# Voids, Layers, and the First Sharp Diffraction Peak in $ZnCl_2$

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The origin of the first-sharp diffraction peak (FSDP) in supercooled liquid $ZnCl_2$ (a network-forming, intermediate strength fluid) is studied by computer simulation. Measures are introduced to characterize *voids* in the spatial distribution of cations and the existence of transient *layered structures* and to clarify their role in producing the FSDP. It is shown that the position of the FSDP is set by the mean intervoid separation and that its intensity is due to density fluctuations with a layered character even well above the glass transition. [S0031-9007(97)05073-4]

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Prepeaks, or first sharp diffraction peaks (FSDPs), appear in the structure factor $S(k)$ of a fluid as the signature of a second length scale in the pair structure. In a one-component liquid, the first (short range) length scale is the nearest neighbor separation $R$, and is related to the position of the principal peak $k_{PP}$ in the structure factor ($\sim 2\pi/R$). In a simple liquid, this also determines the scale of the structure at longer range, through packing requirements. A second (longer) length scale can arise in fluids with more complex interactions for a number of reasons, giving rise to features in the structure factor at *smaller* $k$ than $k_{PP}$. Such FSDPs are observed in widely differing fluid types [1–3]. In Angell's classification [4], fragile liquids (which include atomic and simple ionic ones) are weakly associated and quite mobile at the melting point with the viscosity increasing sharply in the supercooled régime. Strong liquids exhibit an Arrhenius behavior for the viscosity, are viscous at the melting point, and have networklike atomic arrangements. FSDPs are observed in strong [1] *and* fragile [3] fluids, but it is only the former which concern us here. In this case the second length scale reflects *intermediate range order* in the network connections: the slow relaxation of this order under shear may be the origin of the "strong" behavior of the viscosity [5]. It has also been suggested [6,7] that the intermediate range order is linked to the localization of vibrational motions in strong glasses, itself responsible for heat capacity and thermal conductivity anomalies [8] and the appearance of a "boson peak" in various spectroscopies. Despite this interest in the intermediate range order there is no clear consensus on its origin.

Liquid $ZnCl_2$ is an ideal candidate for examination, since diffraction data have been resolved to the partial structure factor level [9] and has been reproduced in computer simulations [10,11]. The diffraction data reveal that the FSDP appears almost exclusively in the cation-cation structure factor [$S_{\mathrm{ZnZn}}(k)$]. The local order consists of a tetrahedral arrangement of $Cl^-$ ions around each $Zn^{2+}$ ion. These tetrahedra corner-link (predominantly) to form the three dimensional network. Computer simulations with a simple ionic pair potential (a rigid ion model, or RIM) predict that the tetrahedral linkage is such as to produce almost linear ($\simeq 160°$) Zn-Cl-Zn bonds—driven by the requirement to maximize the separation of doubly charged $Zn^{2+}$ cations, so that the nearest neighbor separation of a pair of $Zn^{2+}$ ions, $R_{\text{Zn-Zn}}$, is almost twice the Zn-Cl separation. If, however, the interaction model is extended to allow for polarization (polarizable ion model, PIM), bending of the Zn-Cl-Zn bond induces anion dipoles which screen the cation-cation repulsion—thus reducing $R_{\text{Zn-Zn}}$ [11,12].

A comparison of $S_{\mathrm{ZnZn}}$ calculated (using potentials described in [11]) with and without polarization [Fig. 1(a)] shows that the principal peak of the RIM structure factor is split when polarization effects are included, the new principal peak ($k_{PP} \sim 2\pi/R_{\text{Zn-Zn}}$) has moved to larger $k$ (corresponding to the reduction in $R_{\text{Zn-Zn}}$) and an FSDP has appeared at $k_{\mathrm{FSDP}} \simeq 1$ Å$^{-1}$. The new length scale, as signaled by the appearance of the FSDP, has been induced because the closer approach of pairs of Zn ions leads to an *increase* in the cation density at a local level and, as a result, a *reduction* in cation density on a longer length scale [1] relative to what would be expected if the cations distributed themselves uniformly through space under the influence of their coulomb repulsion.

Elliott has suggested that a generic way to explain the new length scale in tetrahedrally coordinated systems is through the average distance between *voids* in the real space structure [13]. The above account of $ZnCl_2$ is clearly compatible with this explanation and snapshots [11] of instantaneous configurations show appreciable inhomogeneities in the spatial distribution of cations, which could be associated with voids. Nevertheless, Elliott's original argument was formulated on a tetrahedral random network model, where voids can be defined geometrically: the concept of a void in a liquid and of an ordering of voids is more difficult to countenance.

We have identified "voids" in the simulated liquid by performing a Voronoi analysis [14,15] of the cation positions in the instantaneous liquid configurations [16]. The *vertices* of the Voronoi polyhedra in a disordered structure define the center of a group of four atoms (which

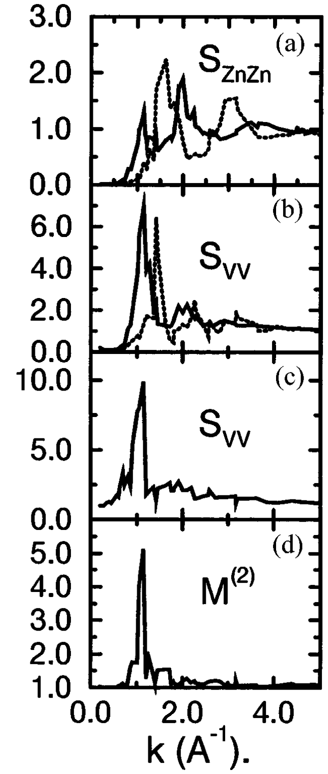

FIG. 1. (a) $S_{\mathrm{ZnZn}}(k)$ for the PIM (solid line) and RIM (dotted) for $\mathrm{ZnCl_2}$ at 700 K. (b) Void-void structure factor, $S_{VV}(k)$ [Eq. (1)] for the RIM (dotted) and PIM (solid line). (c) $S_{VV}(k, \sigma_c)$ for $\sigma_c = 7.0$ a.u. (solid line): the cutoff radius $\sigma_c$ is indicated in Fig. 2. (d) $M^{(2)}(k)$ [Eq. (2)] for the PIM cation distribution.

are mutually nearest neighbors) and are known as the Delaunay simplices (DS) of the structure. Around each DS a circumsphere which passes through the four atoms may be drawn and, since no other atom center lies within the sphere, the radius $\sigma$ of the circumsphere gives a measure of the empty (void) space in between the atoms [17].

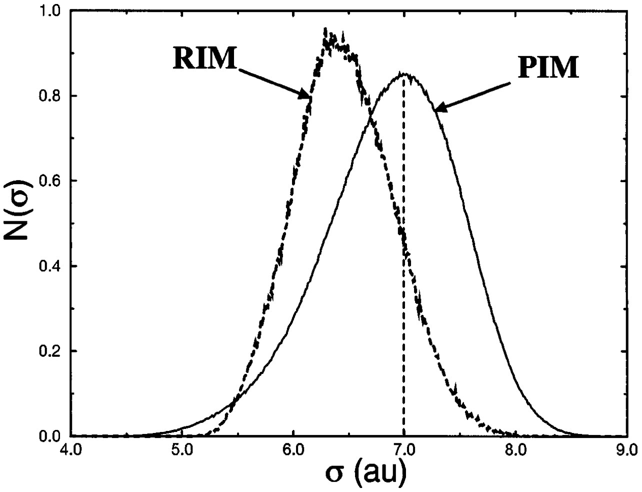

FIG. 2. Circumsphere radii distribution [$N(\sigma)$] for the RIM (dotted line) and PIM (solid). Also indicated on the PIM curve is the cutoff considered for distinguishing large voids.

Figure 2 shows the distribution, $N(\sigma)$ of circumsphere radii for the cation configurations in both the RIM and PIM simulations. The PIM distribution peaks at a larger radius than the RIM and is broader with significant tails to both small and large circumradii. The information in the figure quantifies the idea that the $\mathrm{Zn}^{2+}$ distribution in the RIM is more uniform than in the PIM leading to a smaller average void size and a narrower void distribution.

We can study the relative position of voids in space by treating the DS as the centers of spherical voids, with positions $\{\mathbf{R}^i\}_{i=1\longrightarrow N_V}$, and calculating a structure factor for them, as if they were particles which scattered radiation:

$$S_{VV}(k) = \left\langle N_V^{-1} \sum_{i,j=1}^{N_V} \exp(i\mathbf{k} \cdot \mathbf{R}^{ij}) \right\rangle. \qquad (1)$$

Figure 1(b) shows the PIM and RIM void structure factors, $S_{VV}^{\mathrm{PIM}}$ and $S_{VV}^{\mathrm{RIM}}$ compared with the corresponding zinc partial structure factors, $S_{\mathrm{ZnZn}}^{\mathrm{PIM}}$ and $S_{\mathrm{ZnZn}}^{\mathrm{RIM}}$ [Fig. 1(a)]. $S_{VV}^{\mathrm{PIM}}$ shows two main peaks in the same positions as the FSDP ($k_{\mathrm{FSDP}}$) and the principal peak ($k_{PP}$) in $S_{\mathrm{ZnZn}}^{\mathrm{PIM}}$, with the $k_{\mathrm{FSDP}}$ peak by far the most intense. By contrast, the only feature in $S_{VV}^{\mathrm{RIM}}$ appears very close to the principal peak in $S_{\mathrm{ZnZn}}^{\mathrm{RIM}}$ showing that no new length scale is associated with the voids present in the RIM.

Figure 1(c) shows the normalized void structure factor when only the DS with circumsphere radii larger than a cutoff $\sigma_c = 7.0$ a.u. are included in the calculation of $S_{VV}(k, \sigma_c)$ [Eq. (1)]. As these larger voids are included only in $S_{VV}(k, \sigma_c)$ the intensity of the peak at $k_{\mathrm{FSDP}}$ relative to that at $k_{PP}$ increases, showing that the FSDP position is determined by the separation of the larger voids which are introduced as a consequence of the polarization effects (Fig. 2) on the network structure. The separation between the smaller voids is linked to the nearest neighbor Zn-Zn distance, as in the RIM calculations.

Gaskell and Wallis [18] suggested an alternative explanation for the second length scale. They noted that the wave vector of the FSDP often corresponds to the first Bragg peak position of the associated crystal and argued that the appearance of the FSDP in the liquid and glass reflected the persistence of crystalline intermediate range order in the amorphous phases. They showed that the atomic positions in computer simulations of amorphous $\mathrm{SiO_2}$ exhibited such order [18]. $\delta$-$\mathrm{ZnCl_2}$ is a *layered* crystal, and the first Bragg peak reflects the interlayer spacing. The idea that a liquid could be appreciably layered up to hundreds of degrees above the melting point [19] does not come naturally to those who approach the glass transition from the liquid side. Examination of instantaneous configurations in the $\mathrm{ZnCl_2}$ PIM simulations was not suggestive of layering, and there must always be some anxiety when examining simulations of supercooled liquids that one is not seeing the onset of crystallization.

We have therefore attempted to clarify the relationship between the putative layered nature of the intermediate range order and the observation of the FSDP in diffraction experiments: note that this involves more than can be learned from a study of the pair distribution function or structure factor alone.

A possible way forward is to study the statistics of a (theoretical) scattering experiment carried out on a simulated sample. If, indeed, the sample at some instant contains a layered region which occupies a significant fraction of the whole sample volume, observation of the far field of collimated monochromatic radiation scattered from the sample would reveal a bright twinkle or speckle along a particular direction characterized by the wave vector $\mathbf{k}_l$ which satisfied the Bragg condition for that layer spacing and orientation. If, over a period of time, such a layered region were to disappear and reform at random orientations but the same interlayer spacing, the *time-averaged* scattering pattern would exhibit a ring, composed of the set of all speckles, and the amplitude of the ring would be given by the structure factor $S(|\mathbf{k}_l|)$, as appropriate to an isotropic liquid. In simple liquids, it is believed that the features in $S(k)$ arise because distributed throughout the sample are small groups of particles separated by the characteristic distances of the fluid, each of which is scattering weakly. In this case, there will be simultaneously weak scattering at many points on the ring characterized by $k$. These two situations may be distinguished by looking at the moments of the scattered intensity [20] collected at a series of points over the ring; the latter case corresponds to Gaussian statistics. In the computer simulation, only discrete wave vectors of the form $\mathbf{k}_i = 2\pi/L(l_i, m_i, n_i)$, where $L$ is the cell length and $l_i$ an integer, are available, and we therefore study

$$M^{(2)}(k) = N_k^{-1} \sum_{i=1,N_k} [\langle |A(\mathbf{k}_i, t)|^2 \rangle - S(k)^2]/S(k)^2, \quad (2)$$

where the sum runs over the $N_k$ wave vectors with $|\mathbf{k}_i| = k$ and

$$A(\mathbf{k}_i, t) = N^{-1} \sum_{p,q=1,N} \exp[i\mathbf{k}_i \cdot \mathbf{r}^{pq}(t)] \qquad (3)$$

corresponds to the instantaneous intensity along $\mathbf{k}_i$ [whose average is $S(|\mathbf{k}_i|)$]. $M^{(2)}(k)$ takes a value of 1 for Gaussian statistics and could be significantly larger if layered regions were, in fact, important.

The moments calculated in this way for the $Zn^{2+}$ ions in the PIM simulation are shown in Fig. 1(d). It is clear that the scattering at the position of the FSDP *is* strongly non-Gaussian, whereas the scattering at the principal peak and other values of $k$ is almost Gaussian. Checks confirm the Gaussian nature of the scattering in liquid argon (a typical fragile simple atomic system) at all $k$.

Figure 1(d) lends weight to the suggestion that the scattering at the FSDP in $ZnCl_2$ is due to density fluctuations with a layered character of appreciable spatial extent. However, it is possible that the layering is associated with incipient crystallization whose growth kinetics is slow compared to the run length, rather than a fluctuation of the (metastable) fluid. The stable crystal structure for the PIM potential is indeed the layered $\delta$-$ZnCl_2$ structure. Figure 3(a) shows the evolution of $A(\mathbf{k}_i, t)$ for the six individual wave vectors associated with $k = |2\pi/L(440)|$ ($\simeq 1.05$ Å$^{-1}$) (corresponding to a point on the FSDP in Fig. 1), over a total time of $\simeq 370$ ps ($\equiv 600\,000$ molecular dynamics time steps) for 999 ions at 700 K. We have also calculated the $A(\mathbf{k}_i, t)$ for the voids in the system: this mirrors the behavior indicated in the figure closely. It is clear that particular directions become "bright" for a considerable period of time: the [044] direction, for example, is the most intense for $\simeq 40$ ps and then dies in intensity to be replaced by the [440]. Over the period of the run, each direction becomes transiently bright so that the fluid is isotropic on this time scale. The amplitude of the bright fluctuations is not increasing over the course of run, as would be the case if some crystallite was ripening or growing. At this temperature, the ionic diffusion coefficients are $\sim 2.4 \times 10^{-6}$ cm$^2$ s$^{-1}$, i.e., the fluid is well above the glass transition.

The statistics of the scattering at the FSDP are thus consistent with strong scattering by stable, but relatively long lived density fluctuations with a layered character in the isotropic fluid. However, as noted earlier, we have not readily discerned a layering of the atomic positions in snapshots; any such ordering is much weaker than that illustrated by Gaskell and Wallis [18]. A way of increasing the "contrast" of the layered fluctuations is to show snapshots of the positions of the large voids, identified by the Voronoi analysis earlier, rather than atomic positions. As shown by the strength of $S_{VV}^{\mathrm{PIM}}(k, \sigma_c)$ at $k_{\mathrm{FSDP}}$ relative to $k_{PP}$, the layered order of the large voids is more pronounced than in the atomic positions. Figure 4(a) shows the centers of the voids with circumsphere radii $>7.0$ a.u. clearly demonstrating the

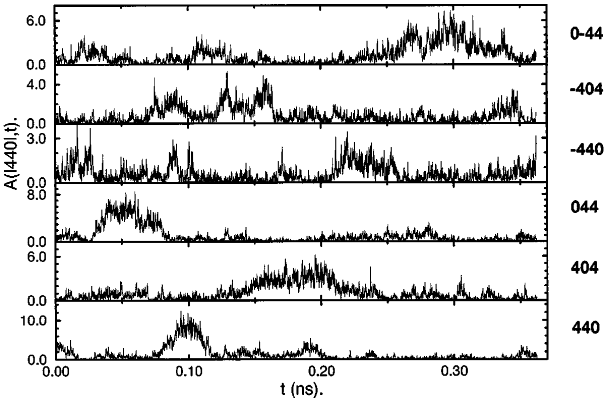

FIG. 3. Evolution of $A_{\mathrm{ZnZn}}(\mathbf{k}_i)$ for the six 440 wave vectors over $\sim 400$ ps in a 999 ion PIM simulation at 700 K.

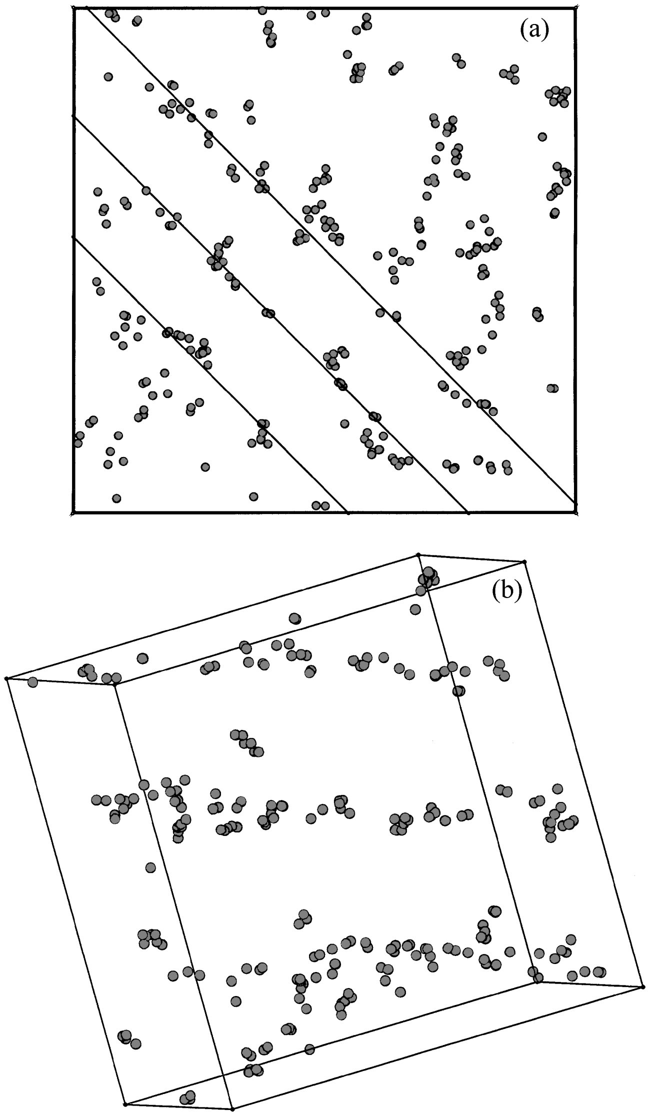

FIG. 4. Molecular graphics "snapshots" of the void structure in (a) liquid $ZnCl_2$ (999 ion system) and (b) partially crystallized $ZnCl_2$ (324 ion system). In both cases only circumspheres above 7.5 a.u. radius are colored. Both sets of circumspheres have been coarse grained for clarity (see text). In (a) the lines are perpendicular to the (440) direction and indicate the layers responsible for the strong scattering in this configuration.

inherent layered structure in the [440] direction. Although one can make out the presence of such layers in the void distribution, the character of the layering is that it is weak and extends over only a portion of the sample. It is useful to judge the strength of the layering by contrasting with a similar picture of the void positions in a smaller (324 ion) simulation run that was observed to partially crystallize [Fig. 4(b)]. Ordering of this clarity results in a scattering amplitude for **k** along the direction perpendicular to the layers, of around 5 times the magnitude of the brightest vector in Fig. 3.

In conclusion, our study indicates that in liquid $ZnCl_2$, the length scale which corresponds to the wave vector of the FSDP is set by the average distance between larger voids in the spatial distribution of cations. The weak ordering of these voids tends to induce cation density fluctuations with a layered character, even in the relatively mobile supercooled fluid range.

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[1] P. S. Salmon, Proc. R. Soc. London A **437**, 591 (1992); **445**, 351 (1994).
[2] M. P. Tosi, D. L. Price, and M-L. Saboungi, Annu. Rev. Phys. Chem. **44**, 173 (1993).
[3] D. Morineau *et al.* (to be published).
[4] C. A. Angell, J. Phys. Chem. Solids **49**, 863 (1988).
[5] M. Wilson and P. A. Madden, J. Phys. Condens. Matter **6**, A151 (1994).
[6] S. R. Elliott, Europhys. Lett. **19**, 201 (1992).
[7] A. P. Sokolov, A. Kisliuk, M. Soltwisch, and D. Quitmann, Phys. Rev. Lett. **69**, 1540 (1992).
[8] R. Orbach, Physica (Amsterdam) **220B**, 231 (1996).
[9] S. Biggin and J. E. Enderby, J. Phys. C **14**, 3129 (1981).
[10] M. Wilson and P. A. Madden, Phys. Rev. Lett. **72**, 3033 (1994).
[11] M. Wilson and P. A. Madden, J. Phys. Condens. Matter **5**, 6833 (1993).
[12] G. Pastore, P. Ballone, and M. P. Tosi, J. Phys. C **19**, 487 (1986); P. Ballone, G. Pastore, J. S. Thakur, and M. P. Tosi, Physica (Amsterdam) **142B**, 294 (1986).
[13] S. N. Taraskin, S. R. Elliott, and M. Klinger, J. Non-Cryst. Solids **193**, 263–266 (1995); J. H. Lee and S. R. Elliott, *ibid.* **193**, 133 (1995); A. Ulherr and S. R. Elliott, *ibid.* **193**, 98 (1995).
[14] J. D. Bernal, Proc. R. Soc. London A **280**, 299 (1964); J. L. Finney, *ibid.* **319**, 495 (1970).
[15] We made use of a program kindly supplied by A. Appelhagen and A. Geiger; see Mol. Phys. **88**, 1337 (1996).
[16] Very similar methods have been introduced recently in D. S. Corti, P. G. Debenedetti, S. Sastry, and F. H. Stillinger, Phys. Rev. E **55**, 5522 (1997).
[17] Y. I. Naberukhin, V. P. Voloshin, and N. N. Medvedev, Mol. Phys. **73**, 917 (1991).
[18] P. H. Gaskell and D. J. Wallis, Phys. Rev. Lett. **76**, 66 (1996).
[19] D. A. Allen, R. A. Howe, N. D. Wood, and W. S. Howells, J. Chem. Phys. **94**, 5071 (1991).
[20] P. N. Pusey and J. G. Rarity, J. Phys. (Paris) **46**, 43 (1985).