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INTERMEDIATE RANGE ORDER IN MODEL LIQUID BINARY ALLOYS

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We study the nature of intermediate range order (IRO) in a 2:1 model liquid binary mixture as the range of the potentials is changed from short to long range.

The calculations were carried out within the Mean Spherical Approximation, and the study focuses on the Bhatia-Thornton partial structure factors. We find evidence of IRO when there is size difference between the atoms in the mixture. However, at the level of description of this work, there appears no way of distinguishing between the IRO in a compound forming or an ionic system.

KEY WORDS: Bhatia-Thornton partial structure factors, size difference effects.

1 INTRODUCTION

The effect of ordering on the structural properties of binary mixtures has been of interest lately. By means of partial structure factors, topological short-range order (TSRO), i.e. a preference of a positional arrangement of neighbors about each particle, and chemical short-range order (CSRO), i.e. a preferred arrangement of a given type of particles for nearest neighbours of a particular type, are studied in different systems.¹

The total structure factor $S(q)$ of a number of liquid binary alloys, molten salts and good glass forming binary liquid mixtures exhibit a distinctive prepeak at low q , referred to as the first sharp diffraction peak (FSDP). The presence of the FSDP is regarded as the signature for the existence of intermediate range order (IRO) in these systems, extending beyond nearest-neighbour distances.²

A study of the experimental Bhatia-Thornton partial structure factors³ for a number of liquid and amorphous binary systems⁴ reveals that for different systems the partial structure factors contribute in different ways to IRO even though the overall effect on the local structure is similar. Hence it is of interest to study these possible contributions in the context of model liquid binary alloys. As a result there have been a number of

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studies adopting a charged hard sphere model (CHS)^{5,6} and also a sticky hard sphere model (SHS)⁷ to find out the interplay between different effects in establishing the nature of IRO.

In this paper we study the nature of IRO in 2:1 model liquid mixtures as the range of the potentials are changed from short to long range, namely from potentials resembling SHS to almost “ionic” order. This is achieved by employing a solution for the hard sphere Yukawa (HSY) binary mixtures within the mean spherical approximation (MSA) in order to study the structural changes which may take place as the potentials are extended beyond the hard cores. We also include a few SHS results for comparison.

2 THEORY AND RESULTS

The HSY potential for a binary mixture with one-Yukawa tail outside the core is

$$\phi_{ij}(r) = \begin{cases} \infty & 0 < r \leq d_{ij} \\ A_{ij} \frac{e^{-zr}}{r} & r \geq d_{ij} \end{cases}, \quad (1)$$

where A_{ij} and z are the strength and inverse-range parameters, respectively. For repulsive Yukawas between like and attractive between unlike particles, $A_{11}, A_{12} > 0$ and $A_{12} < 0$. The d_{ij} denote the hard sphere diameters, such that $d_{ij} = (d_{ii} + d_{jj})/2$.

The Ornstein-Zernike equation for the above potential has been solved analytically by Blum and Høye (BH)⁸ using the factorization method⁹ in the MSA.

We present results for two extreme cases in the MSA, one which mimics the SHS situation; the other which probes a long-ranged potential. The ensuing parametrisation is discussed below. The choice of parameters has been dictated by the requirement of comparing partial structure factors of similar magnitude in the two extreme cases under study.

In both cases we assume the pre-exponential factor to satisfy the “charge neutrality” condition¹⁰

$$c_1 A_{11}^{1/2} + c_2 A_{22}^{1/2} = 0,$$

where c_i ($i = 1, 2$) is the concentration of species i , such that $c_1 + c_2 = 1$. This gives

$$A_{11} = 4A_{22},$$

for the 2:1 mixtures studied in this work.

For the first case, we extend the prescription proposed by Ciccariello and Carraro¹¹ for the one component HSY fluids, and link the structure of the HSY mixtures with that

of the SHS mixtures by setting

$$\beta A_{12} = -z_s t_{12} e^{z_s d_{12}}, \quad (2)$$

where β is the inverse of Boltzmann's constant k_B times the temperature T , z_s is the value of z at which the HSY mimics the SHS, and t_{12} is a coefficient related to the SHS stickiness parameter¹². Moreover we choose βA_{22} to have a small value ($=0.2 \text{ \AA}$) so that the interaction between like particles effectively probes the hard repulsive core. For the same reason we take a relatively large value of the inverse-range parameter, $z d_{11} = 5$ which, with a SHS stickiness parameter $\tau_{12} = 2$ ($\tau_{ii} = 0$), gives $\beta A_{12} = -337.303 \text{ \AA}$ via Eq. 2.

For the second case we choose $A_{12} = -\sqrt{A_{11}A_{22}}$, which becomes $-2A_{22}$ for the 2:1 mixture in hand, so that "charge neutrality" is exactly satisfied. Here we choose $\beta A_{22} = 2.5 \text{ \AA}$ and $z d_{11} = 0.9$ to ensure both that like particles effectively "see" the soft repulsion and that the potential is reasonably "long ranged".

To obtain the HSY structure factors, we have used the numerical algorithm proposed by Arrieta *et al.*¹³, combined with Pastore's criteria¹⁴ to select the physical solution of the system. In all cases we have chosen d_{11} as the unit of length and $k_B T$ as the unit of energy.

In order to study partial structure factors of comparable magnitude we choose, for both the SHS and HSY case which mimics it, the packing fraction $\eta = 0.45$. For the long-range HSY we choose $\eta = 0.34$. In order to differentiate between the two we shall refer to the former as the "compound forming" HSY and the latter as the "ionic" HSY. The difference in the roles of η for the two cases takes care of the smaller density found in systems where an "ionic potential" is the dominant inter-

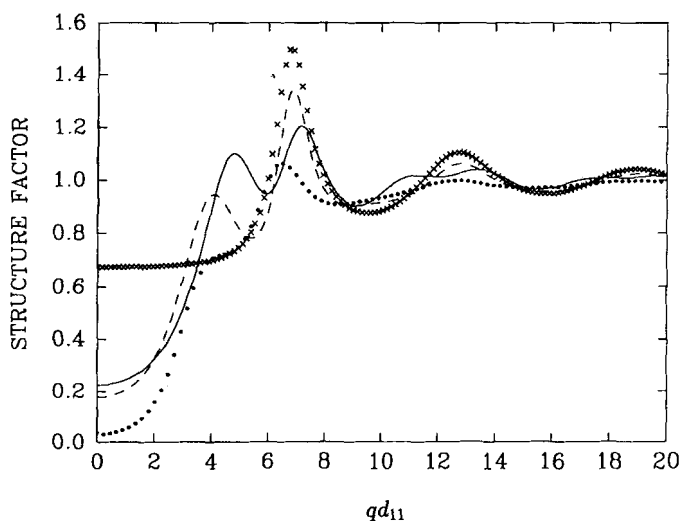


Figure 1 (a) $S_{11}(q)$ for the $\alpha = d_{22}/d_{11} = 1$ case. For parametrisation see text. Solid line shows the SHS result; dashed line the CF HSY; dotted line the ionic HSY and cross line the HS ($\eta = 0.45$).

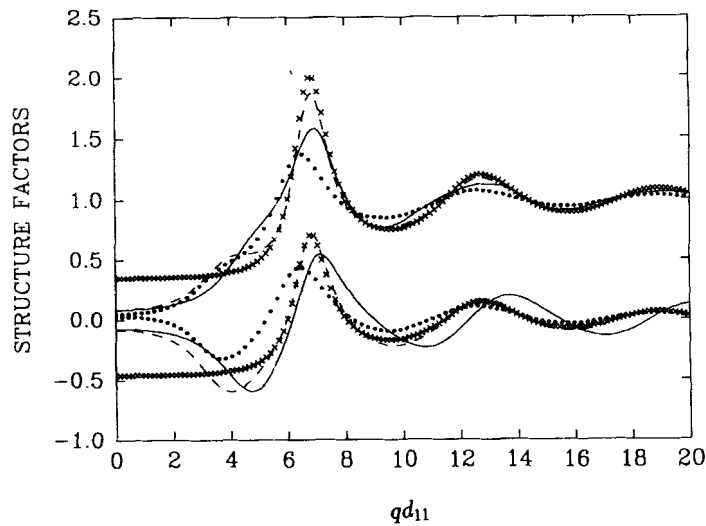


Figure 1 (b) $S_{22}(q)$ (upper set of curves), and $S_{12}(q)$ (lower set of curves) for the $\alpha = 1$ case. Solid line shows the SHS result; dashed line the CF HSY; dotted line the ionic HSY and cross line the HS ($\eta = 0.45$).

action. The size effect is studied by considering the cases where $d_{22}/d_{11} \equiv \alpha = 1$, and $\alpha = 2$.

The BT partial structure factors resulting from the above parametrisation are shown in Figures 2 and 4. The Ashcroft-Langreth (AL) partials $S_{ij}(q)$ for the HSY potential are also included together with those for the hard sphere (HS) potential to more clearly identify the position of the prepeaks.

In Figure 1 we show the AL partial structure factors for equal diameters, $\alpha = 1$. In Figure 1(a), we find that the prepeak in $S_{11}(q)$ of HSY system becomes more pronounced as the HSY potential goes from long-ranged to the sticky limit, while the position of the prepeak is at lower values of q for the “compound forming” system, at $qd_{11} \approx 4$, compared to $qd_{11} \approx 5$ for the “ionic” case. We regard this prepeak as the signature of CSRO. Figure 1(b) shows the results for $S_{22}(q)$ and $S_{12}(q)$. The prepeak in $S_{22}(q)$ is only a shoulder for the “compound forming” case and is barely observable in the SHS limit. The first minima in $S_{12}(q)$ nearly coincide with the position of the prepeak in $S_{11}(q)$.

In Figure 2(a) we show $S_{NN}(q)$, the density fluctuations partial structure factor, for the case $\alpha = 1$. The position of the first peak is almost the same in all cases, with that of the ionic case slightly displaced towards a lower q . The differences between the SHS and the “compound forming” HSY are due to the differences in the range and strength between the like potentials, and the fact that we are solving in two different approximations, as the former is solved in the Percus-Yevick approximation¹². We associate the position of this peak, at $qd_{11} \approx 7$, to TSRO. The fact that it is largely insensitive to the range of the potential suggests that it mainly results from the repulsive core. In Figure 2(b) we show both the concentration fluctuations partial structure factor $S_{cc}(q)$, and the cross correlation between the density and concentration fluctuations $S_{Nc}(q)$. For the particular case $\alpha = 1$, the “ionic” HSY $S_{Nc}(q) = 0$ for all values of q . The position of the first

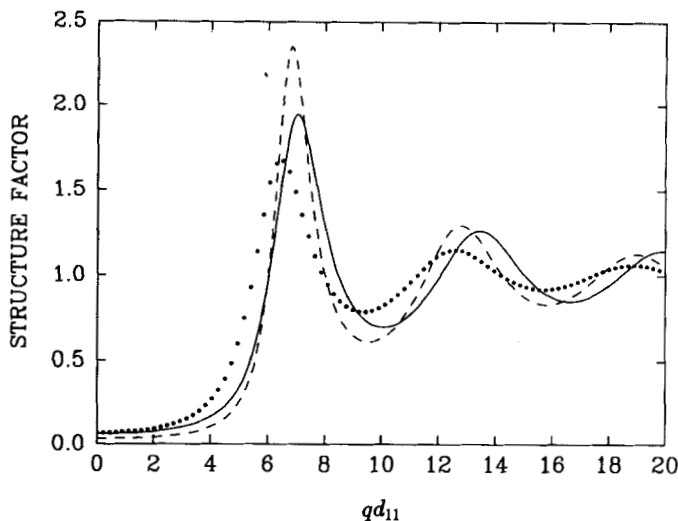


Figure 2 (a) Density fluctuations partial structure factor $S_{NN}(q)$ for the $\alpha = d_{22}/d_{11} = 1$ case. For parametrisation see text. Solid line shows the SHS result; dashed line the CF HSY; and dotted line the ionic HSY.

peak of $S_{cc}(q)$ corresponds, in all cases, to that found for the prepeak in $S_{11}(q)$ which we have already associated with CSRO.

We now turn to Figures 3 and 4 where we present the results for the $\alpha = 2$ case.

The heights of the prepeaks in $S_{11}(q)$ surpass those of the first peaks in all the cases studied here, as shown in Figure 3(a). Figure 3(b) shows that the positions of the first

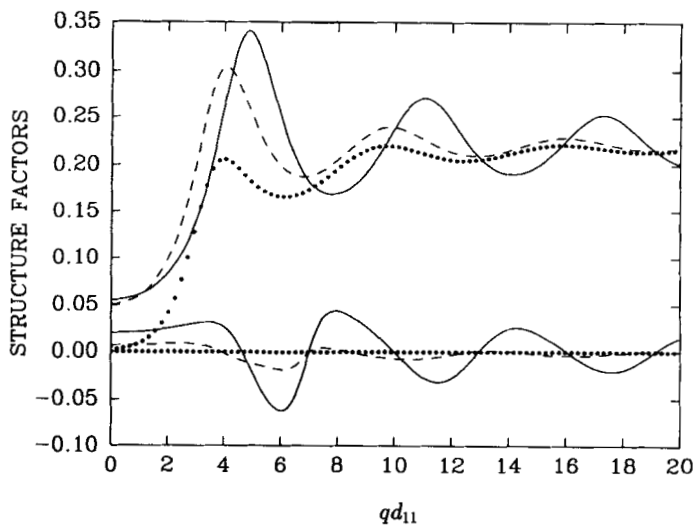


Figure 2 (b) Concentration fluctuations partial structure factor $S_{cc}(q)$ (upper set of curves), and crossed fluctuations partial $S_{Nc}(q)$ (lower set of curves) for the $\alpha = 1$ case. Solid line shows the SHS result; dashed line the CF HSY; and the dotted line the ionic HSY.

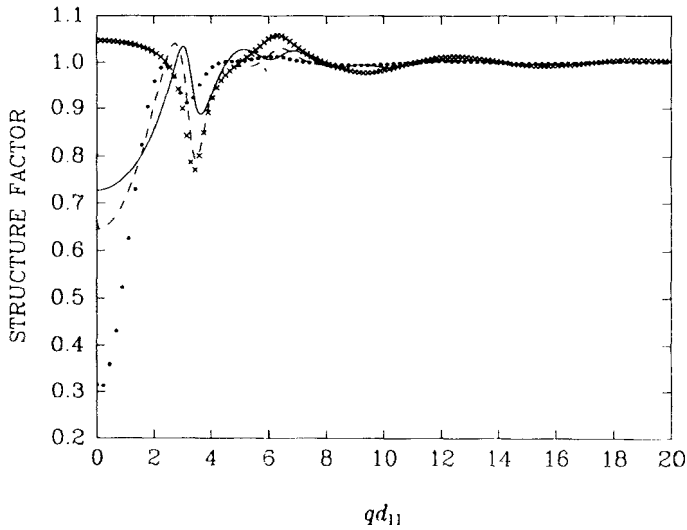


Figure 3 (a) $S_{11}(q)$ for the $\alpha = 2$ case. For parametrisation see text. Solid line shows the SHS result; dashed line the CF HSY; dotted line the ionic HSY and cross line the HS ($\eta = 0.45$).

dips in $S_{12}(q)$ again almost coincide with the prepeaks in $S_{11}(q)$, and are located at $qd_{11} \approx 3.4$. Relative to the $\alpha = 1$ case, the positions of the first peaks of $S_{22}(q)$ are shifted to the lower values of q , and are now close to the position of the prepeaks in $S_{11}(q)$.

The BT partial structure factors are shown in Figure 4. We find that the peaks for both $S_{NN}(q)$ and $S_{cc}(q)$, and the dip of $S_{Nc}(q)$ at the same value as the prepeak in $S_{11}(q)$

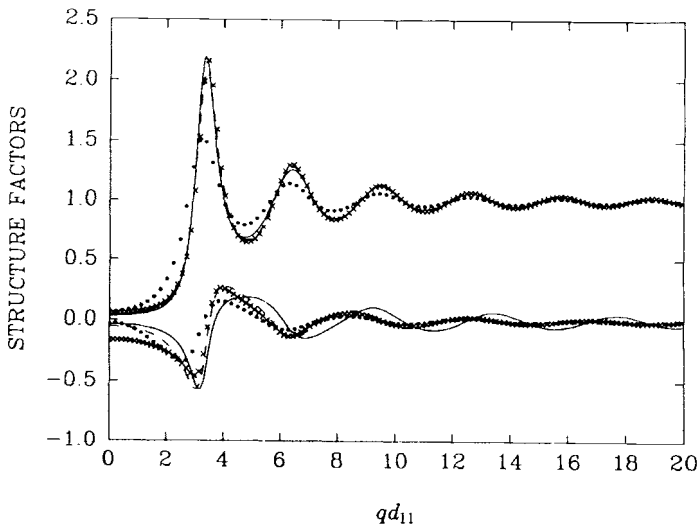


Figure 3 (b) $S_{22}(q)$ (upper set of curves), and $S_{12}(q)$ (lower set of curves) for the $\alpha = 2$ case. Solid line shows the SHS result; dashed line the CF HSY; dotted line the ionic HSY and cross line the HS ($\eta = 0.45$).

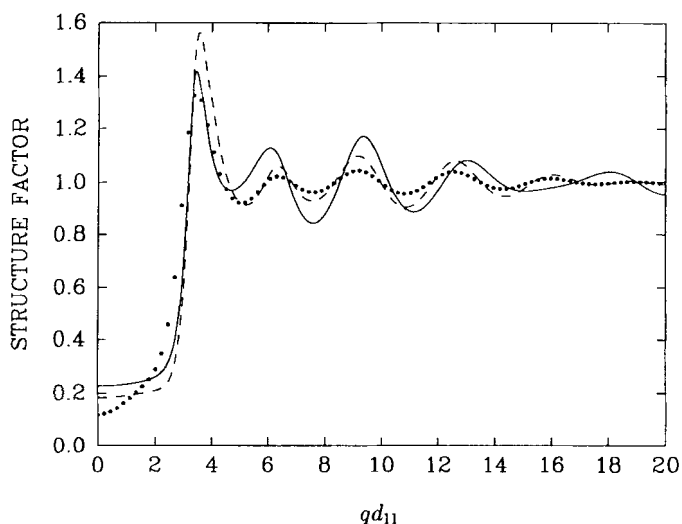


Figure 4 (a) Density fluctuations partial structure factor $S_{NN}(q)$ for the $\alpha = 2$ case. For parametrisation see text. Solid line shows the SHS result; dashed line the CF HSY; and dotted line the ionic HSY.

are a clear indication of IRO. This is also clearly indicated by the three peaks in $S_{NN}(q)$ in the range $qd_{11} \approx 3.4$ to 9.3 . We note: (i) since no parameter has changed other than the size difference, it is the size difference which changes the system from what is normally described as a CSRO system to IRO^{1,5} (ii) both “compound forming” and “ionic” systems yield similar results.

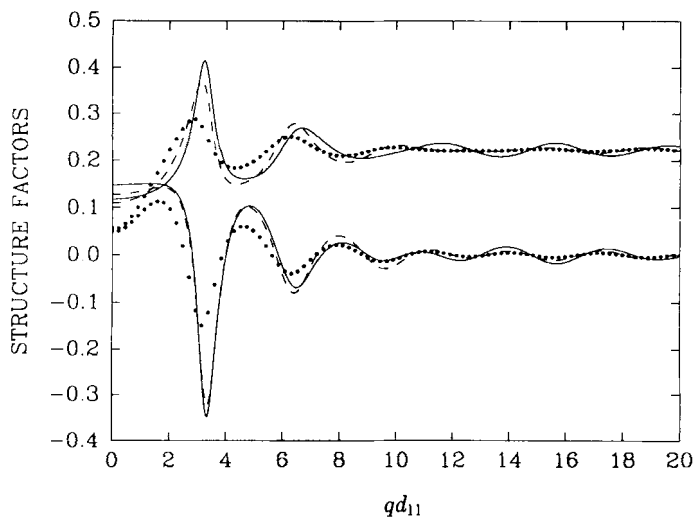


Figure 4 (b) Concentration fluctuations partial structure factor $S_{cc}(q)$ (upper set of curves), and crossed fluctuations partial $S_{Nc}(q)$ (lower set of curves) for the $\alpha = 2$ case. Solid line shows the SHS result; dashed line the CF HSY; dotted line the ionic HSY.

3 CONCLUSIONS

The possible origins of IRO in model liquid binary mixtures have been studied within the BT formalism using the MSA HSY solution for two extreme cases; one mimics “compound forming”, the other “ionic” behaviour. The HS and SHS cases have been included for comparison.

For the equal size case we find evidence of the existence of chemical short range order (CSRO) and this is indicated by the concentration fluctuations; for the case of size difference between the atoms we find evidence of intermediate range order in the model liquid binary mixture. The position of the first sharp diffraction peak (FSDP), to which all partials contribute, is located at $qd_{11} \approx 3.4$, which is about the same value found by Iyetomi and Vashista⁵ for the charged spheres model liquid used in their calculations. At this level of description it appears that there is no way of distinguishing whether IRO has been caused by ionic ordering or compound forming. The results of this work raise the question as to whether the range of the potentials is indeed important in the setting up of IRO.

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References

1. M. L. Saboungi, W. Geertsma and D. L. Price, *Ann. Rev. Phys. Chem.* **41** (1990) 207.
2. S. C. Moss and D. L. Price, in *Physics of Disordered Materials*, eds. D. Alder, H. Fritzsche and S. R. Ovshinsky (Plenum, New York, 1986), p. 77.
3. A. B. Bhatia and D. E. Thornton, *Phys. Rev. B* **2**, (1970) 3004.
4. P. S. Salmon, *Proc. R. Soc. (London) A* **437** (1992) 591.
5. H. Iyetomi and P. Vashista, *Phys. Rev. B* **47** (1970) 3063.
6. J. Boronat and M. Silbert, Submitted to *Phys. Chem. Liq.*
7. Jun Wang, I. L. McLaughlin, P. S. Salmon and M. Silbert (unpublished results).
8. L. Blum and J. S. Høye, *J. Stat. Phys.* **19** (1978) 317.
9. R. J. Baxter, *Aust. J. Phys.* **21** (1968) 563.
10. D. J. Gonzalez and M. Silbert, *J. Phys. F: Met. Phys.* **18** (1988) 2353.
11. S. Ciccariello and C. Carraro, *Phys. Rev. A* **38** (1988) 4121.
12. B. Barbooy, *Chem. Phys.* **11** (1975) 357.
13. E. Arrieta, C. Jedrzejek and K. N. Marsh, *J. Chem. Phys.* **86** (1987) 3607.
14. G. Pastore, *Mol. Phys.* **63** (1988) 731.