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Another look at the melting temperature of colloidal crystals in the completely deionized suspension

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Abstract: Melting temperature (T_m) of colloidal crystals of monodispersed polystyrene and silica spheres has been measured for the *completely* deionized suspensions as a function of sphere concentration. More than 3 weeks are needed before achievement of the completely deionized state. T_m increases substantially as the deionization process of the suspension proceeds. The most reliable values of T_m observed for the completely deionized suspensions are successfully analyzed again with the theory of Williams et al. The new T_m values are compared also with the theory of Robbins et al., which treats the repulsive Yukawa potential between colloidal spheres.

Key words: Colloidal crystals – melting temperature – deionization – polystyrene spheres – silica spheres

Introduction

Melting temperature (T_m) of colloidal crystals, which is one of the most important thermodynamic parameters, has been measured and discussed by Williams et al. [1] for the first time. Recently, this author has measured the melting temperatures for the deionized suspensions of monodispersed polystyrene and silica spheres having various diameters ranging from 85 to 212 nm by reflection spectroscopy and also by the naked eye [2–4]. However, quite recently we found that it took a very long time, more than 3 weeks, before the aqueous suspensions of colloidal spheres were deionized *completely* with the mixed beds of ion-exchange resins, and, furthermore, the critical concentration of melting was very sensitive to the degree of deionization. Thus, a series of measurements of the melting temperatures of the colloidal crystals has been made again in this report. The most reliable new data of T_m are analyzed with the theories of Williams–Crandall–Wojtowicz and Robbins–Kremer–Grest. It should be further mentioned that giant colloidal single crystals have appeared only for the *completely* deionized suspension [5], and the completeness in the deionization of suspension is very important.

Experimental

Materials

D1C25, D1C27, D1B76, D1P30, D1K88, and D1B72 were polystyrene spheres purchased from Dow Chemical Co. VN1001 was also polystyrene spheres kindly donated by Nippon Zeon Co. (Tokyo). Colloidal silica spheres of CS-61, CS-81, CS-91, CS-121, and CS-161 were gift from Catalyst & Chemicals Ind. Co. (Tokyo). CS-22 is the colloidal silica spheres prepared by us previously [6]. Diameters (d) and standard deviations (δ) from the mean diameter, which were determined from electron microscopy, are listed in Table 1 along with other characteristics and parameters. The charge densities of strongly acidic groups on the spheres were determined by conductometric titrations with a Wayne–Kerr autobalance precision bridge, model B331, mark II (Bognor Regis, Sussex). These spheres were carefully purified several times using an ultrafiltration cell (model 202,

Table 1. New sets of parameters for the completely deionized suspensions

Sphere	d (nm)	δ (nm)	Charge density ($\mu C/cm^2$)	ϕ_{350}	10^{-3} C	A
D1C25	85	6	1.5	0.0034	117	5.2
D1C27	91	6	2.0	0.001	283	7.35
D1B76	109	3	2.1	0.001	300	7.55
D1P30	109	27.8	0.62	0.0017	242	7.0
D1K88	137	16	0.58	0.0022	257	7.2
D1B72	173	7	1.0	0.002	241	7.01
VN1001	192	6	0.50	0.0012	274	7.3
CS-61	81.2	11.5	0.60	0.0035	185	6.4
CS-81	103	13.2	0.38	0.0018	242	7.0
CS-91	110	4.5	0.48	0.0014	245	7.0
CS-121	136	10.9	0.40	0.0017	260	7.2
CS-22	178	9	0.52	0.00083	300	7.5
CS-161	184	18.6	0.47	0.0026	228	6.9

ϕ_{350}: colloidal concentration in volume fraction where T_m becomes 350 °K.

membrane: Diaflo XM300, Amicon Co.). Then the stock samples were treated on a mixed bed of cation- and anion-exchange resins (Bio-Rad, AG501-X8 (D), 20–50 mesh) for several months. Water used for the purification and for suspension preparation was deionized by using cation- and anion-exchange resins (Puric-R, type G10, Organo Co. (Tokyo)), purified by a Milli-Q reagent grade system (Millipore Co., Bedford, Massachusetts), and further treated with the ion-exchange resins of Bio-Rad.

Determination of melting temperature

The colloidal suspensions were prepared in a test tube (disposable culture tube, borosilicate glass, Corning Glass Works, Corning, New York; 11 and 13 mm, inside and outside diameters) shielded very tightly with Parafilm (American Can Co., Greenwich, Connecticut). The suspensions co-existed with a small amount of Bio-Rad resins. In order to attain the completely deionized suspension, the suspensions in the test tubes were mixed up-and-down several times a day and allowed to stand more than 3 weeks.

The test tubes containing the completely deionized suspension were immersed into a water bath which was made from smooth quartz glass and contained deionized water, a cooling tube and a heater. Temperature of the bath was raised very slowly from 8° to 92°C during 3 or 4 h. Melting temperature was determined with the naked eye, i.e., the brilliant iridescent colors and/or colloidal single crystals disappeared distinctly at the melting point.

Results and discussion

Significant effect of the degree of deionization upon the melting temperature

Williams et al. [1] have measured, for the first time, the melting temperature of colloidal crystals of monodispersed polystyrene spheres as a function of sphere concentration. Quite recently, this author [2] measured the melting temperatures of the colloidal crystals having different degrees of deionization of suspension. Figure 1 shows three sets of melting temperatures of polystyrene spheres measured by Williams et al. [1] (shown by open circles; reported 1976), by this author (crosses; 1991) [2] and this work (triangles; 1993). The sphere samples of the last two papers are monodispersed polystyrene spheres (diameter = 109 nm) purchased from Dow Chemical Co., and believed to be the same as those used by Williams et al. Clearly, the melting temperatures increased significantly as years reported, especially in the range of low concentrations of spheres. This increase is undoubtedly due to improvement in the degree of deionization of the suspension. It is not clear how long the suspensions in the experiments of Williams et al. were treated with the

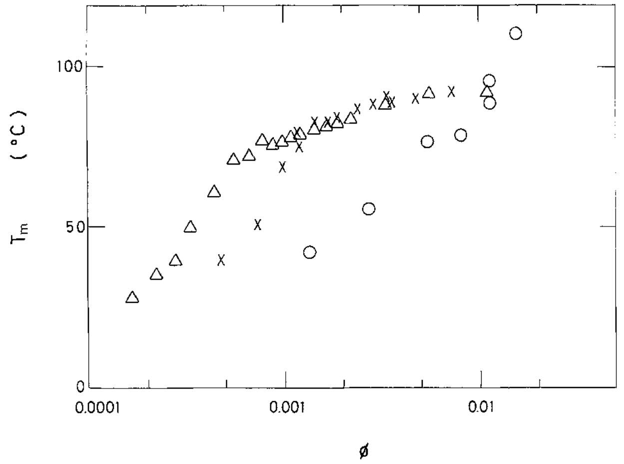

Fig. 1. Plots of T_m of deionized suspensions of polystyrene spheres (diameter = 109 nm) against ϕ. ○: Williams et al. [1] (reported 1976), ×: Okubo (1991), △: this work

ion-exchange resins and what kind of the resins were used. Data shown by crosses were taken 2 *or* 3 *hours* after suspension was set in a quartz observation cell containing the Bio-Rad ion-exchange resins. Newest data of this work were measured *more than* 3 *weeks* after suspension preparation with the resins. The melting temperatures were the same within experimental errors for all samples when they were coexisted with the resins more than 3 weeks and shorter than 3 months. Specific conductivities of the suspensions coexisted with resins more than 3 weeks were always smaller than 0.1 μs/cm with a cell of 1.3 cm^{-1} in its cell constant, though the values scattered rather significantly for each sample. In some cases the specific conductivities of completely deionized suspensions were similar to or even smaller than that of the deionized water used for suspension preparation. Thus, it is concluded that the deionization reaction is very slow, unexpectedly, and the most reliable data of melting temperature for the completely deionized suspension can be obtained after the resin treatment of more than 3 weeks. This author believes that the limit of completely deionized suspension is reached in this work and our attainment of the completeness in the deionization process will not be overcome in the future. It should be further noted that the critical concentration of melting at the given temperature, ϕ_{350}, which will be described later, for example, shifted substantially toward much lower concentrations as the deionization proceeded.

Observation of iridescent colors and colloidal single crystals

Suspensions of comparatively high concentrations displayed strong iridescent colors, though the suspensions themselves are not so transparent and rather milky. The iridescent colors changed as the incident light against the cell surface were changed ranging blue and red. This beautiful color is, of course, ascribed to the Bragg diffraction of light through the ordered arrays of spheres in the colloidal crystal. When the suspension was diluted, the single crystals or the crystallites became observable with the naked eye. Generally speaking, size of the single crystals increased sharply as sphere concentration decreased. Very large single crystals ranging 2 to 8 mm were observed for the highly deionized suspensions a bit higher than the critical concentration of melting [5, 7].

Most of single crystals were rock-like, especially in the comparatively concentrated suspensions. In many cases, triangular crystals, displaying various colors, e.g., red, orange, green, yellow, and blue were observed. Cube-like, pentagonal, and hexagonal islands were seen in some cases, as well as cone-like forms. Plate-like crystals have often been observed in diluted suspensions. Note that the colloidal single crystals described above are formed in the bulk phase of suspension via *homogeneous* nucleation. However, pillar-like and rather small single crystals can also be observed at the surface of the cell wall. These crystals may form after the *heterogeneous* nucleation mechanism [5, 7].

Generally speaking, size of the single crystals increased as the suspension temperature raised. However, for suspensions close to the melting temperature colloidal crystals became small again and they moved vigorously with translational and rotational Brownian movement. This blinking phenomenon was striking, resembling the blinking lights on a Christmas tree [8]. The blinking occurred also in this work, for example, for D1C25 suspension at $\phi = 0.00039$ above 79 °C and ceased at 84 °C, i.e., the melting temperature. Furthermore, CS-61 at $\phi = 0.0044$ blinked between 76° and 80.5 °C (melting temperature). Above the melting temperature, the colloidal crystals disappeared abruptly and sharply. Thus, melting temperature was determined rather easily and precisely with the naked eye with the accuracy of ± 0.1 °C. It should be mentioned that the melting processes were not observed so sharply, however, for the colloidal spheres larger than 170 nm, since the suspensions were milky and not very transparent, even in the diluted concentrations, so that the crystals were not clearly recognizable in the bulk phase.

Comparison of the new data of melting temperatures with the theory of Williams et al.

The melting temperatures (T_m) observed in this work are given by open circles in Figs. 2 and 3 for polystyrene spheres and Figs. 4 and 5 for silica spheres, respectively. All the suspensions coexisted with the mixed beds of cation- and anion-exchange resins (Bio-Rad) in the bottom of the test tubes for *more than* 3 *weeks* before the observation. The T_m-values kept constant irrespective of time of deionizing process when the suspensions were deionized more than 3 weeks. All of the experiments were carried out in the course of very slow ascending temperature. The T_m–ϕ curves

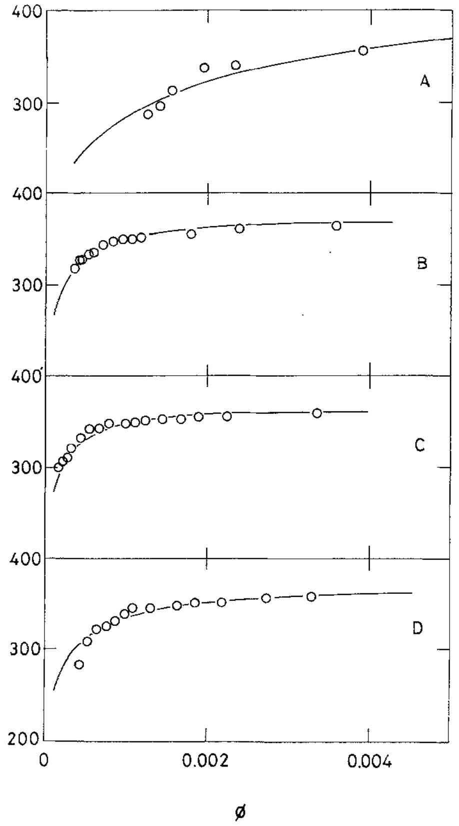

Fig. 2. Melting temperature of completely deionized suspensions of D1C25 (A), D1C27 (B), D1B76 (C), and D1P30 (D). The solid line is calculated from equation of Williams et al. [1] using the parameters C and A given in the table

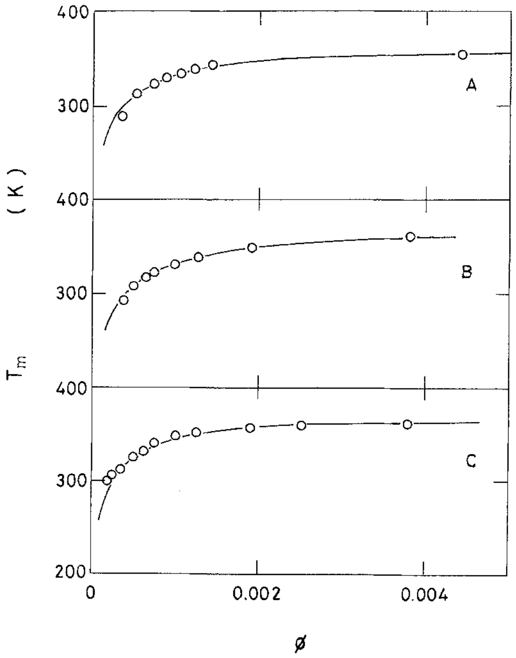

Fig. 3. Melting temperature of completely deionized suspensions of D1K88 (A), D1B72 (B), and VN1001 (C). The solid line is calculated from equation of Williams et al. [1] using the parameters C and A given in the table

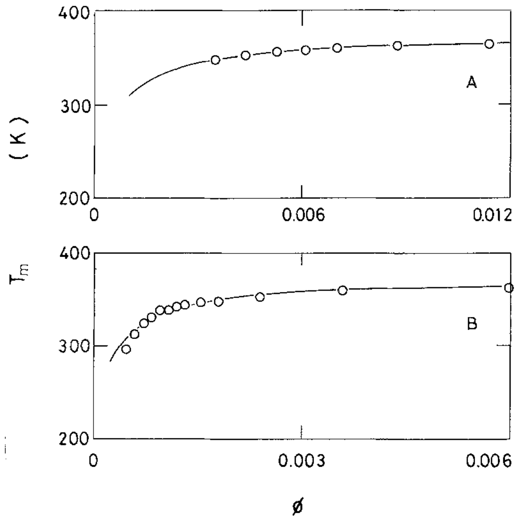

Fig. 4. Melting temperature of completely deionized suspensions of CS-61 (A) and CS-81 (B). The solid line is calculated from equation of Williams et al. using the parameters C and A given in the table

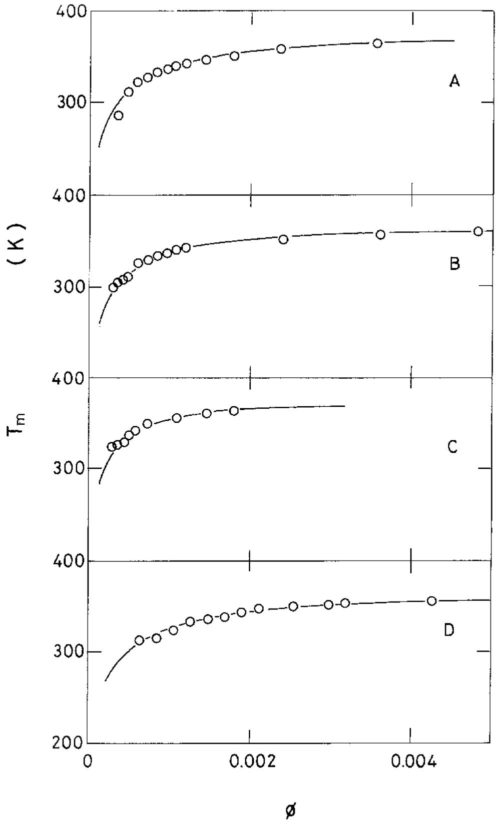

Fig. 5. Melting temperature of completely deionized suspensions of CS-91 (A), CS-121 (B), CS-22 (C) and CS-161 (D). The solid line is calculated from equation of Williams et al. using the parameters C and A given in the table

shifted significantly toward the lower ϕ values when this work was compared with the previous ones [2, 3]. The suspensions reported previously may be deionized uncompletely. This means that the melting temperature is very sensitive to the degree of deionization of the suspension. We believe that the data of T_m observed in this work are the most reliable ones for the completely deionized suspensions among the reference values reported so far. Generally speaking, T_m values were sensitive to sphere concentration, especially in the range of low temperatures. In other words, T_m increased sharply at low sphere concentrations and the saturation of T_m occurred at high concentrations.

The sphere concentrations, at which T_m equals 350 K, ϕ_{350}, are listed in Table 1. They were lower than the reference values reported previously [2]. The ϕ_{350}-values were almost insensitive to the sphere size in the range between 90 and 190 nm, and ϕ_{350} values of D1C25 ($d = 85$ nm) and CS-61 (81 nm) seems to be two-fold larger than those of the other spheres examined.

Following Williams et al. [1], melting temperature of colloidal crystals is given by Eq. (1):

$$T_m = C\phi^{1/3}\exp(-A\phi^{1/6})\{\phi^{-1}\ln\phi^{-1} - (\phi^{-1} - 1)\ln(\phi^{-1} - 1)\}^{-1}, \tag{1}$$

where ϕ is the concentration of spheres in volume fraction. C and A are constants. Equation (1) was fitted to our data by adjusting the values of C and A. The solid curves in Figs. 2 to 5 are best-fitted examples of representation. Agreement between the observation and theory was excellent, as is clear in the figures. The constants C and A thus estimated are compiled in Table 1. Both C and A values for D1B76 spheres (diameter = 109 nm) were 0.160 and 6.0, 0.211 and 6.6, and 0.300 and 7.55 for the values of Williams et al. [1] (reported 1976), Okubo [2] (1991), and this work, respectively. The main reason for the increase of the parameters with the year reported may be the difference in the *degree of deionization* of suspension.

The heat (enthalpy) of melting and entropy of melting are given by Eqs. (2) and (3), respectively [1].

$$\Delta H = Nk_BC\phi^{1/3}\exp(-A\phi^{1/6}), \tag{2}$$

$$\Delta S = Nk_B[\phi^{-1}\ln\phi^{-1} - (\phi^{-1} - 1)\ln(\phi^{-1} - 1)], \tag{3}$$

where N is the sphere number per cm^3, and k_B is Boltzmann's constant. Figures 6 and 7 show the ΔH values evaluated using the parameters C and A estimated, and Eq. (2) for polystyrene and silica spheres, respectively. Kind of spheres seems to have no influence on the absolute values of ΔH. In most cases, ΔH decreased slightly from 23 to 20 kJ/mol as ϕ increased from 0.001 to 0.004. The effect of size of spheres was not so significant except those of very small spheres (D1C25 and CS-61). ΔS decreased monotonously in the range from 80 to 40 J/mol K as ϕ increased from 0.001 to 0.02. Note that ΔS is independent of parameters C and A, and also of the degree of deionization of suspensions.

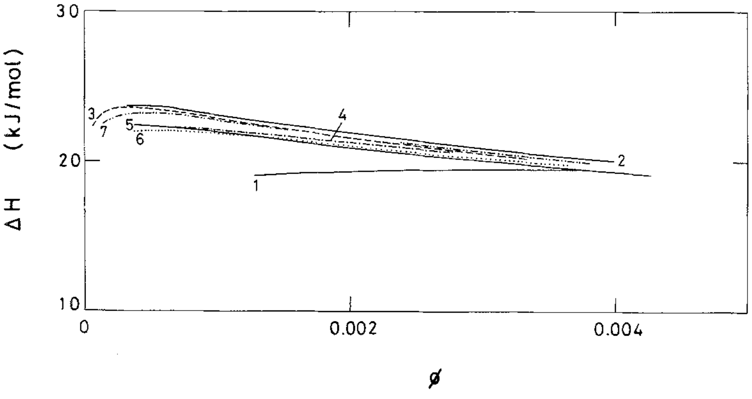

Fig. 6. Heat of melting estimated from the equation of Williams et al. [1] using the parameters C and A given in the table. 1) D1C25, 2) D1C27, 3) D1B76, 4) D1P30, 5) D1K88, 6) D1B72, 7) VN1001

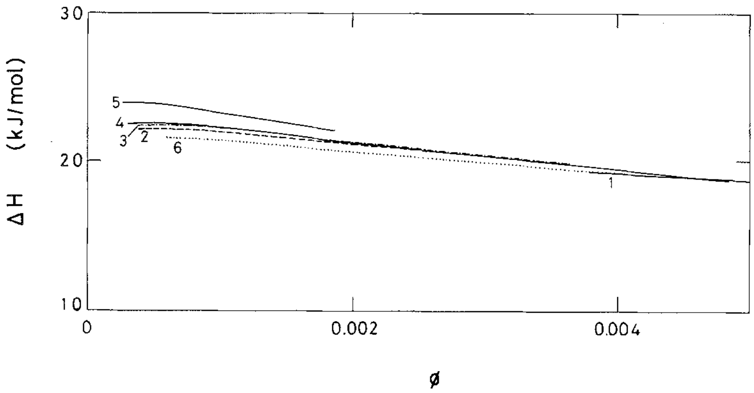

Fig. 7. Heat of melting estimated from the equation of Williams et al. using the parameters C and A in the table. 1) CS-61, 2) CS-81, 3) CS-91, 4) CS-121, 5) CS-22, 6) CS-161

Comparison of the new phase diagram with the theory of Robbins et al.

Robbins et al. [9, 10] obtained a phase diagram theoretically using a repulsive Coulomb (Yukawa) potential. The phase diagram contains both a melting transition and a transition between fcc and bcc subphases. Figure 8 shows the phase diagram in terms of λ and k_BT/U_a, where λ is the ionic parameter given by Eq. (4):

$$\lambda = \kappa \iota \, , \tag{4}$$

where κ is the inverse of Debye-screening length (D_l), and ι is the average intersphere separation. The Debye length is given by

$$D_l = (4\pi e^2 n/\varepsilon k_B T)^{-1/2} \, , \tag{5}$$

where e is the electronic charge, ε is the dielectric constant of the solvent and n is the concentration of free-state cations (H^+) and anions (OH^-) in deionized suspension, given by $n = n_c + n_0$. Here, n_c is the concentration (number of ions per cm^3) of *diffusible* counter-ions (H^+ ions) and n_0 is the concentration of both H^+ and OH^- from the dissociation of water. In this work n_0 was taken to be 2×10^{-7} (mol/dm^3) $\times N_A \times 10^{-3}$ cm^{-3}, where N_A is Avogadro's number. In order to estimate n_c, the fraction of free counter-ions (β) must be known. Values of β have been determined for colloidal spheres of various sizes and charge densities [11–15]. The β value changes dramatically depending on both the size and charge density of the spheres. The total number of stoichiometric charges on a sphere is the only factor needed to determine the β value. β for D1B76 spheres was estimated to be 0.1.

The energy parameter, k_BT/U_a is given by

$$k_BT/U_a = (\varepsilon \iota k_B T/Z^2 e^2)\exp(\lambda) \, , \tag{6}$$

where Z is the effective charge number of a colloidal sphere obtained as the stoichiometric number of charges multiplied by the β value. T is the

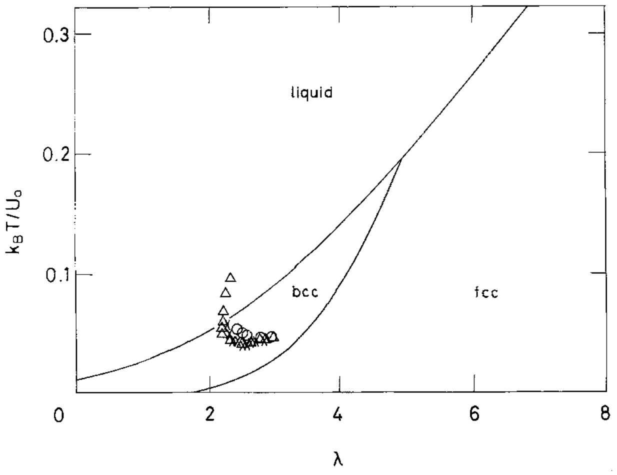

Fig. 8. Plots of k_BT/U_a against λ. ○: Experimental data for the phase transition of deionized suspension of polystyrene spheres (diameter = 109 nm) between liquid and crystal structures (Williams et al. [1]), ×: data for the transition of D1B76 suspension between liquid and bcc structures (Okubo [2] 1991), △: this work. $\beta = 0.1$, $Z = 490$, ——: theory of Robbins et al. [9]

melting temperature obtained experimentally. Plots of k_BT/U_a against λ are shown in Fig. 8. Solid curves are the theoretical ones separating liquid-like and crystal-like, or bcc and fcc structures [10]. Open circles are experimental points reported by Williams et al. [1] for the phase transition between liquid-like and crystal-like structures. Crosses are the data reported previously by us [2]. Triangles are the experiments in this work. Agreement between the theory and the experiment is satisfactory. Furthermore, all the data locate around places similar to each other. However, note that dependence of the energy parameter on the λ values is not always explained nicely by the theory. One of the reasons for the discrepancy may be that the concentration of the diffusible ions in the diluted suspension is quite low and close to the total concentration of H^+ and OH^- dissociated from water, 2×10^{-7} mol/L.

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References

1. Williams R, Crandall RS, Wojtowicz PJ (1976) Phys Rev Lett 37:348
2. Okubo T (1991) J Chem Phys 95:3690
3. Okubo T (1992) J Chem Phys 96:2261
4. Okubo T (1992) Colloid Polym Sci 270:1018
5. Okubo T (1992) Naturwissenschaften 79:317
6. Okubo T (1992) Ber Bunsenges Phys Chem 96:61
7. Okubo T (1993) Colloid Polym Sci 271:190
8. Okubo T (1992) J Colloid Interface Sci 153:587
9. Kremer K, Robbins MO, Grest GS (1986) Phys Rev Lett 57:2694
10. Robbins MO, Kremer K, Grest GS (1988) J Chem Phys 88:3286
11. Vanderhoff W, van de Hul HJ, Tausk RJM, Overbeek J. ThG (1970) In: Goldfinger G (ed) Clean Surfaces: Their Preparation and Characterization for Interfacial Studies. Dekker, New York
12. Schaefer DW (1977) J Chem Phys 66:3980
13. Alexander S, Chaikin PM, Grant P, Morales GJ, Pincus P, Hone D (1984) J Chem Phys 80:5776
14. Okubo T (1987) Ber Bunsenges Phys Chem 91:1064
15. Okubo T (1988) J Colloid Interface Sci 125:380

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