I-T Polyamorphism in Molecular Liquids

So far the only quantity known as the order parameter that distinguishes liquids from gases is density. However, a recent experimental confirmation of the very existence of the pressure-induced “structural” transition between stable liquids of black phosphorus lends strong impetus to reconsideration on the concepts of liquids. As represented by amorphous ice, such polyamorphism in metastable states has been known for a long time. Very recently we found that the melting curve of the low-pressure crystalline phase of a molecular crystal $\mathrm{SnI_4}$, which is known to undergo pressure-induced solid-state amorphization, has a maximum at around 2 GPa. This means that an abrupt change in liquid density takes place at that pressure, which is expected to be attributable to liquid-liquid phase transition. The purpose of the project is not only to experimentally reveal the transition but also to construct the statistical-mechanical model for the transition from which order parameters other than the density characterizing the polyamorphism can be extracted.

I-T-1 Construction of an Interaction-Site Model for Molecular Systems

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Our target substance is a molecular crystal $\mathrm{SnI_4}$, which exhibits a variety of structural and electrical properties under high pressures.[1] Although our model crystalline with octupole-octupole interactions entered as the first nonvanishing contribution to the perturbed part exhibited considerably higher melting points[2] compared to the experimental results,[3] investigations on the liquid state utilizing this model is still attractive, since no experimental information under high pressures has been as yet available. However, actual numerical computations are much time-consuming. Hence, to set up a new interactions-site model that can deal with molecular systems more efficiently in the simulations is by no means trivial.

Let us suppose molecular systems consisting of electrically neutral molecules with internal degrees of freedom. We assume that the intermolecular interactions are given by the sum of the interactions between the interaction sites within a molecule. The constituent interaction is proportional to the inverse power s of a distance between the interaction sites. Let $\mathbf{r}_i$ be the center-of-mass position of the ith molecule. The position of the kth interaction site relative to $\mathbf{r}_i$ is given by $\alpha^k \mathbf{p}_i^k$, $\mathbf{p}_i^k$ being fixed to the molecule. We locate a “charge” at the interactions site, which is denoted by $\zeta_i^k(s)$. The quotation marks are intended to mean that the charges are ordinary electric charges when $s = 1$, but otherwise, they are virtual whose magnitude yields the units of [energy][(length)^s] when multiplied with each other. This generalization of the concept of charges allows us to treat the interaction sites in a unified fashion without regarding the Coulombic interaction sites as being special. We then arrange these molecules in a p-dimensional computational cell, whose basis vectors are given by $[\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_p] = \mathbf{h}$. When the periodic boundary condition is imposed, the position of kth interaction site within ith molecule in mth image cell is given by $\mathbf{r}_m + \mathbf{r}_i + \alpha^k \mathbf{p}_i^k = \mathbf{r}_m + \mathbf{r}_i^k(\alpha^k)$. Here, $\mathbf{r}_m = \mathbf{h}\mathbf{m}$, $\mathbf{m}$ being the vector whose components are all integers. Then, total intermolecular interaction is given by $\Phi = \Sigma_s \Phi(s;p)$ with

$$\Phi(s;p) = \frac{1}{2}\sum_{m}\sum_{i}\sum_{k\in i}\sum_{j}\sum_{l\in j}\frac{\varsigma_i^k(s)\varsigma_j^l(s)}{\left|\mathbf{r}_m + \mathbf{r}_{ij}^{kl}(\alpha^k(s);\alpha^l(s))\right|^s},$$

where $\mathbf{r}_{ij}^{kl}(\alpha^k(s);\alpha^l(s)) = \mathbf{r}_i^k(\alpha^k) - \mathbf{r}_j^l(\alpha^l)$. The lattice sums appearing in this expression corresponds to a special case of the generalized zeta function of pth order developed by the author.[4] Derivation of the final expression for $\Phi(s;p)$ together with some examples of its implementation will soon be reported.

References

1) N. Hamaya, K. Sato, K. Usui-Watanabe, K. Fuchizaki, Y. Fujii and Y. Ohishi, *Phys. Rev. Lett.* **79**, 4597–4600 (1997).
2) K. Fuchizaki and K. Nagai, *Solid State Commun.* **132**, 305–308 (2004).
3) K. Fuchizaki, Y. Fujii, Y. Ohishi, A. Ohmura, N. Hamaya, Y. Katayama and T. Okada, *J. Chem. Phys.* **120**, 11196–11199 (2004).
4) K. Fuchizaki, *J. Phys. Soc. Jpn.* **63**, 4051–4059 (1994).