Thermal compression of colloidal crystals: Paradox of the repulsion-only assumption

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It is demonstrated that the Sogami potential, which contains both repulsive and attractive components, can account for the experimental data on photothermal compression of colloidal crystals much more satisfactorily than the purely repulsive DLVO potential. The Sogami theory gives a natural explanation for the non-space-filling nature of the crystals with an experimentally realistic value for the effective surface charge on the particles. A fundamental paradox of the DLVO theory is that in the case of thermal compression, when the whole dispersion is heated, it predicts no contraction at all, in contradiction to the experimental results.

Colloidal phenomena have traditionally been interpreted in terms of the purely repulsive DLVO (or Yukawa) potential.[1,2] However, recent experimental techniques are providing results which cannot be explained by the repulsion-only assumption without additional *ad hoc* assumptions. These results have largely been accumulated on latex sphere dispersions, which show pronounced structural inhomogeneities, including a two-state structure of a localized ordered structure in dynamic equilibrium with a liquidlike phase,[3,4] the formation of large stable voids,[5,6] and a two-state structure of a liquidlike phase in equilibrium with a gaslike phase.[7] These results definitely indicate the presence of an attractive interaction in addition to the widely accepted repulsion, as shown in the Sogami theory.[8] The Sogami potential, which contains both repulsive and attractive components, accounts not only for the existence of the structural inhomogeneities but also for the reentrant phase transition,[9] for the reversible phase transition in the *n*-butylammonium vermiculite clay system[10] and for the positive adsorption of cationic micelles near a cationic monolayer.[11]

The presence of the attraction has been criticized on various grounds. These criticisms contain errors. For example, Overbeek's criticism[12] of the Sogami theory violated the Gibbs-Duhem equation.[13] According to Smalley,[14] Overbeek's omission of the macroion contribution to the free energy leads to the implausible conclusion that "there is no free energy associated with the electrical double layers." The use of the enlarged sphere concept[15-19] led to the likewise implausible conclusion[20] that Perrin's interpretation[21] was wrong and that the Avogadro number may not be 6.02×10^{23}. In addition to these basic imperfections in arguments in favor of the repulsion-only assumption, dialectical errors in the traditional way of reasoning have also been pointed out. For example, by using computer simulations, Sood[22] was the first to show that both the repulsive DLVO potential and the Sogami potential give good agreement with observed structure factors, thereby showing that the repulsive DLVO potential cannot be claimed to be the only correct

one. Ito, Sumaru, and Ise[23] also showed that the elastic modulus of colloidal crystals can be reproduced satisfactorily not only by the repulsive DLVO potential but also by the Sogami potential. In the present article we demonstrate that the Sogami potential can account for experimental data on thermal compression of colloidal crystals much more satisfactorily than the repulsive DLVO potential.

Rundquist *et al.*[24] studied the thermal compression of regular crystalline arrays of dyed sulfonated polystyrene spheres. They used absorption of high intensity radiation by the dye to induce local heating of the crystalline array and probed the variation in the lattice parameter by Kossel line analysis. Following the traditional method of analysis, they interpreted the observed compression in terms of the repulsive DLVO potential. The essential experimental facts are as follows: (i) Low ionic strengths ($< 10^{-5}$ M) were used, (ii) the sphere diameter was 830 Å, (iii) the (bare) surface charge of the particles (Z) was $2370e$, where e is the electronic charge, (iv) the structure was bcc, (v) the sphere volume fraction was 2% (it was noted that higher volume fractions lead to the fcc structure), and (vi) the interparticle separation distance was 2450 Å.

We first consider the geometric facts (ii) and (iv)-(vi) and ask the question "Is the structure space filling ?" We denote the nearest-neighbor separation by b, and the length of the usual cubic (nonprimitive) unit cell by c. By the Pythagoras theorem, $c = 2b/\sqrt{3}$. Assuming the Kossel line analysis to be accurate to three significant figures,[25] $b = 2450$ Å implies $c = 2830$ Å. Let V_{cell} be the volume of the unit cell, given by $V_{cell} = c^3 = 2.27 \times 10^{10}$ Å^3. The volume occupied by one sphere, V_p, the volume of the primitive unit cell, is given by $V_p = 1.13 \times 10^{10}$ Å^3. Let V_s be the volume of a sphere (radius a). Since $a = 415$ Å, $V_s = 2.99 \times 10^8$ Å^3. The volume fraction in the bcc structure (r_c) is therefore given by $r_c = V_s/V_p = 0.0264$. The spheres occupy 2.64% of the dispersion volume within the bcc structure. Comparing this with the global volume fraction (r_b) of 2%, the

answer to our question is no. The bcc structure must coexist with a less dense phase, that is, it is part of a two-state structure. This proves the existence of a net attractive force at fixed interparticle distance[26] and invalidates the use of a purely repulsive potential, which must lead to a space-filling structure.

It is thus necessary and legitimate to use the Sogami potential instead of the repulsive DLVO potential. Ideally we should apply (via, for example, a Brownian dynamics simulation) the full Sogami potential,[8] given by Eq. (1),

$$U^G = \varepsilon^{-1}\{Ze \sinh(\kappa a)/\kappa a\}^2$$

$$\times \{(1 + \kappa a \coth\kappa a)/R - \kappa/2\}e^{-\kappa R} , \tag{1}$$

where U^G is the Gibbs pair potential, ε the dielectric permittivity, Ze the surface charge, κ the inverse Debye screening length, and R the interparticle separation. However, we get a good qualitative insight into the behavior of the system by simply equating the observed interparticle separation (b) with the position (R_m) of the minimum in $U^G(R)$, given in Ref. 8

$$R_m = \{\kappa a \coth\kappa a + 1$$

$$+ [(\kappa a \coth\kappa a + 1)(\kappa a \coth\kappa a + 3)]^{1/2}\}/\kappa . \tag{2}$$

With $a = 415$ Å, we set $R_m = b = 2450$ Å. Then we find κ from Eq. (2) to be 2.19×10^{-3} Å^{-1}. This solves the geometric problem easily: the spheres are constrained to sit at their observed interparticle separation by the long-range attractive tail in the Sogami potential and so, quite naturally, do not adopt a space-filling structure.

We wish to show how easy it is to solve Eq. (2) over the experimentally accessible range. Noting that the numerator in Eq. (2) is a function of the product of a with κ only, we write $R_m = f(a\kappa)/\kappa$ and construct Table I. The second column of the table expresses R_m as the number of Debye screening lengths at the potential minimum, which lies between 4 and 10. Note that experimentally, the secondary minimum between colloidal particles always lies between 4 and 10 Debye lengths.[27] DLVO theory, which balances a κ-independent attractive force (van der Waals force) with a repulsive force which decays exponentially with κ (double-layer force) has no explanation to offer for this global fact. By contrast, the Sogami theory, in which both the repulsion and attraction are

TABLE I. Sogami minimum (R_m) in terms of the number of Debye screening lengths (κR_m) and the number of particle radii (R_m/a).

$a\kappa$	$f(a\kappa) = \kappa R_m$	R_m/a
0	4.828	∞
0.1	4.833	48.3
0.5	4.997	9.99
1.0	5.471	5.47
1.5	6.175	4.12
2.0	7.025	3.51
2.5	7.956	3.18
3.0	8.929	2.98
3.5	9.920	2.83

electrical in origin, naturally predicts that colloidal particles must sit at a roughly constant number of Debye lengths in the secondary minimum. Hunter[27] quotes $7/\kappa$ as the typical separation, exactly as we would expect from the Sogami potential.

However, since κ is *a priori* unknown, and the radius of the particles is much easier to measure, it is better to convert R_m into a number of particle radii by dividing the second column of Table I by the first. The results are given in the third column of Table I. Returning to the example case, $R_m/a = 5.9$ and the calculation gives $a\kappa = 0.91$, from which $\kappa = 2.19 \times 10^{-3}$ Å^{-1}, as stated.

We now ask the question "Is this a reasonable value for κ in view of facts (i) and (iii)? The relationship between κ and the electrolyte concentration (c) for a univalent electrolyte in water at 25 °C is given by Eq. (3),

$$\kappa^2 = 0.107c , \tag{3}$$

where κ is expressed in Å^{-1} and c is in moles per liter (M). In the example case, $\kappa = 2.19 \times 10^{-3}$ Å^{-1} corresponds to $c = 4.49 \times 10^{-5}$ M. This only fits with fact (i), that the background ionic impurity concentration is less than 10^{-5} M, if the counterions make the dominant contribution to κ. Fact (iii) is easiest to address if we convert c into a number density (n) per Å^{-3}, using

$$n = 6.02 \times 10^{-4}c \tag{4}$$

giving $n = 2.70 \times 10^{-8}$ Å^{-3}. If we use the analytic surface charge to calculate n, which we represent by n_a, then fact (iii) tells us that there are 2370 charges in 1.13×10^{10} Å^3, that is, $n_a = Z/V_p = 2370/1.13 \times 10^{10} = 2.09 \times 10^{-7}$ Å^{-3}. If the dispersion is perfectly deionized, then $n/n_a = 0.13$ to 2 significant figures, the limit of experimental accuracy in such determinations.

This value can be compared with the number of effective charges on latex spheres with SO_3H groups determined by transference measurements.[28] The ratio n/n_a was 0.10 for $Z = 17000$ for similar particles to those studied by Rundquist *et al.*[24] The value $n/n_a = 0.13$ for $Z = 2370$ calculated above fits in perfectly sensibly with this result. The renormalized charge used by Rundquist *et al.*,[24] $Z_{eff} = 1150$, gives $n/n_a = 0.49$. Such a value is appropriate for soluble polyelectrolytes, whereas it is not so for polystyrene sulfonate latex spheres, as shown by Ito, Ise, and Okubo.[28]

We note that the interpretation in terms of the repulsive DLVO potential cannot explain the observed interparticle separation and does not give a reasonable value for the effective surface charge on the spheres. By contrast, the Sogami potential has now given a consistent explanation of all the facts (i) to (vi).

Now, the main point. Rundquist *et al.*[24] do not state the temperature at which $b = 2450$ Å was observed. In order to proceed, we choose $T = 25$ °C without affecting our qualitive conclusions. The essential equation is

$$\kappa^2 \propto 1/\varepsilon T \tag{5}$$

and the basic facts we need are in Table II, which suffices to calculate the T dependence of the Sogami minimum over the experimentally accessible range.

TABLE II. The inverse Debye screening length, κ, between 0 and 50 °C.

T (°C)	ε^a	εT (K)	κ/κ_{298}
0	87.90	24 000	0.988
10	83.96	23 760	0.993
20	80.20	23 500	0.998
25	78.55	23 410	1.000
30	76.60	23 210	1.004
40	73.17	22 900	1.011
50	69.88	22 570	1.018

[a]Taken from D. G. Archer, P. Wang, J. Phys. Chem. Ref. Data **19**, 371 (1990).

FIG. 1. Comparison of the Sogami prediction for the thermal compression of colloidal crystals with that of Rundquist et al. (Ref. 24) (DLVO prediction).

Note that it is only the product εT which enters into the calculation, given in the third column of the table. Application of Eq. (5) enables us to construct the fourth column of the Table, but we should note that κ^2 is also proportional to c (or n) so we have had to choose a temperature dependence for c, which in turn depends on the effective surface charge. We made the simplest possible choice, namely $c(T)=$ constant. This is a weak point, but it makes the T dependence of b directly comparable with that of Rundquist et al.,[24] who made the same approximation. Fixing $\kappa=2.19\times10^{-3}$ Å at 25 °C then gives us the T dependence of κ and hence the T dependence of R_m, shown in Fig. 1. In order to compare with the calculation of Rundquist et al.,[24] we have assumed that their ΔT (Kelvin) is equal to the temperature in degrees centigrade.[29]

With respect to the Sogami calculation, we first note that the total thermal compression between 0 and 50 °C is 59 Å, which is a 2.4% compression, easy to measure by Kossel line analysis. Secondly we note that two competing factors are involved. While the Debye screening length contracts by approximately 3.0% across this range, the major factor leading to the thermal compression, this is partially offset by the fact that the number of Debye screening lengths at the Sogami minimum increases by approximately 0.6%, leading to an overall contraction of 2.4%. The second factor is clear from the second column of Table I.

Although the graph makes the deviation between the two calculations seem quite pronounced, it is worth noting that the plots are qualitatively similar (both nearly linear with a slight concavity with respect to the temperature axis). From 0 to 50 °C, the contraction is 1.3% according to the repulsive DLVO potential and 2.4% according to the Sogami potential. In the former case, the "repulsion" between the particles becomes weaker and in the latter case, the attraction becomes stronger. If we take one single fact (the thermal compression of colloidal crystals) in isolation, we cannot distinguish between the two potentials.

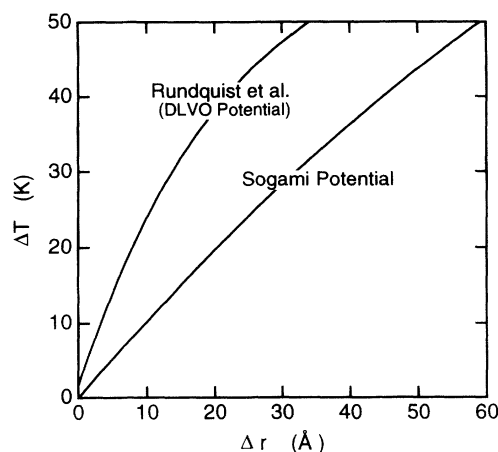In this case, the non-space-filling nature of the ordered

structure is the first fact that must be taken into account. The second important fact is that Ise et al.[30] reported a qualitatively similar temperature dependence of the interparticle separation in a latex dispersion for the case when the whole dispersion was heated. The repulsive DLVO potential only offers a superficially plausible explanation for photothermal compression, when there are external "cold" regions to compress the laser-heated region (a nonequilibrium situation). In the case of thermal compression (an equilibrium situation), the repulsive DLVO theory would predict no contraction at all. This is because the particles are always repelling each other (the van der Waals forces are negligible at separations of the order of 0.1 to 1 μm), so they must fill the dispersion container homogeneously irrespective of the temperature and so should show no variation of lattice parameter in the case when the whole dispersion is heated. We emphasize that the claim in the paper of Rundquist et al.[24] that the lattice is compressed by repulsions arising from the surrounding unheated parts of the lattice is unwarranted, in spite of the qualitatively correct result of their calculation, namely that the lattice is compressed on heating.

This type of problem is an example of a subtle kind of logical or dialectical error. When it is shown that the repulsion-only assumption can account for one particular phenomenon and the counterinterpretation in terms of the attraction-repulsion assumption is ignored, the reader is left with the impression that the repulsive DLVO (or Yukawa) potential is the only correct one. We have demonstrated that similar results can be obtained using either the repulsive DLVO potential or the Sogami potential for the photothermal compression of colloidal crystals. It is only when we take a global view of the properties of the system that the advantage of the Sogami potential (the attraction-repulsion assumption) becomes apparent.

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