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1999 J. Phys.: Condens. Matter 11 A237

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# $\alpha$ and $\beta$ relaxation processes in $\text{ZnCl}_2$ —a computer simulation study

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Received 2 October 1998

**Abstract.** Results for the single-particle motion in a realistic simulation model of the intermediate-strength, network-forming liquid  $\text{ZnCl}_2$  in the vicinity of its melting point are presented. The shape of the self-intermediate scattering function, as seen in incoherent neutron scattering experiments, is compared, qualitatively, with the predictions of the mode-coupling theory.

## 1. Introduction

There is enduring interest in identifying the critical features of the interatomic interactions responsible for the observable differences between strong and fragile glass-forming liquids [1]. Fragile liquids tend to be unassociated van der Waals (e.g. *o*-terphenyl) or simple ionic ( $\text{CaKNO}_3$ ) liquids, whereas strong ones are network-forming ionic liquids such as  $\text{SiO}_2$  or hydrogen bonded systems (glycerol, probably best regarded as intermediate). The different behaviour of macroscopic observables, like the viscosity and the heat capacity at the glass transition, may be rationalized in terms of the ‘energy landscape’ picture [2], though no firm connections between the landscape topology and the elementary interactions has been made. Strong systems often show characteristic differences in more microscopic observables, such as the greater prominence of ‘boson peaks’ in spectra, and the signature of intermediate-range order in diffraction data, but whether these phenomena are intrinsically linked to their strength continues to be debated [1, 3].

A great deal has been learnt through the application of the mode-coupling theory (MCT) about the way that fragile fluids approach the structural arrest which precedes the glass transition [4]. The underlying scenario is that a diffusing molecule is trapped in its cage of neighbours for a characteristic cage relaxation time. The cage relaxation is expressed in terms of the relaxation of the fluctuations in the fluid density on a particular length scale which, in fragile fluids, turns out to be the scale of the distance of closest approach of the particles (i.e. roughly the cage radius). Because the relaxation of the fluid density is itself governed by particle diffusion, the MCT equations acquire a particular self-consistent form, which allows the general shape of relaxation functions to be predicted and certain scaling relationships to be extracted. These seem to be obeyed quite well for many fragile systems. For idealized situations (notably hard spheres) the full MCT equations can be evaluated quantitatively and successful parameter-free comparisons within experiment [5] (and simulation [6]) made. These analyses are not immediately suggestive of reasons for the distinction between strong and fragile fluids (the MCT has only been fully evaluated for hard spheres and, more recently,

for simple molecular liquids [7]). There appears to be no rôle for the boson peak and the intermediate-range order which appear to be strong-liquid characteristics. Attempts to apply the MCT scaling relationships to experimental data on strong fluids have met with mixed success. Meyer *et al* recently [8] reported good agreement for a multicomponent metallic glassformer, whereas in glycerol [9] and  $\text{ZnCl}_2$  [10] the presence of a boson peak in the frequency window of interest prevents a detailed examination. In  $\text{B}_2\text{O}_3$  [11] only ‘remnants’ of MCT behaviour are reported. Recently, Sciortino and co-workers [12] have examined MCT predictions for the slow dynamics with very long simulations on supercooled SPC/E water, which shows strong-liquid characteristics. They report quantitative agreement in this time window.

Simulation studies should help to unravel the relationship between the interaction potential and observable behaviour. Extensive simulation studies of strong ( $\text{SiO}_2$ ) and fragile (e.g. Lennard-Jones mixture) fluids have been made previously—it seems that devising interaction models which recapture the generic properties for the extremes of strength/fragility is more straightforward than for covering the middle ground. On the other hand, at the extremes it is difficult to compare realistic simulations with actual observed behaviour in the region of the structural arrest. For  $\text{SiO}_2$ , this is because experiments have not been performed at the very high temperatures at which the arrest takes place. For fragile systems, molecules of rather complicated shape must be used to avoid crystallization, and this makes *realistic* simulations too time consuming. For such reasons, *quantitative* comparisons with real observation in this region have not been made, especially for the microscopic phenomena like the boson peak and the intermediate-range order. For  $\text{ZnCl}_2$ , which is an intermediate-strength liquid [1], the structural arrest occurs in a temperature range at which detailed diffraction and spectroscopic measurement are possible [10, 13, 14]. Furthermore, it has proven possible to devise a ‘realistic’ interaction potential [15] which reproduces the experimentally observed features and yet which is sufficiently simple to allow the long runs, and large system sizes, necessary to study the structural arrest in simulations.

In previous work with the same simulation model [16, 17], we have examined the ‘vibrational’, short-time part of the relaxation, including an account of the nature of ‘sound modes’ in this system. We have also considered the fluid structure predicted with this model, especially in regard to the intermediate-range order [18, 19]. In this paper we will examine the single-particle motion in the region of the structural arrest, as seen in the self-intermediate scattering function, in order to examine how well this quantity conforms (at a qualitative level) to the predictions of the MCT. The behaviour of the collective motion (density relaxation) will be described elsewhere.

## 2. Simulation runs

The  $\text{ZnCl}_2$  simulations were carried out with the polarizable ion potential model (PIM), which has previously been shown to reproduce structural properties of the liquid very well [15, 18, 19]. In particular, with this model, the ‘covalent’ aspect of the local structure—that the mean Zn–Zn separation is very similar to the Cl–Cl [13]—is attributed to polarization of the  $\text{Cl}^-$  ions which results in a bending of the Zn–Cl–Zn ‘bonds’ between the tetrahedrally coordinated zinc ions [15]. This polarization-induced change in the local structure is associated with the appearance of a prepeak in the structure factor [19], which signals a non-trivial intermediate-range order in the network of  $\text{ZnCl}_4$  tetrahedra.

With this simulation model, we find that the system is able to freeze (at constant density) at temperatures below 650 K [19, 20] (the experimental melting point is 598 K). With the PIM potential, freezing into the experimentally observed  $\delta$ - $\text{ZnCl}_2$  structure is found. Temperatures

in the range 700–600 K turn out to be (see below) most suitable for studying the ‘supercooled’ liquid dynamics. In this range, the structural relaxation is taking place on the 100 ps–1 ns timescale, i.e. a much longer timescale than would be the case for a fragile atomic fluid near its freezing point. The rate of freezing decreases with increasing simulation cell size and it has proved possible to prepare metastable liquids for sufficiently long to study the dynamics. Nevertheless, we continuously monitor the structure factor and abandon runs in which the onset of crystallization is detected (by the appearance of strong peaks in the structure factor corresponding to Bragg peaks of the crystal).

In preparing simulations with which to study dynamics in supercooled liquids, care must be taken to ensure that the lengths of the runs and the simulation cell size are adequate to study the phenomena of interest [21, 22]. For this reason calculations have been undertaken with cells containing 999 and 2001 ions, and we will illustrate the system size effects in the course of describing our results. Care must also be taken to ensure that after a run at a particular temperature has been prepared, sufficient time is allowed to elapse for full structural relaxation to take place before gathering data at the new temperature. For this reason, our runs have been performed in sequence, cooling at constant volume, and with the configuration taken from the end of one run being used as the starting point for a run at a lower temperature. Only small temperature changes ( $\sim 25^\circ\text{C}$ ) were allowed between runs and the density was not changed. After reducing the temperature, at least two structural relaxation times (to be defined below) from the higher temperature were allowed to elapse before statistics were collected. This criterion seemed to produce reproducible results; shorter equilibrium periods gave relaxation functions which resemble those obtained at the higher temperature from which the simulation was prepared. Give that our calculations are made with the PIM, which is more expensive to evaluate than the pair potentials which have hitherto been used in simulations to study the glass transition, these considerations mean that the calculations were very demanding on computing resources. A full list of the simulations from which data was gathered is given in table 1.

**Table 1.** Simulation run lengths over which data were collected.

System size	$T$ (K)	Steps	Time step (fs)	Total time (ns)
999	700	770 000	0.61	0.466
	650	843 800	1.21	1.020
2001	700	439 500	0.73	0.319
	600	1464 200	1.45	2.125

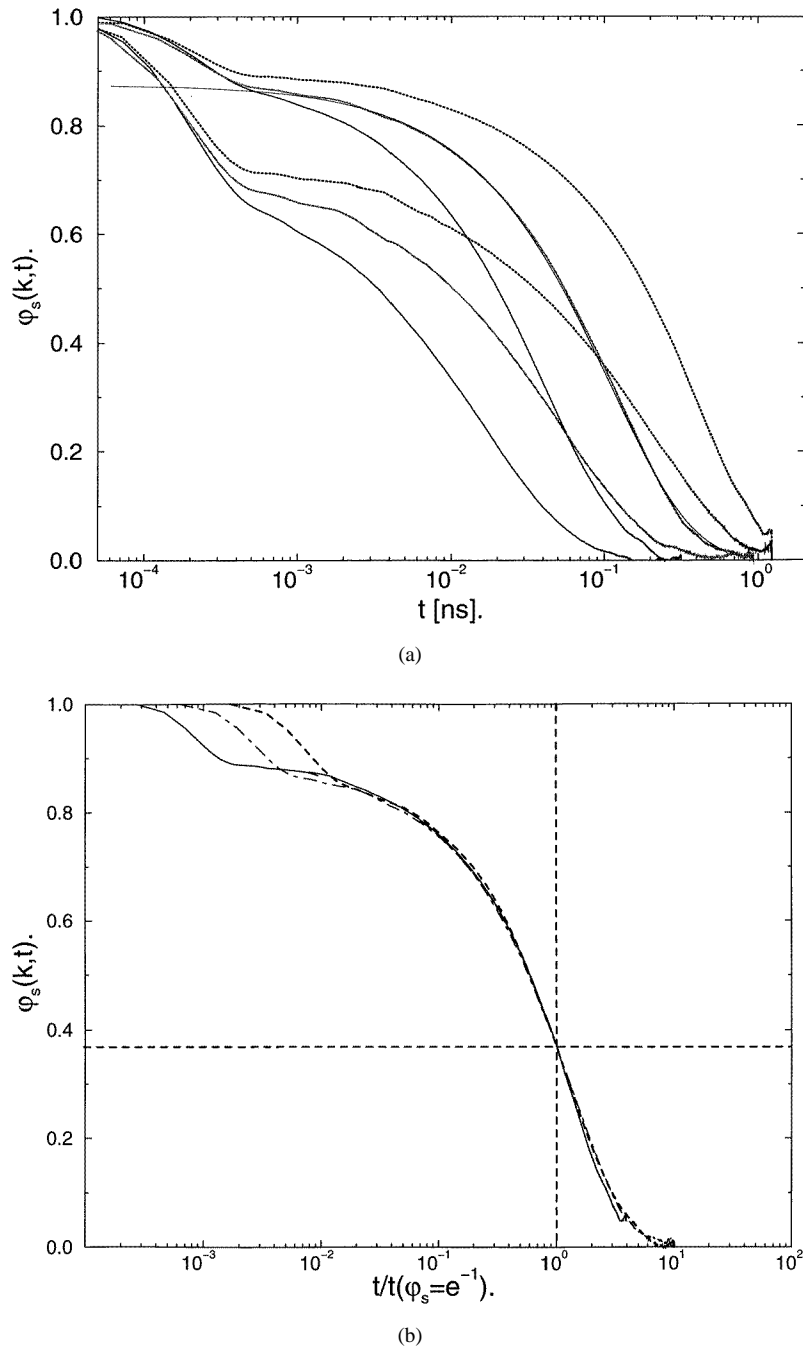
### 3. Single-particle dynamics—the self-intermediate scattering function

The self-intermediate scattering function is given by

$$\varphi_s(q, t) = \langle e^{iq \cdot (r^i(t) - r^i(0))} \rangle \quad (1)$$

where  $r^i$  is the position of ion  $i$  and  $q$  plays the rôle of scattering vector in an incoherent neutron scattering experiment.

In figure 1(a) we show results for  $\varphi_s(q, t)$  of the  $\text{Zn}^{2+}$  ions at three temperatures and at wavevectors of 1.14 and  $1.97 \text{ \AA}^{-1}$  corresponding to points on the peaks of the first sharp diffraction peak [19] and principal peak in  $S_{\text{ZnZn}}$ ; very similar results are obtained for the corresponding function of the  $\text{Cl}^-$  ions. The figure shows the development of the now familiar two-step relaxation as the system is cooled below 700 K. The short-time decay reflects the dephasing of the vibrations of the ions around their (instantaneous) local potential energy



**Figure 1.** (a) Self-intermediate scattering function,  $\varphi_s(q, t)$ , for  $\text{Zn}^{2+}$  ions at 1.14 and 1.97  $\text{\AA}^{-1}$  and temperatures of 700, 650 and 600 K. The smooth line shows a stretched exponential (KWW) fit to one of the curves. (b) 1.14  $\text{\AA}^{-1}$  after scaling the time axis, to indicate time/temperature superposition in the  $\alpha$  relaxation régime.

minima, as described in detail in [23]. This initial decay takes  $\varphi_s$  towards a plateau,  $f_s(q)$ , which becomes more pronounced and extended as the temperature is lowered. Finally, the

long-time  $\alpha$  process sets in, relaxing  $\varphi_s$  to zero. The physical significance of the plateau is that it gives the time range in which the particles are confined by their immediate neighbours, and the  $\alpha$  process reflects the break-up of this ‘cage’. The MCT predicts this general shape qualitatively and, for fragile fluids, makes specific predictions about the shape of the relaxation function in the region about the plateau which is known as the  $\beta$  relaxation régime. The short-time region, where the relaxation function moves towards the plateau, is called the fast- $\beta$  and at longer times, where the function decays away from the plateau to link up with the long-time  $\alpha$  relaxation, it is known as the slow- $\beta$  régime.

### 3.1. The long-time, $\alpha$ relaxation

Our results for  $\text{ZnCl}_2$  as concerns the  $\alpha$ -relaxation of  $\varphi_s(q, t)$  are consistent with those which have been obtained previously for fragile fluids [24] and also for  $\text{SiO}_2$  [25] and water [12]. The *shapes* of the functions in the  $\alpha$  relaxation régime for the same value of  $q$  but at different temperatures are preserved very well. This can be seen (figure 1(b)) by plotting the function versus the reduced time  $t/\tau_\alpha$ , where  $\varphi_s(q, \tau_\alpha) = e^{-1}$ . The long-time parts of the curves for different temperatures fall onto a master-curve, i.e. they obey the ‘time–temperature superposition principle’ over this part of the relaxation behaviour.

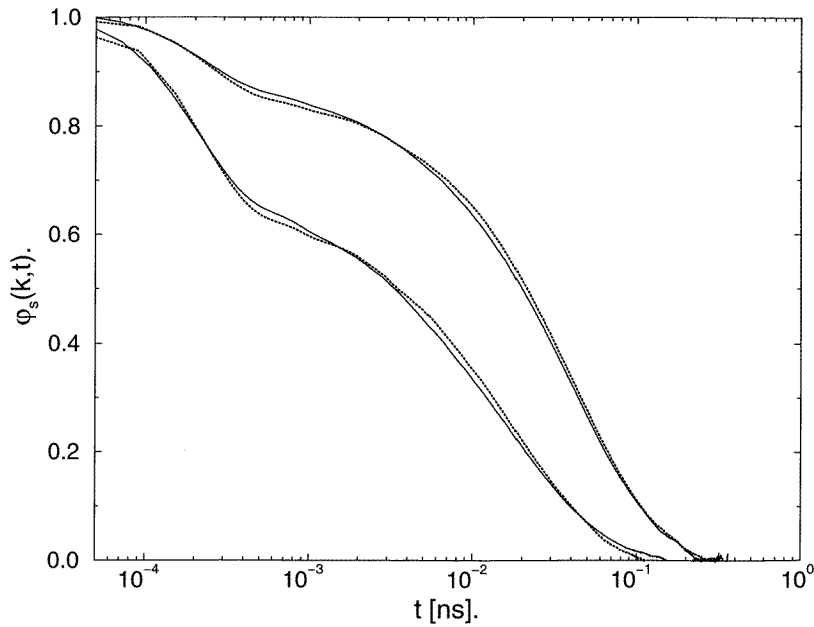
The long-time behaviour is well presented by a stretched exponential (or Kohlrausch–Williams–Watts–KWW) form

$$\varphi_s(q, t) = A_s(q) e^{-(t/\tau_s(q))^\beta} \quad (2)$$

and we have fitted this function to the data in order to extract the  $q$  and  $T$  dependence of the parameters  $A_s(q)$ ,  $\tau_s(q)$  and  $\beta$ . An example of such a fit is illustrated in figure 1(a). As discussed by other workers [24], these parameters are not wholly independent and we have found it best to treat  $\beta$  as a fixed parameter and then allow the other parameters to vary freely in each fit. This process is not sanctioned by theory. The KWW functional form is found to provide a numerically satisfactory representation of the MCT solutions at finite  $q$  [26] if  $\beta$  is allowed a weak  $q$  dependence. It is difficult to test the theory at the requisite level of detail to detect this effect unless the data are noise-free and the range of time over which the fit is to be applied is prescribed. We use the KWW fits as convenient ways for data reduction, and to examine whether the self-motion in  $\text{ZnCl}_2$  shows significant differences from that in other fluids where  $\varphi_s(q, t)$  has been examined in the same way [24]. We find that  $\beta = 0.85$  provides a good agreement of shape over a wide range of  $q$  and  $T$ . Similar fits for fragile fluids tend to give smaller  $\beta$  values, but our value is similar to that obtained from neutron data for the strong metallic glassformer studied by Meyer *et al* [8]. Angell and co-workers have documented the fact that values for the stretching exponent tend to be closer to unity for strong systems [27]. Dreyfus *et al* [10] found a comparatively large value of  $\beta$  ( $\sim 0.8$ ) was required to fit the  $\alpha$  peak in depolarized light scattering experiments.

Within this fitting procedure,  $A_s(q)$  is *approximately* [24] the height of the plateau in  $\varphi_s(q, t)$ ,  $f_s(q)$ , known as the ‘non-ergodicity parameter’ in MCT and as the Lamb–Mössbauer factor in experimental incoherent neutron scattering studies. It is expected to be only weakly dependent on temperature and to vary in an approximately Gaussian way with  $q$ . We find that both these expectations are fulfilled quite well by the data.

The temperature dependence of  $\tau_s(q)$  follows that of the diffusion coefficient extracted from the long-time behaviour of the mean square displacement. Its  $q$  dependence is somewhat more complicated. For (relatively) small  $q$ , up to about the position of the prepeak in the Zn–Zn structure factor,  $\tau_s(q)^{-1}$  appears to be almost quadratic in  $q$ . This corresponds to the prediction of a short-step diffusion model for the relaxation time of  $\varphi_s(q, t)$ . If, on the time and length



**Figure 2.** The figure illustrates system size effects on  $\varphi_s(q, t)$ , showing data obtained for 2001 (full curve) and 999 (dashed) ion simulations at 700 K and at wavevectors of  $1.14 \text{ \AA}^{-1}$  (top) and  $1.97 \text{ \AA}^{-1}$ .

scale of interest, many independent diffusive hops contributed to the particle translation, the process would be Gaussian and the relaxation time would be  $\tau_s(q)^{-1} = D^2$  [28]. However, the process would also be Markovian and an exponential relaxation for  $\varphi_s(q, t)$  would be predicted, whereas we find stretched exponential behaviour at long times, albeit with a low degree of stretching compared to more fragile systems. It has been suggested that this power should be related to the value of  $\beta$  through  $\tau_s(q) \propto q^{-2/\beta}$  and it may be that our observation is also consistent with this relationship, given the large value of  $\beta$ , the limited range of  $q$  available and the limitations imposed by the fitting procedure for the KWW function. In the supercooled region, non-Gaussian behaviour is to be expected on short length scales, since particles trapped within their cage are overwhelmingly more likely to jump back in the direction from which they have emerged rather than make an independent motion in another direction. Hence, especially at large  $q$ , corresponding to short, intra-cage distances, one might expect this correlated aspect of the particle motion to affect the statistics of the relaxation process, even at long times. At larger  $q$  values our results show a much slower increase of  $\tau_s(q)^{-1}$  with  $q$ —closer to linear than quadratic. This result should be treated with some caution, as we have assumed a constant  $\beta$  value in the KWW fits, and it may be that the change in behaviour of  $\tau$  is a consequence of a change in the degree of stretching. However, in analyses of combined neutron and nmr spin-echo data for glycerol, Wüttke *et al* [29] report a cross-over from diffusive behaviour at low  $q$  to dependence of the relaxation time on a fractional power of  $q$  for larger  $q$ .

### 3.2. The $\beta$ region—emergence of a ‘boson’ peak

Whereas the results obtained for the long-time behaviour are in qualitative accord with what has been previously been found for fragile fluids and with the predictions of the MCT, very

different behaviour is observed in the fast- $\beta$  region for  $\text{ZnCl}_2$ . In the  $\beta$  region, MCT predicts that the shape of the relaxation function for different  $q$  values should be identical in a region around the plateau (the ‘first scaling régime’)

$$\varphi_s(q, t) = (1 - f_s(q)) + f_s(q)g(t/\tau) \quad (3)$$

where  $g$  is a universal function and  $\tau$  a  $q$ -independent time. Further,  $g$  should approach the plateau value from above as  $(t/\tau)^{-a}$  in the fast- $\beta$ , and drop below it as  $-(t/\tau)^b$  in the slow- $\beta$  regions. The exponents  $a$  and  $b$  are connected by certain scaling relationships. It should be noted that adherence to the scaling behaviour is predicted only asymptotically close to the structural arrest by the theory, and so examining how well the data conforms to the scaling form of equation (3) should not be seen as a *test* of the theory; however, the scaling form has been found to describe fragile systems over a surprisingly wide range of conditions, and we examine  $\text{ZnCl}_2$  in this light.

As is already clear from figure 1, the approach of  $\varphi_s(q, t)$  to the plateau has a weakly oscillatory character, so that the function undershoots the plateau and rises towards it. This is not predicted by the MCT, nor is it observed in simulations of fragile atomic fluids [24], but similar behaviour is seen in simulations of silica [25]. The oscillation becomes more pronounced as  $q$  increases. Its frequency is only weakly dependent on temperature and  $q$ , which means that the time constants which characterize the fast- $\beta$  part of the relaxation function cannot be linked to those which describe the relaxation away from the plateau; these, as seen above, exhibit strong  $T$  dependences.

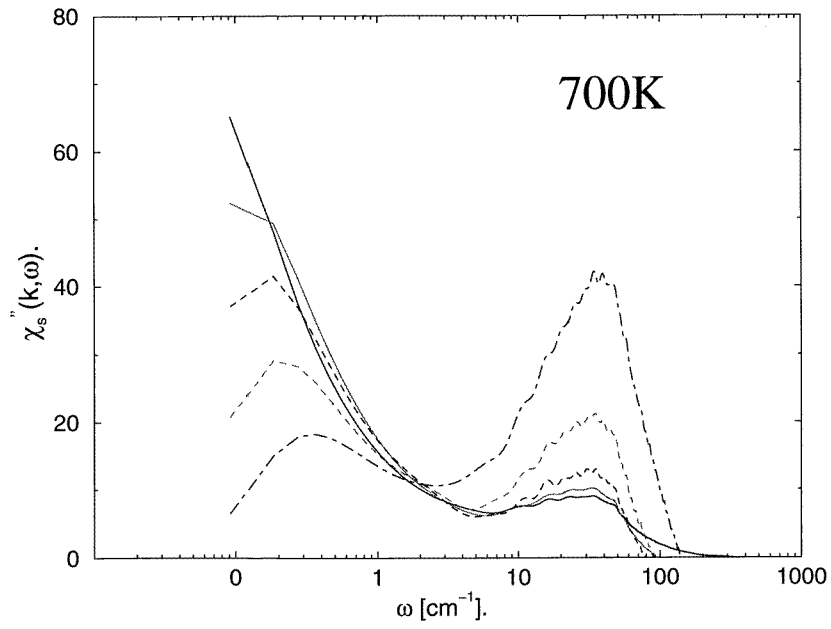
Lewis and Wahnström [30] first showed that the structure in the  $\beta$  region may depend markedly on system size and Kob *et al* [31] have shown that the effect is more pronounced in strong liquids. In figure 2 we contrast the shapes of  $\varphi_s(q, t)$  at the same value of  $q$  and  $T$  in simulations for 999 and 2001 ions. The oscillatory structure is more pronounced in the 999-particle system, and even more pronounced in smaller systems not reported here. Furthermore, there also appears to be an effect on the  $\alpha$  relaxation with the 999-ion system exhibiting a slightly slower  $\alpha$  relaxation. A similar effect was reported in [31]: it is as if the network in the smaller system is more rigid. Although the effect is small, it occurs systematically at many wavevectors, indicating that it is beyond the statistical errors. We regard the 2001 particle results as reliable with regard to system-size effects in the  $\beta$  region. In  $\text{SiO}_2$ , Horbach *et al* [31] have shown that still larger systems are required, but we note that the network in  $\text{SiO}_2$  is considerably stiffer than that in  $\text{ZnCl}_2$ , and, experimentally,  $\text{ZnCl}_2$  is considerably more fragile than  $\text{SiO}_2$ .

The presence of this additional structure and the fact that the range of the scaling régime is expected to vary with  $q$  mean that it is easier to check the extent to which the scaling form applies by examining the spectrum of  $\varphi_s(q, t)$  in the susceptibility representation

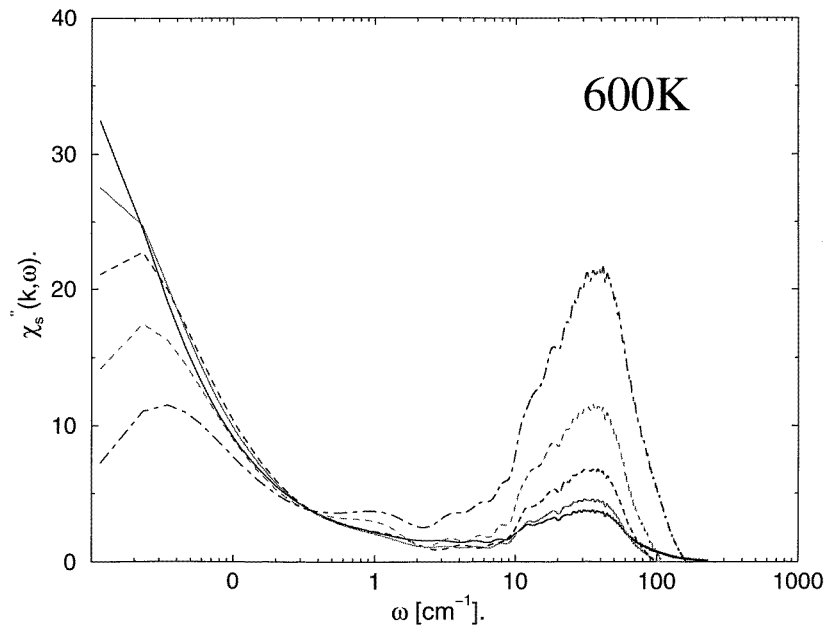
$$\chi_s''(q, \omega) = \omega \mathcal{R} \int_0^\infty dt e^{i\omega t} \varphi_s(q, t). \quad (4)$$

In this representation, the shape of the time correlation function around the plateau is reflected in the shape of the susceptibility around the minimum between the low-frequency  $\alpha$  peak and the high-frequency microscopic region. Figure 3 shows the susceptibilities calculated for several  $q$  values and at two temperatures. At the lower temperature, their shapes in the minimum region agree well for several  $q$  values especially on the low-frequency side of the minimum, showing conformity with the scaling behaviour in the *slow*-beta régime. As  $q$  increases, the range of frequency over which this scaling behaviour applies becomes smaller, so that at the largest  $q$  value it does not conform anywhere. For the higher temperature, the range of applicability of scaling is even more limited. At both temperatures, scaling is not observed on the high-frequency side of the minimum in the susceptibility, corresponding to the





(a)



(b)

**Figure 3.** The susceptibilities of  $\varphi_s(q, t)$  at a series of wavevectors from the 2001-ion runs at 700 and 600 K are shown. Wavevectors of 0.91, 1.14, 1.45, 1.97 and 2.97  $\text{\AA}^{-1}$  in order of low  $\alpha$ -peak frequency are shown.

fast- $\beta$  region. Furthermore, the very steep increase of the susceptibility out of the minimum on the high-frequency side is incompatible with the allowed values of the MCT exponent  $a$ .

These phenomena are the consequences of the oscillatory structure seen in  $\varphi_s(q, t)$  in the time domain. Similar ‘non-MCT’ behaviour has been reported in experimental studies of non-fragile systems in the fast- $\beta$  region, including  $\text{ZnCl}_2$  [10].

The bump, clearly seen in the 600 K susceptibility in the 10–20  $\text{cm}^{-1}$  frequency range, is the boson peak in the simulated system, and is directly linked to the ‘overshoot’ of the plateau in the fast- $\beta$  of the time correlation function. Inelastic neutron scattering spectra [14] exhibit a broad boson peak in  $\text{ZnCl}_2$  at 0.4 THz ( $\sim 14 \text{ cm}^{-1}$ ) at 300–400 K and the Raman data [10] show a peak at 17–30  $\text{cm}^{-1}$  (dependent on fitting procedure and temperature), so that the peak in the simulated system is in the correct frequency range. The ‘bump’ becomes more pronounced for larger  $q$  values, showing that it is associated with small-amplitude motions, and is considerably less distinct at 700 K, despite the fact that the  $\alpha$  relaxation is still well separated from the fast- $\beta$  region at this temperature.

One of the outstanding general questions to be answered about strong and intermediate fluids is whether the boson peak reflects dynamical events which are intimately linked to the approach to structural arrest in these liquids (which would indicate an incompleteness in its description by present versions of the MCT) or whether it is simply caused by some ‘trivial’ local vibration which happens to be at very low frequency and annoyingly obscures the underlying MCT behaviour. Answering this question, even with the aid of the detail available in simulation, has proven frustratingly difficult. Elsewhere [17] we have (tentatively) linked the origin of the excess vibrational density of states in  $\text{ZnCl}_2$  to torsional motions of the network around centres where pairs of  $\text{Zn}^{2+}$  ions are linked by a *bridging pair* of  $\text{Cl}^-$  ions. The overwhelmingly predominant motif of the network connections involves vertex-sharing between the  $\text{ZnCl}_4$  tetrahedra and these bridging sites are regarded as intermediates in the refolding of the network. These connections suggest a tantalizing link between the boson peak and the structural relaxation, but further work will be required before any firm conclusions may be drawn.

## Acknowledgments

The work was supported by EPSRC grant GR/L/49369. MW thanks the Royal Society for a fellowship.

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