I-N 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. Recently, we have succeeded, through *in situ* synchrotron x-ray diffraction measurements under high pressures and temperatures, in unveiling the presence of a liquid-to-liquid structural phase transition in a molecular liquid SnI_4. This discovery offers the first evidence of the thermodynamically stable transition found in general compounds other than elements. The purpose of the present project is on the basis of theoretical, computational as well as experimental investigations to construct the statistical-mechanical model for the transition from which local order parameters characterizing the polyamorphism can be extracted.

I-N-1 Murnaghan’s Equation of Motion Revisited

FUCHIZAKI, Kazuhiro
(IMS and Ehime Univ.)

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The expression known as Murnaghan’s equation of state in high-pressure research community is mathematically a correct solution to the equation of bulk modulus but is valid only within a very limited parameter space. Moreover, the equation of state in question exhibits a peculiar behavior at high pressures when fitted to compression data. An alternative expression with a much wider range of validity is given. No peculiarity appears in the resultant compression curve. The latter expression thus provides a new tool as an infinitesimal-strain equation of state for quick estimate of compression characteristics of substances.

I-N-2 Polyamorphism in Tin Tetraiodide

FUCHIZAKI, Kazuhiro[1]; HASE, Takaki[2]; YAMADA, Akihiro[2]; HAMAYA, Nozomu[3]; KATAYAMA, Yoshinori[4]; FUNAKOSHI, Ken-ichi[5]
([1]IMS and Ehime Univ.; [2]Ehime Univ.; [3]Ochanomizu Univ.; [4]JAEA; [5]JASRI)

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The experimental evidence for a thermodynamically stable liquid-to-liquid transition to occur has been given thus far only for liquid phosphorus. This transition is regarded as an allotropic transition in noncrystalline states. Then, one might ask whether there can be a general polymorphic transition in noncrystalline states. Such polyamorphism in equilibrium states has been searched for a long time. Here, we present firm evidence that there exist two types of phases in a molecular liquid SnI_4 below and above about 1.5 GPa, where the melting curve of the crystalline phase has an apparent break. Structure factors of the liquids were obtained through *in situ* synchrotron x-ray diffraction measurements performed under pressures from 1 atm up to 3.4 GPa. At lower pressures below 1.5 GPa higher-wavenumber components of the structure factor can be well explained by an ideal gas structure consisting of molecules with regular tetrahedral symmetry. The presence of molecules is also confirmed by the fact that the positions of the two principal peaks in the reduced radial distribution functions inverted from the structure factors, which corresponds to two kinds of intramolecular separation, are almost independent of pressures applied as far as the pressure is below 1.5 GPa. However, with increasing pressure beyond 1.5 GPa, the two peaks are going to merge, the situation having been found in high-pressure amorphous structure in which molecular dissociation proceeds. We conclude from these observations that the lower-pressure liquid is a molecular liquid, whereas polymerization takes place on the higher-pressure side.

I-N-3 New Method for Inversion from Structure Factors to Radial Distributions

FUCHIZAKI, Kazuhiro
(IMS and Ehime Univ.)

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Although one of the advantages of using synchrotron radiation is its wide energy range available to scattering experiments, the situation is a bit different in the energy-dispersive type of measurements employed upon high-pressure experiments utilizing a multi-anvil type apparatus. The effective energy range is restricted by scattering angles; it is limited down to several degrees to avoid strong forward scattering on the one hand while a upper bound is limited up to ~16 degrees to obtain scattered intensities with reasonable S/N ratio on the other. The actual wavenumber window, Λ, is thus limited both in low and high k directions. If the structure factors with a finite window Λ is naively Fourier transformed to obtain radial distribution functions, G, they will suffer from spurious peaks originated from this finite truncation. Applying some window functions to reduce the truncation effects is not recommended because it severely modifies the peak height of G. Hence, a new method has been devised in which no Fourier inversion is invoked. The method relies on the maximum entropy principle to yield G according to the relation involving an observed structure factor and a Lagrange’s multiplier, λ, as input. G determined based on the relation agrees well with that obtained through the reverse Monte Carlo calculations of the structure factor, and found to be robust against a choice of the value for λ.

I-N-4 Changes in Orientational Correlations in a Molecular Liquid on Compression

FUCHIZAKI, Kazuhiro[1]**; NEZBEDA, Ivo**[2]**;**
KALYUZHNYI, Y. V. [3]
([1]IMS and Ehime Univ.; [2]Czech Acad. Sci.; [3]Natl. Acad. Sci. Ukraine)

[*J. Chem. Phys.* submitted]

Evolution in local molecular configuration in a molecular liquid, especially in orientational correlations, with increasing pressure is of primary interest. This aspect was investigated conducting molecular dynamics simulations for a molecular liquid SnI_4. The method of the simulations is basically the same as that employed previously$^{1)}$ except that the shape of the MD cell was fixed to be cubic with only its size allowed to vary.

The structure factor, *S*, obtained at ambient pressure attains remarkable agreement with the experimental result. Moreover, its components with wavenumbers beyond ~2.7 A^{-1} are hardly affected by thermodynamic conditions applied as well as the precise nature of the intermolecular interactions. The region beyond k ~ 2.7 A^{-1} corresponds to the lengths within the intramolecular distance. In fact, the behavior of *S* over this length scale is quantitatively explained by the ideal gas model consisting of freely rotating tetrahedral molecules. However, the behavior in the low-*k* region is strongly affected by the intermolecular correlations. The primary peak shifts in higher-*k* direction upon compression, reflecting the shrinkage of the system as a whole, whereas the height of the peak increases, implying that the spatial correlation develops due to, mainly, hard-core repulsion between the molecules. The first small peak located at ~1 A^{-1}, which diminishes in height, is from the spatial correlation between the central tins; in the structure factors obtained through RISM calculations with no interactions between tin atoms, the corresponding peak never appears. A unique orientational order parameter that can capture the intermolecular orientational correlation is discussed. We found on the basis of the behavior of the order parameter that population of nearest neighbor molecular pairs which are in vertex-to-face configuration increases on compression.

References

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