,²⁰ and also transiently in Limmer and Chandler's,²³ should finally serve to model the behavior of one of computing technologies important phenomenologies!

Concluding remarks

The study of inhomogeneous aspects of liquid and polymer structures, and the associated thermodynamics (where there is a need for additional parameters beyond the usual P and T to properly specify the state of the system) has many intriguing aspects which this Discussion has helped to expose and clarify. Hopefully many of these complexities will become better understood in the coming decade as additional experimental tools and theoretical concepts are applied.

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