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Mesoscopic structure in near-critical mixtures of D_2O and 3-methylpyridine with salts

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Small-angle neutron scattering (SANS) experiments were performed on mixtures of 3-methylpyridine, D_2O, and salts to investigate concentration fluctuations and structures in the vicinity of the critical point. The SANS profiles of ternary mixtures with large critical temperature shifts can be analyzed by the sum of the concentration fluctuation and a scattering from spherical clusters. The size of the clusters increases as the critical point is approached. These results can be interpreted in terms of a strong coupling of the critical fluctuation and the solvation effect of salt ions.

1. Introduction

The solvation effect plays an important role in various fields of natural science. One of the most interesting issues regarding the solvation effect is its large influence on near-critical binary mixtures with polar and non-polar liquids. Experimentally, it is well known that the addition of salt ions to a binary mixture causes a shift of the critical temperature (Hales *et al.*, 1966). Many investigations have been performed to reveal the effect of ions in near-critical solutions. Takamuku *et al.* (2001) performed large-angle X-ray scattering (LAXS) and small-angle neutron scattering (SANS) measurements in water/acetonitrile and water/dioxane mixtures and suggested that the addition of salt ions, such as NaCl, accelerated phase separation by attracting polar molecules. In addition, several authors have shown that nanometer-scale clusters are formed, even far from the critical temperature (Misawa *et al.*, 2004; Jacob *et al.*, 1999). Misawa *et al.* (2004) investigated the structure of a near-critical ternary mixture, water/1-propanol/KCl, by SANS measurement and a reverse Monte Carlo analysis, and showed that a water layer of several tens of Å existed in the one-phase region.

A mixture of water and 3-methylpyridine (3MP) is known to have a large salt effect on the critical temperature. This binary mixture is completely miscible at room temperature and separates into two phases with increasing temperature at 310.3 K. With the addition of salt ions, it has been reported that the critical temperature decreases (Narayanan & Kumar, 1994) due to the creation of nano-sized microclusters in the one-phase region (Jacob *et al.*, 1999). On the other hand, several authors have investigated the critical phenomena of a water/3MP/NaBr system by means of light scattering (Jacob *et al.*, 1998; Anisimov *et al.*, 2000; Wagner *et al.*, 2004; Hernandez *et al.*, 2003; Kostko *et al.*, 2004; Unni, 2006). Jacob *et al.* showed that critical behaviors can be expressed by crossover from the three-dimensional Ising behavior to the mean-field behavior and concluded that an additional length scale exists competing with the correlation length of the concentration fluctuation. Anisimov *et al.* also suggested the formation of a microheterogeneous phase due to the clustering of ions and molecules.

Recently, Onuki & Kitamura (2004) theoretically showed that the addition of salt ions to a near-critical binary mixture induces a long-period structure. Furthermore, our SANS measurements show that such a structure is formed in ternary mixtures with D_2O/3MP and a salt such as LiCl, NaBr and $MgSO_4$ near the critical point (Sadakane *et al.*, 2006). This evidence suggests that this large structure is induced by collaboration between the solvation effect and the critical fluctuation.

In the present study, we obtained further SANS results on critical fluctuation and large structures in the near-critical region. The effects of the strength of solvation and salt concentration were investigated. We confirmed that large clusters (about 1000 Å) exist even in the one-phase region. The clusters become larger as the critical point is approached. These results reveal that strong coupling of the critical fluctuation and the solvation effect of salt ions induces more distinct clusters of solvated ions.

2. Experimental

2.1. Samples

A binary mixture of 3MP and heavy water (D_2O) was prepared at a critical composition, *i.e.* 27.11 wt% 3MP and 72.89 wt% D_2O (Narayanan & Kumar, 1994). At this concentration, the critical temperature is known to be 310.3 K (Sadakane *et al.*, 2006). 3MP (98% purity) and D_2O (99% purity), purchased from Nacalai Tesque and EURISO-TOP, respectively, were mixed without further purification. To investigate the solvation effects of salt ions, each salt was dissolved in this binary mixture: LiCl (99.0% purity, Nacalai Tesque), NaBr (99.0% purity, Wako Pure Chemical Industries, Ltd), NaCl (99.5% purity, Nacalai Tesque), KCl (99.0% purity, Wako Pure Chemical Industries, Ltd), and $MgSO_4$ (99.0% purity, Nacalai Tesque). The weight percent of salts ($\chi_{\rm salt}$) and critical temperatures are summarized in Table 1.

2.2. SANS measurements

SANS measurements were performed with the small-angle neutron scattering spectrometer SANS-U at JRR-3M of the Japan Atomic Energy Agency (JAEA) (Okabe *et al.*, 2005). A 7.0 Å incident neutron beam with a wavelength resolution of 10% was used, and the scattered neutrons were collected with a two-dimensional position-sensitive proportional counter placed at 8 and 12 m from the sample position. The modulus of the scattering vector, Q (= $4\pi\sin\theta/\lambda$, where λ is the wavelength, and 2θ is the scattering angle), ranged from 3.9×10^{-3} to 5.2×10^{-2} Å^{-1}. Each sample was kept in a quartz

Table 1
Weight percent of salts ($\chi_{\rm salt}$) and critical temperatures estimated from experiment (T_c).

Salt	$\chi_{\rm salt}$ (wt%)	T_c (K)
LiCl	0.21	307.8
LiCl	1.40	300.0
LiCl	12.49	287.1
NaBr	0.37	307.7
NaCl	0.38	303.4
NaCl	1.94	288.5
KCl	0.49	302.7
KCl	2.47	286.1
$MgSO_4$	0.06	307.1
$MgSO_4$	0.16	303.3
$MgSO_4$	0.77	285.2

cell 2 mm thick. These cells were placed in a temperature-controlled chamber with a temperature accuracy of better than 0.1 K. Measurement times were varied from 600 to 1800 s, depending on the scattering intensity. The observed two-dimensional scattering intensity patterns were azimuthally averaged, and corrected for transmission, background scattering, and sample thickness. They were scaled to absolute differential scattering cross-sections using a secondary standard sample made of Lupolen (a polyethylene slab calibrated with the incoherent scattering intensity of vanadium).

3. Results

Scattering intensities below $Q = 2.5\times10^{-2}Å^{-1}$ increased significantly near the critical point in all of the mixtures. The SANS profile of the binary mixture D_2O/3MP follows the Ornstein–Zernike function (Stanley, 1971) as

$$I_{\rm OZ}(Q) = \frac{I_0}{1+\xi^2Q^2}, \qquad (1)$$

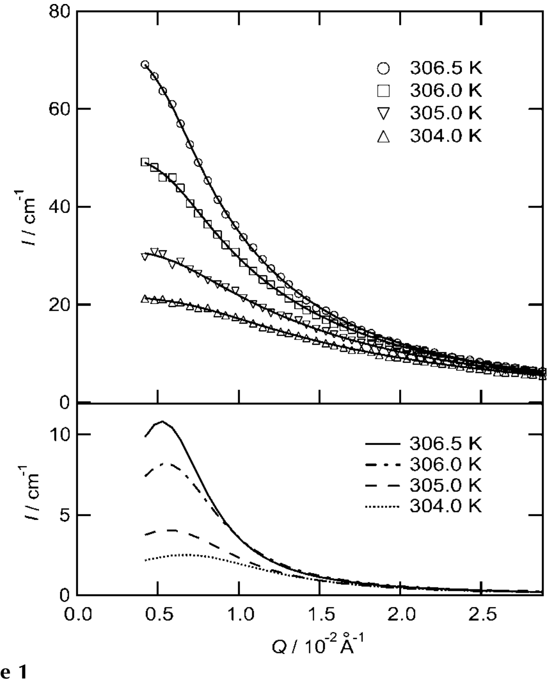

Figure 1
The upper figure shows the SANS profile of D_2O/3MP/LiCl ($\chi_{\rm LiCl} = 0.21$ wt%) and the fitting function, equation (2). The lower figure is the long-range periodic structure indicated by the second term of equation (2).

where ξ is the correlation length due to the concentration fluctuation near the critical point, and I_0 is the forward scattering proportional to the osmotic compressibility. The obtained temperature dependencies of I_0 and ξ follow the critical phenomenon of the three-dimensional Ising universality class: the critical indices are $\gamma = 1.24$ and $\nu = 0.63$ (Narayanan & Kumar, 1994). As shown in our previous paper (Sadakane *et al.*, 2006), the SANS profiles of D_2O/3MP and small amounts of LiCl, NaBr and $MgSO_4$ can be well explained by the function for a lamellar structure proposed by Nallet *et al.* (1990) as

$$I_{\rm Nallet}(Q) = \frac{I_0}{1+\xi^2Q^2} + \frac{A}{1+\xi'^2(Q-2\pi/d)^2}, \qquad (2)$$

where A, ξ' and d are the amplitude, correlation length and characteristic repeat distance of a long-range periodic structure, respectively. The first term corresponds to the concentration fluctuation of D_2O and 3MP, and the second term indicates the periodic structure. Fig. 1 shows the SANS profile of a ternary mixture of D_2O/3MP with LiCl ($\chi_{\rm LiCl} = 0.21$ wt%) with the fitting function given by equation (2). The temperature dependence of I_0 and ξ estimated with equation (2) is consistent with the three-dimensional Ising behavior. The temperature dependence of the second term is shown in the lower part of Fig. 1. The long-range periodic structure grows as the critical temperature is approached (Sadakane *et al.*, 2006).

Fig. 2 shows the SANS profile of D_2O/3MP/KCl at 301.0 and 301.5 K. These profiles have several shoulders, especially in the low-Q region, and can not be explained by equation (2), which is shown by the solid line. Similar scattering patterns were observed with samples containing high concentration of LiCl, NaCl and $MgSO_4$.

To analyze the data, we assumed spherical clusters in this region and applied the following function,

$$I_{\rm sp}(Q) = \frac{I_0}{1+\xi^2Q^2} + C\int_0^\infty f(R)\left|F(Q,R)\right|^2 dR, \qquad (3)$$

where

$$f(R) = \left(\frac{Z+1}{R_m}\right)^{Z+1} R^Z \exp\left[-\left(\frac{Z+1}{R_m}\right)R\right] / \Gamma(Z+1), \qquad (4)$$

and

$$F(Q,R) = \frac{\sin(QR) - QR\cos(QR)}{(QR)^3}. \qquad (5)$$

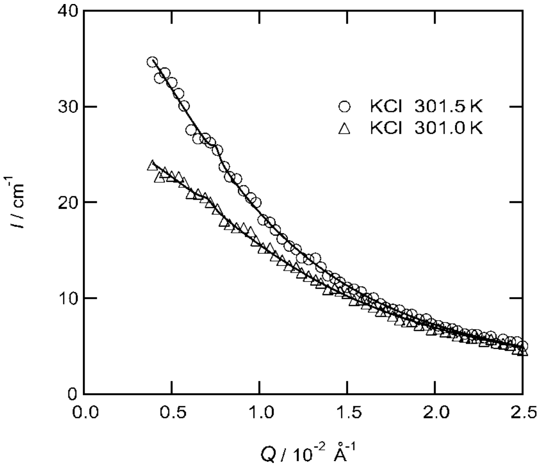

Figure 2
SANS profile of D_2O/3MP and KCl ($\chi_{\rm KCl} = 0.49$ wt%) at 301.0 and 301.5 K with the fitting function given by equation (2).

The first term in equation (3) indicates the critical fluctuation of D_2O and 3MP, and the second term corresponds to the form factor from spherical clusters with a Schultz size distribution. Here, R is the radius of a cluster, Z is a width parameter, R_m is the mean radius of cluster, Γ is the gamma function, and C is related to the number of clusters.

Fig. 3 shows the same SANS profile as in Fig. 2 (D_2O/3MP/KCl) with the fitting function given by equation (3). The several shoulders observed in the low-Q region can be well explained by the fitting. The temperature dependence of I_0 and ξ estimated with equation (3) is consistent with three-dimensional Ising behavior.

The estimated cluster size, R_m, increases as the critical point is approached. These findings indicate that a mesoscopic-sized cluster is formed near the critical point and both the size and number increase as the critical point is approached. The same behaviors were observed in ternary mixtures with LiCl ($\chi_{LiCl} = 12.49$ wt%), NaCl ($\chi_{NaCl} = 1.94$ wt%), KCl ($\chi_{KCl} = 2.47$ wt%) and $MgSO_4$ ($\chi_{MgSO_4} = 0.16$ and 0.77 wt%).

4. Discussion

The SANS profiles for mixtures of D_2O, 3MP and salt were analyzed using two types of scattering functions, depending on the kind of salt and the salt concentration. One is for periodic structures [equation (2)] for samples with low concentrations of LiCl, NaBr, NaCl and $MgSO_4$, and the other is for spherical clusters [equation (3)] for other samples. Both scattering functions include characteristic length scales: d is the repeat distance of the periodic structure in equation (2), and R_m is the size of the spherical clusters in equation (3).

Fig. 4(*a*) shows the temperature dependence of the critical fluctuation, ξ, and repeat distance, d, derived from equation (2) for mixtures with a low salt concentration. Fig. 4(*b*) shows the temperature dependence of ξ and R_m derived from equation (3) for other mixtures. The trends of temperature dependence of d and R_m are nearly identical: both d and R_m increase with an increase of the correlation length, ξ. This suggests that the origin of the extra peaks in the critical fluctuation, interpreted as 'long-period structure' and 'large clusters', should be the same. The difference between the two functions may be due to the distinctness of the induced clusters. When the concentration of a salt is low, indistinct clusters are formed and only a single shoulder is observed in the critical scattering, and we applied the fitting function given by equation (2) in the previous study (Sadakane *et al.*, 2006). On the other hand, more distinct clusters are formed when the salts are present at rather high concentrations. In the present study, we applied the fitting function given by equation (3), and all of the SANS profiles with salt ions could be explained. This supports the assumption that 'large clusters' might be more essential.

Fig. 5 summarizes the salt concentration dependence of the shift in the critical temperature ΔT. Spherical clusters were observed in samples with large ΔT. Thus, when the temperature shift is large, mesoscopic-sized clusters are distinct. This finding also suggests that the clusters have the same origin as the critical temperature shift. We believe that large clusters are generated by a coupling of the critical fluctuation and the preferential solvation of salt ions by water molecules. These structures could be emphasized under a strong solvation effect.

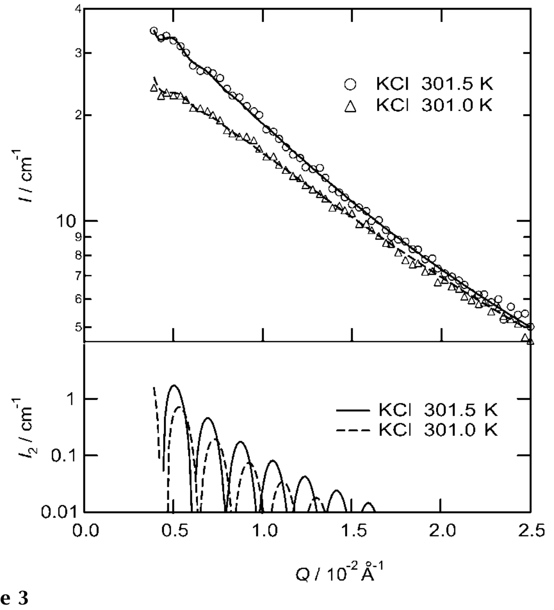

Figure 3
The upper figure is the temperature variation from D_2O/3MP and KCl ($\chi_{KCl} = 0.49$ wt%) at 301.0 and 301.5 K. The lower figure is the fitted scattering function from spherical clusters indicated by the second term of equation (3).

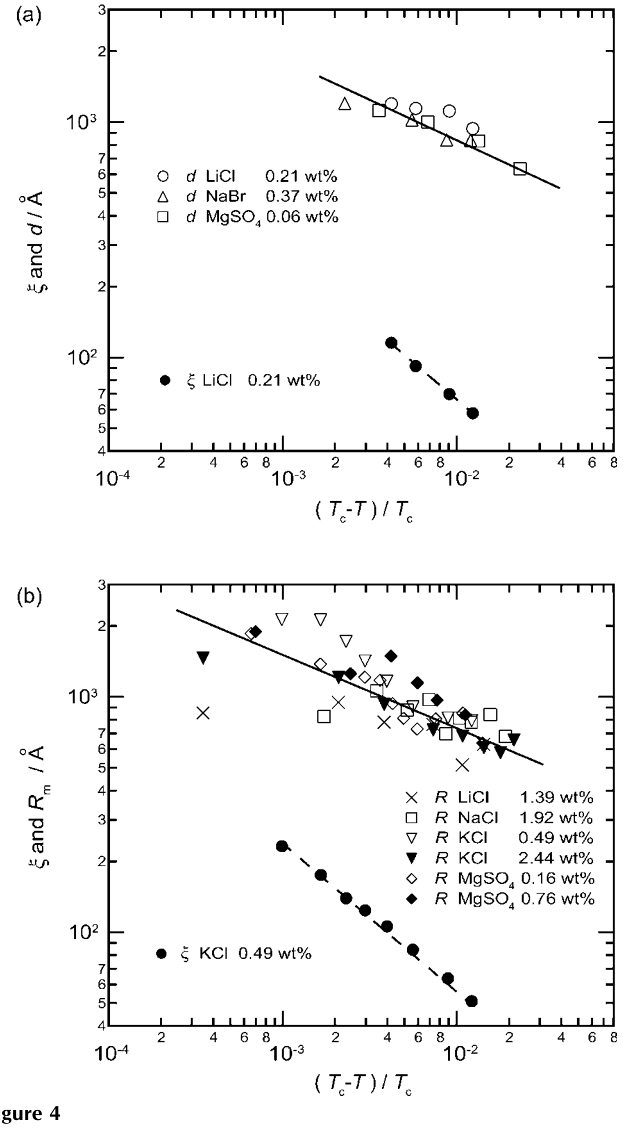

Figure 4
(*a*) Temperature dependence of the correlation length, ξ, and repeat distance, d. (*b*) Temperature dependence of the correlation length, ξ, and radius of a cluster, R_m. In both figures, the solid line is a guide for the eye, and the dotted line is derived from three-dimensional Ising fitting.

Table 2

Radii of cations and anions used in our experiment. *r* is the crystal radius of each ion. These values were estimated by Pauling (1927) and Nightingale (1959).

Ion	*r* (Å)
Li^+	0.60
Na^+	0.95
K^+	1.33
Mg^{2+}	0.65
Cl^-	1.81
Br^-	1.95
SO_4^{2-}	2.90

As we mentioned in Section 1, Onuki & Kitamura (2004) applied the Ginzburg–Landau theory to phase separation and critical phenomena in mixtures with polar liquids and electrolytes, and suggested that strong coupling of the critical fluctuations and the solvation effect induces a large-period structure near the critical point. Their theory is qualitatively consistent with our result. However, there are some differences. Firstly, according to the theory, the scattering function indicating a long-period structure can be written as

$$I(Q) = \frac{I_0}{1 + (1 - \gamma^2/(1 + \lambda^2 Q^2))\xi^2 Q^2}, \tag{6}$$

where γ is a dimensionless parameter that corresponds to the difference in the strengths of the cation and anion, and λ is the Debye screening length. However, our SANS data can not be explained by equation (6), especially in the low-Q region (Sadakane *et al.*, 2006). Secondly, the theory predicts that ΔT increases when smaller ions are dissolved in a binary mixture. Furthermore, the large structure is enhanced when a smaller cation and larger anion are dissolved. To compare our results with their theory, the radii of the salt ions in each sample are summarized in Table 2. Based on the size of the ions, the effect of salt on ΔT is expected to follow the order LiCl ~ $MgSO_4$ > NaCl > NaBr > KCl, according to the theory. Furthermore, based on the difference in size between the cation and anion, large cluster formation is expected theoretically to be in the order LiCl ~ $MgSO_4$ > NaBr > NaCl > KCl. However, in our experiment, the salt-dependence of ΔT is $MgSO_4$ > NaCl ~ KCl > LiCl > NaBr, and the size of the cluster is KCl ~ $MgSO_4$ > NaCl > LiCl > NaBr. Therefore, our results are not quantitatively fully consistent with the theoretical expectation.

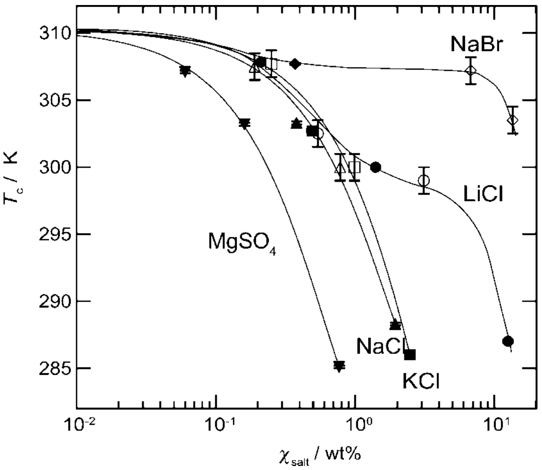

Figure 5

Salt concentration dependence of the critical temperature determined by SANS measurements and visual observations. Filled circles indicate T_c values of samples with LiCl, filled triangles NaCl, filled squares KCl, filled diamonds NaBr and crosses $MgSO_4$. Open symbols indicate the respective data obtained by the cloud point method.

So far, many researchers have tried to identify the origin of the temperature shift upon the addition of salts with nanometer-scale clusters (Misawa *et al.*, 2004; Jacob *et al.*, 1999). However, such small-cluster formation may not be efficient for inducing phase separation because the concentration fluctuation should increase to several thousand Å. In our results, mesoscopic-sized clusters are formed near the critical point and they grow as the critical point is approached. Furthermore, the clusters are more distinct in the case of a large critical temperature shift ΔT. Therefore, our result is suggestive for explaining the decrease in the critical temperature upon the addition of salts.

Finally, it should be noted that the fitting function, equation (3), should be modified, since mesoscopic clusters would not be strictly spherical in shape. In addition, we can not say that the fitting with equation (3) is improved compared with that with equation (2): χ^2 values from equation (2) are 3.74 for 301.0 K and 7.29 for 301.5 K, whereas those from equation (3) are 6.63 and 6.73, respectively. Further experiments and theoretical analyses will be needed to reveal the details of large-cluster formation.

5. Conclusions

We performed SANS experiments to investigate the concentration fluctuation and structures in the vicinity of the critical point. When a small amount of salt is added, the SANS profiles indicate the existence of a long-period structure. On the other hand, the SANS profiles from ternary mixtures of D_2O/3MP with a large amount of salt can be analyzed while assuming spherical clusters. The clusters increase in size as the critical point is approached. These findings suggest the origin of the shift in critical temperature upon the addition of salts to binary mixtures with polar and non-polar liquids.

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References

Anisimov, M. A., Jacob, J., Kumar, A., Agayan, V. A. & Sengers, J. V. (2000). *Phys. Rev. Lett.* **85**, 2336–2339.

Hales, B. J., Bertrand, G. L. & Hepler, L. G. (1966). *J. Phys. Chem.* **70**, 3970–3975.

Hernandez, M. P. & Ortega, F. & Rubio, R. G. (2003). *J. Chem. Phys.* **119**, 4428–4436.

Jacob, J., Kumar, A., Anisimov, M. A., Povodyrev, A. A. & Sengers, J. V. (1998). *Phys. Rev. E*, **58**, 2188–2200.

Jacob, J., Kumar, A., Asokan, S., Sen, D. Chitra, R. & Mazumder, S. (1999). *Chem. Phys. Lett.* **304**, 180–186.

Kostko, A. F. & Anisimov, M. A. & Sengers, J. V. (2004). *Phys. Rev. E*, **70**, 026118.

Misawa, M., Dairoku, I., Honma, A., Yamada, Y., Sato, T., Maruyama, K., Mori, K., Suzuki, S. & Otomo, T. (2004). *J. Chem. Phys.* **121**, 4716–4723.

Nallet, F., Roux, D. & Milner, S. T. (1990). *J. Phys. (Paris)*, **51**, 2333–2346.
Narayanan, T. & Kumar, A. (1994). *Phys. Rep.* **249**, 135–218.
Nightingale, E. R. (1959). *J. Phys. Chem.* **63**, 1381–1387.
Okabe, S., Nagao, M., Karino, T., Watanabe, S., Adachi, T, Shimizu, H. & Shibayama, M. (2005). *J. Appl. Cryst.* **38**, 1035–1037.
Onuki, A. & Kitamura, H. (2004). *J. Chem. Phys.* **121**, 3143–3151.
Pauling, L. (1927). *J. Am. Chem. Soc.* **49**, 765–790.
Sadakane, K., Seto, H. & Nagao, M. (2006). *Chem. Phys. Lett.* **426**, 61–65.
Stanley, H. E. (1971). *Introduction to Phase Transitions and Critical Phenomena.* Oxford University Press.
Takamuku, T., Yamaguchi, A., Matsuo, D., Tabata, M., Kumamoto, M., Nishimoto, J., Yoshida, K., Yamaguchi, T., Nagao, M., Otomo, T. & Adachi, T. (2001). *J. Phys. Chem. B*, **105**, 6236–6245.
Unni, P. K. M. (2006). *J. Chem. Phys.* **124**, 054505.
Wagner, M., Stanga, O. & Schroer, W. (2004). *Phys. Chem. Chem. Phys.* **6**, 580–589.