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Nucleation and clustering: a microscopic study of the aggregation behaviour in metastable solutions

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Abstract

The aggregation state of metastable solutions has been studied by small angle neutron scattering. The variation of the scattering curves was monitored during continuous cooling for aqueous solutions of ND_4Cl. The analysis of the data indicates the existence of finite-sized domains responsible for the variation of the scattering density on undercooling. The data have been analyzed using a Percus–Yevick hard-sphere model which gives cluster sizes between 10 and 30 nm with an average interparticle distance of 100–200 nm.

1. Introduction

The metastable state of supercooled solutions is usually explained on the thermodynamic basis of nucleation theory. The basic features described by the classical droplet model of Becker and Doring [1] seem to be valid and have also been confirmed by different independent approaches, such as the continuous model or Monte Carlo simulations [2,3]. Nevertheless, its validity continues to be mainly qualitative for most systems and only in a few particular situations (e.g., condensation from the vapour) have the prediction of the theory been verified in a quantitative way.

Solution systems are typical examples where the quantitative predictions of the theory fail. Aspects such as the long induction periods observed and the microscopic nature of the metastable state are not yet understood. The main source of experimental data concerned with nucleation in solutions is based on the information which can be obtained concerning the critical size of nuclei when the experimental conditions are close to the limiting attainable supersaturation. On the contrary, there is little information which refers to the nucleation kinetics in the early stages of the process and at low or intermediate supersaturation. The influence of these precursor stages, in the nucleation behaviour near the critical limit of supersaturation, is also unknown.

The existence of an appreciable population of clusters, during the time interval corresponding to the macroscopic metastable range of concentrations, is a problem considered in recent work dealing with this topic and may have considerable impact on the understanding of the mechanism of liquid–solid transitions. The existence of local minima, given the stability of aggregates less than the critical size, is supported from a thermodynamic point of view, when the radius dependence of the surface tension is included in the Gibbs free energy balance for nucleation. This treatment, largely based on the Tolman

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[4] and Buff [5] studies on surface tension, has been reviewed by Rasmussen [6] and more recently an empirical approximation for the particular case of solutions has been developed by Larson and Garside [7].

This problem is mainly experimental in that data are very scarce and even the existence of a stable concentration of clusters has not been clearly demonstrated to date. In this work small angle neutron scattering (SANS) has been applied to the study of supersaturated aqueous solutions. To the authors' knowledge, no previous studies of the metastable behaviour of solutions have been performed using SANS.

2. Experimental

2.1. Selection of the sample

The experiments were limited to wery soluble substances, e.g., ND_4Cl, for several reasons. First, solutions of highly soluble salts can be considered as the most favourable for the formation of clusters of an appreciable size, because of their low surface free energy. Second, the temperature dependence of solubility provides good experimental conditions for generating different supersaturated states, with an induction time for nucleation greater than the time needed to collect several diffraction patterns. The third requirement was to obtain a good contrast between the solvent and the solute aggregates, for which deuterated substances were employed.

The solutions were prepared by heating an excess amount of H_2O for 12 h at the selected saturation temperature and then filtering with normal laboratory filter paper. After preheating, a second filtration was made with a 2 μm filter (Sartorius). The final saturation temperature (65°C) was determined for such conditions by slowly heating the sample until dissolution was reached.

2.2. Experimental procedure

The experiments were carried out using the D11 small angle diffractometer at the Institut Laue–Langevin (ILL) in Grenoble. This instrument has a high incident neutron flux which facilitates measurements in the region near zero angle. The incident wavelengths used for preliminary experiments were 5 and 12 Å. The sample–detector distances were varied to cover the interval between 5 and 20 m the final conditions employed in the experiments were $\lambda = 10$ Å and sample to detector distance of 5 m. A standard silica cell (1 mm thickness) was used as sample container. It was sealed at the top to avoid evaporation of the solvent.

The supersaturation was generated by cooling. A stepwise procedure was followed in varying the temperature from the saturation temperature (65°C) until

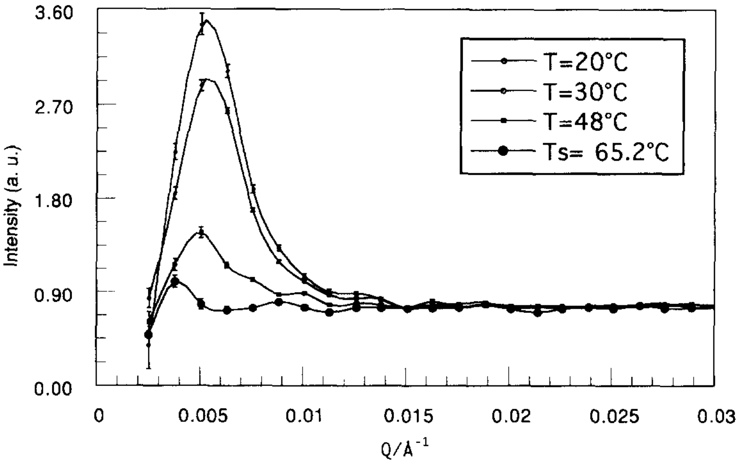

Fig. 1. Evolution of the corrected scattered intensity with undercooling for ammonium chloride solution. Continuous lines are cubic splines fitted to the experimental datapoints.

crystallization was reached (20°C) and several spectra were stored at different levels of supercooling. The state of the sample was visually checked after each run to see if crystallization had occurred within the time interval needed for collection of a single spectrum.

2.3. Data reduction

To obtain the sample contribution to the scattered intensity as a function of Q, the momentum transfer ($Q = (4\pi/\lambda)\sin(q/\theta)$), the raw data from the D11 instrument were corrected for the background from the sample container and non-linearities in the response of the detector cells. The calculations were performed using the software package for isotropic data analysis available at the ILL [8].

The spatial variations of the efficiency of the multidetector cells were corrected by performing an experiment with a highly incoherent scatterer which provides a nominally flat spectrum, independent of Q. Irregularities in this spectrum can be considered as a result of variations in the efficiency of the detector cells which are then used to normalize the sample spectra. In the present case, since only relative values of intensity are needed, the complete set of experiments was normalized to the same water spectrum.

3. Results

3.1. General scattering patern on undercooling

The intensity variation with undercooling for the ND_4Cl solutions, starting from saturation, until the instant where crystallization takes place is illustrated in Fig. 1. A common trend is followed as a function of the supersaturation, which consist of an increase in the scattered intensity, together with an extension of the scattering region to high Q-values during the undercooling. From a qualitative point of view, this behaviour indicates a progressive variation in the aggregation state of the sample, as indicated by both the number and the size of the scattering entities as a function of the supersaturation. The progressive displacement to higher angles indicates a larger contribution to the scattering curve from the smaller particles as the supersaturation increases. The upper limit in the Q-axis, where a relevant scattering exists, is 0.015 $\mathring{A}^{-1}$ which correspond to the last spectrum taken before crystallization.

3.2. Particle size and structure factor for the metastable solution

In the treatment of data from SANS experiments, it is usual to consider the scattering entities as single particles, characterized by a form factor $P(Q)$. The experimental intensity is then separated into two factors, $P(Q)$ and $S(Q)$,

$$I(Q) = \phi P(Q) S(Q), \qquad (1)$$

where $\phi = N/V$ is the number density of the particles or individual scatterers in the sample. $S(Q)$ plays the role of a structure factor, which describes the spatial distribution of the particles. For small Q, the form factor can be approximated using the well-known Guinier expression [9]

$$P(Q) = V^2(\rho - \rho_0)^2 \exp\left(Q^2 R_g^2/3\right) \quad (QR_g \ll 1). \qquad (2)$$

The structure factor, $S(Q)$, in Eq. (1) can be related to the pair-correlation function, $g(r)$, which for an isotropic system in three dimensions takes the form

$$S(Q) = 1 + 4\pi\phi \int_0^\infty |\, g(r) - 1 \,| \, r^2 \frac{\sin(Qr))}{Qr} \, \mathrm{d}r. \qquad (3)$$

The value of $S(Q)$ was approximated analytically, assuming the Percus–Yevick hard sphere model (PYHS) for the solute structure and using the expression of Ashcroft and Lekner [10] which relates the value of $S(Q)$ to both the hard sphere diameter, ξ, and the packing fraction, η. In this case it is assumed that the self-organization in the solution leading to the structure factor arises from the formation of depleted regions in the supersaturation during cluster growth [11]. Therefore, the physical interpretation of the hard sphere diameter is connected with the low supersaturation regions around a cluster of radius, R, where the growth of another cluster is inhibited.

The fits of the SANS patterns generated from this model to the experimental data were carried out by the minimization of Eq. (1), using the Marquardt

Table 1
Fitted values of η, ξ and R at different temperatures from the PYHS model

T (°C)	η	ξ (nm)	R (nm)
20.0	0.53	213	28
30.0	0.54	188	27
48.8	0.59	210	18
65.5	0.59	216	14

algorithm [12], the adjustable parameters being η, ξ and R. The results of the deconvolution of the experimental spectra into $P(Q)$ and $S(Q)$ for four supersaturation values are shown in Figs. 2(a)–(d). The corresponding values of η, ξ and R are listed in Table 1. As can be see from Fig. 2 there is an increase in the particle radius with superaturation from the order of 10 nm at low undercooling degree to 30 nm near the limit of critical supersaturation. The average interparticle distance also varies between 100 and 200 nm.

4. Discussion

The above SANS experiments yield direct evidence for the existence of finite sized domains, responsible for the variations in the scattering curve with overcooling. These results are consistent with the idea that a stable population of molecular clusters exists in supersaturated solutions. From the Percus–Yevick model, it follows that the aggregation state of the sample at the discrete values of supersaturation studied can be described as being formed of molecular clusters, with sizes between 10 and 30 nm and a

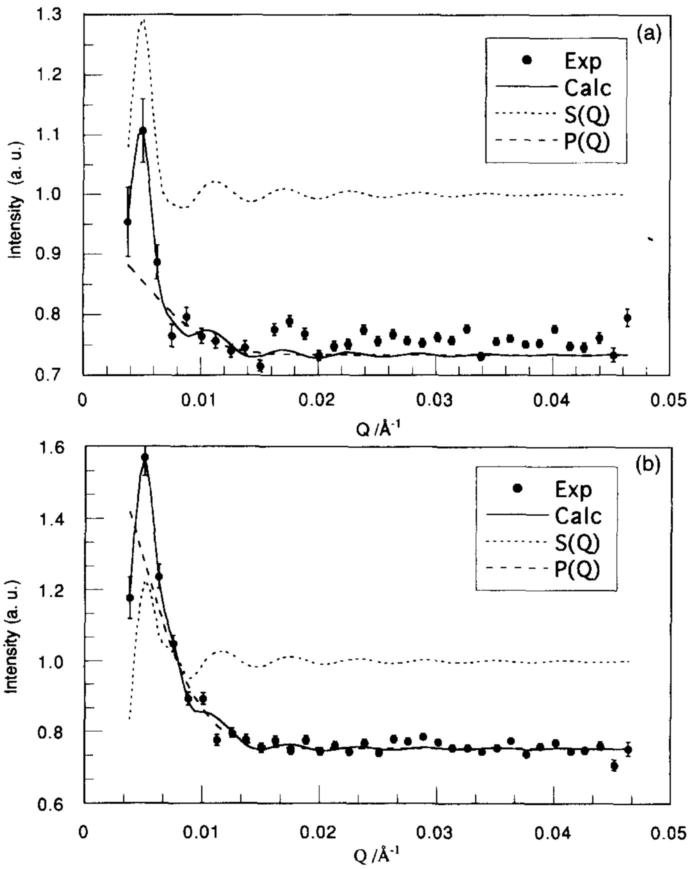

Fig. 2. Deconvolution of the experimental intensity into the structure and form factors using a Percus–Yevick hard-sphere model. (a) At the saturation temperature; (b)–(d) for different degrees of undercooling (ΔT = 17.2, 35.2, 45.2°C, respectively).

spatial arrangement which results from the formation of depleted regions in the supersaturation around the crystallites during the clustering process. In addition, the supersaturation has been found to be the main source of the variation in the aggregation state as results from the modelling of the particle size evolution.

In several experiments, repeated three times at the same temperature, there were no noticeable changes in the scattering function. Hence there is no evidence of a coarsening process during the time period needed to collect three spectra (30 min), which allows a preferred cluster size to be assigned to a particular level of supersaturation. This is in good agreement with the usual results of experiments, based on the induction time procedure, to study crystallization behaviour by macroscopic techniques. In such cases, the reliability of the results is much lower compared to those from the continuous cooling method.

5. Conclusions

The experiments reported here reveal the existence of inhomogeneities in the bulk metastable solution, varying in size from about 10 to 30 nm and with interparticle distances in the range 100–200 nm. The analysis of the scattering patterns also suggest that the aggregation state of the samples is mainly determined by the supersaturation rather than the time.

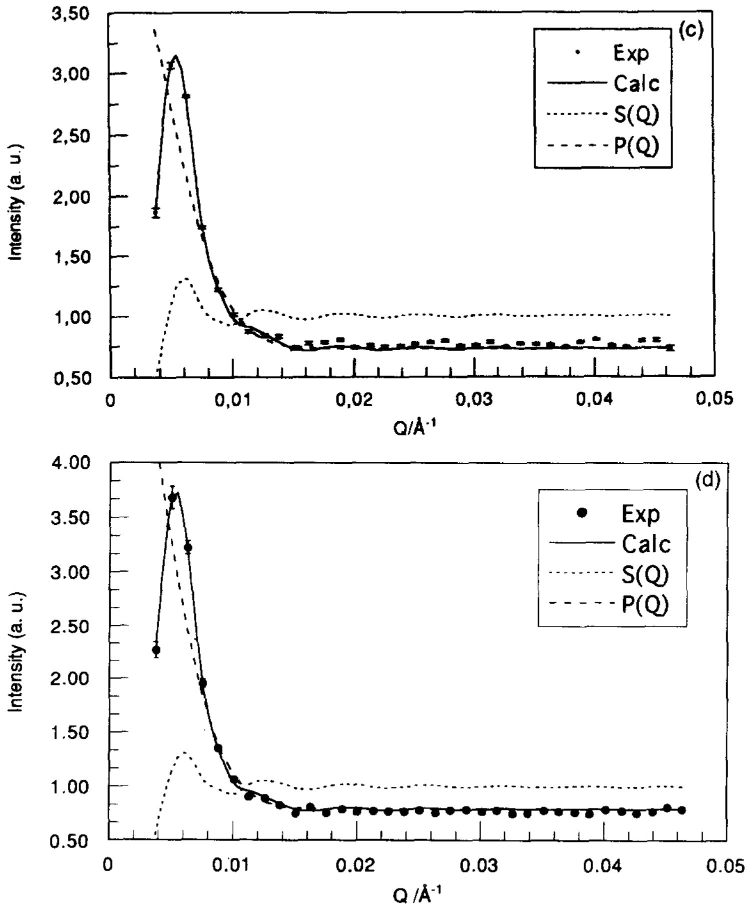

Fig. 2 (continued).

References

[1] R. Becker and W. Doring, Ann. Phys. 24 (1935) 719.
[2] M. Casandro and E. Olivieri, J. Stat. Phys. 17 (1977) 229.
[3] M. Kalos, J. Lebowitz, O. Penrose and A. Sur, J. Stat. Phys. 18 (1978) 39.
[4] R.C. Tolman, J. Chem. Phys. 17 (1949) 339.
[5] F.P. Buff, J. Chem. Phys. 19 (1951) 1591.
[6] D.H. Rasmussen, J. Cryst. Growth 56 (1986) 88.
[7] M.A. Larson and J. Garside, J. Cryst. Growth 116 (1992) 41.
[8] R.E. Ghosh, ILL Technical Report, no. 89GH02T (1989).
[9] J. Texeira, in: Growth and Form, ed. H.E. Stanley and N. Ostrowsky, NATO ASI Series (NATO, Boston, MA, 1986) p. 145.
[10] N.W. Ashcroft and J. Lekner, Phys. Rev. 145 (1966) 83.
[11] G. Banfi, V. Degiorgio and B. Speit, J. Appl. Phys. 74 (1993) 6925.
[12] IMSL Math. Library User's Manual (IMSL Houston, 1987) ch. 8.