LETTER TO THE EDITOR

Mapping of charge polydispersity onto size polydispersity in colloidal suspensions

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Abstract. The variational principle based on the Gibbs–Bogoliubov inequality is used to map the thermodynamic and structural properties of a charge-polydisperse colloidal suspension onto those of a polydisperse reference hard-sphere fluid. The predictions of this mapping are tested by molecular dynamics simulations.

Polydispersity of charge and size is a natural and unavoidable characteristic of charge-stabilized colloidal suspensions and micellar systems (for a review see, e.g., [1]). Since the charge carried by the particles is proportional to the area of their surface, charge polydispersity is larger than the polydispersity of the particle diameters. For spherical particles to which the present discussion is restricted, size polydispersity may be conveniently modelled by a hard-sphere (HS) system with a continuous distribution of diameters σ. If one is interested in structural properties, this model is particularly attractive, since an analytic solution of the Percus–Yevick (PY) closure exists for the continuous set of pair distribution functions $g_{\sigma\sigma'}(r)$ [2, 3].

In this letter we show that the polydisperse HS fluid is also a useful reference system for the investigation of the pair structure of charge polydisperse and micellar fluids. In particular, we show how the charge polydispersity may be related to the size polydispersity of the underlying HS reference system.

We consider a suspension of colloidal particles with number density ρ and charges $q_i = Z_i e$ distributed according to the normalized charge distribution function $P(Z)$. The mean charge and charge polydispersity p_Z are defined by

$$\overline{Z} = \int_0^\infty P(Z) Z \, \mathrm{d}Z \tag{1a}$$

$$p_Z = \frac{1}{\overline{Z}} \left(\int_0^\infty P(Z)(Z - \overline{Z})^2 \, \mathrm{d}Z \right)^{1/2}. \tag{1b}$$

If the van der Waals interactions may be neglected (which is, in particular, the case when the dielectric permittivities of the particles and the solvent are close), the familiar DLVO potential [4] between particles i and j may be cast in the Yukawa form:

$$V_{ij}(r) = U_0 \frac{a}{r} \frac{Z_i Z_j}{\overline{Z}^2} \exp\left[-\kappa \left(\frac{r-a}{a} \right) \right] \equiv Z_i Z_j U(r) \tag{2}$$

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where $r = |r_i - r_j|$, $\kappa = 1/\lambda$ is the inverse Debye screening length, due to the counter ions and added salt, and a and U_0 are characteristic length and energy scales. The corresponding units of temperature and density are U_0/k_B and a^{-3}. Note that the strong Coulomb repulsion between colloidal particles prevents them from coming as close as their diameter, thus masking any size polydispersity.

The monodisperse version of the model (i.e. all Z_i equal) has been investigated via extensive molecular dynamics (MD) simulations by Robbins *et al* [5]. In the present work we study the thermodynamic and structural properties of the polydisperse system by relating it to a polydisperse HS reference system having the same number density ρ and temperature T and diameters distributed according to a normalized size distribution function $P_0(\sigma)$; the mean diameter $\overline{\sigma}$ and size polydispersity p_σ are defined by relations similar to (1).

The mapping of the polydisperse Yukawa model (2) onto the polydisperse HS reference system is conveniently carried out via the Gibbs–Bogoliubov inequality [6], which yields an upper bound to the free energy of the system of interest in terms of the known free energy and the pair structure of the reference system. Using a suitable parametrization of the reference system (e.g. the diameter of a monodisperse HS fluid) minimization of the upper bound has led to good estimates of the static properties of simple liquids [7]. The Gibbs–Bogoliubov inequality is easily generalized to the polydisperse situation of present interest, according to

$$\frac{F^{\mathrm{ex}}}{V} \leqslant \frac{F_0^{\mathrm{ex}}}{V} + \frac{1}{2}\rho^2 \int_0^\infty \mathrm{d}\sigma \int_0^\infty \mathrm{d}\sigma' \, P_0(\sigma)P_0(\sigma') \int \mathrm{d}^3r \, g_{\sigma\sigma'}(r)Z(\sigma)Z(\sigma')U(r) \qquad (3)$$

where V is the volume, F^{ex} and F_0^{ex} denote the excess Helmholtz free energies of the polydisperse Yukawa and of the polydisperse HS systems respectively, while $g_{\sigma\sigma'}(r)$ is the pair distribution function for pairs of HS with diameters σ and σ'. The free energy F_0^{ex} of the reference HS system may be calculated from a knowledge of the Ornstein–Zernike direct correlation function $c_{\sigma\sigma'}(r)$ by thermodynamic integration:

$$\frac{F_0^{\mathrm{ex}}}{V} = k_B T \rho^2 \int_0^\infty \mathrm{d}\sigma \int_0^\infty \mathrm{d}\sigma' \, P_0(\sigma)P_0(\sigma') \int_0^1 \mathrm{d}\gamma \, (\gamma - 1) \int \mathrm{d}^3r \, c_{\sigma\sigma'}(r; \{\gamma P_0(\sigma)\rho\}) .$$
$$(4)$$

For explicit calculations, we have used the analytic PY expressions for $g_{\sigma\sigma'}(r)$ [2,3] and $c_{\sigma\sigma'}(r; \{\rho\})$ [8] in equations (3) and (4). The variational calculation proceeds then as follows. For a given temperature T, the polydisperse Yukawa system is entirely characterized by the density ρ and the charge distribution function $P(Z)$. The reference system, taken at the same temperature T and density ρ, is then completely specified by the mapping function $Z(\sigma)$ appearing in equation (3), which associates a charge Z with a given diameter and vice-versa. This mapping uniquely defines the size probability density $P_0(\sigma) = P(Z(\sigma))\mathrm{d}Z/\mathrm{d}\sigma$ of the HS reference system. The right-hand side of equation (3) is finally minimized with respect to the set of variational parameters contained in the mapping function $Z(\sigma)$.

In practice, we have chosen for the latter a simple linear form

$$Z(\sigma) = \overline{Z} + \alpha \frac{(\sigma - \overline{\sigma})}{\overline{\sigma}} \qquad (5)$$

which involves two variational parameters, the slope α and the mean diameter $\overline{\sigma}$. For large polydispersities, more complicated mapping functions, involving additional

variational parameters, may be necessary. The calculations described below were carried out for a simple box distribution of charges:

$$P(Z) = \begin{cases} 1/(\tilde{Z}_2 - \tilde{Z}_1) & \text{for } \tilde{Z}_1 < Z < \tilde{Z}_2 \\ 0 & \text{otherwise}. \end{cases} \tag{6}$$

In view of the linear form of the mapping function (5), the size distribution function $P_0(\sigma)$ is also a box distribution (6), characterized by the variational parameters $\overline{\sigma}$ and α, or alternatively by the minimum and maximum diameters σ_1 and σ_2, with $\sigma_\nu = \overline{\sigma} + (\overline{\sigma}/\alpha)Z_\nu - \overline{Z}$ and $\nu = 1, 2$. Once the free energy F of the charge polydisperse system has been estimated from (3) for several densities, the (osmotic) pressure p follows from numerical differentiation of F with respect to ρ.

In addition to the variational calculations, we have carried out a few MD simulations of the polydisperse Yukawa fluid, in order to test the predictions of the former. These simulations are similar to those of Dickinson and co-workers for the complete DLVO potential [9]. The charges of $N = 500$ particles were sampled uniformly from the box distribution (6), i.e.

$$Z_j = \tilde{Z}_1 + \left(j + \frac{1}{2}\right)\left(\frac{\tilde{Z}_2 - \tilde{Z}_1}{N}\right) \qquad 1 \leqslant j \leqslant N. \tag{7}$$

The forces between particles were calculated from the pair potentials (2) and the equations of motion were integrated using the Verlet algorithm and the standard constant-temperature constraint [10]. The main outputs relevant to the present work were the averaged and charge-averaged pair distribution functions $g(r)$ and $g_Z(r)$, defined by

$$g(r) = \frac{1}{\rho N}\left\langle \sum_{i \neq j}^{N} \delta(r - r_i + r_j) \right\rangle \tag{8a}$$

$$g_Z(r) = \frac{1}{\rho N \overline{Z}^2}\left\langle \sum_{i \neq j}^{N} Z_i Z_j \delta(r - r_i + r_j) \right\rangle. \tag{8b}$$

The latter yields directly the pressure according to the virial theorem for a charge polydisperse system

$$p = \rho k_\mathrm{B} T - \frac{2\pi}{3}\rho^2 \overline{Z}^2 \int_0^\infty dr\, g_Z(r) \frac{dU}{dr} r^3. \tag{9}$$

Some typical results of the variational calculation are summarized in figures 1 and 2. In figure 1, the optimal values of the parameters $\overline{\sigma}$ and α in equation (5) are plotted versus the charge polydispersity p_Z, together with the resulting size polydispersity p_σ of the HS reference system, and the variational estimate of the free energy of the polydisperse Yukawa system; these results are shown for a fixed value of the inverse screening length κ. In figure 2, the dependence of the previous quantities on κ is plotted for a fixed value of the charge polydispersity p_Z. For fixed κ, the mean diameter $\overline{\sigma}$, and the slope α, which is simply the ratio of polydispersities, p_Z/p_σ, hardly vary with the charge polydispersity p_Z. Note that, as expected, the size polydispersity that yields the lowest free energy is considerably smaller than the charge
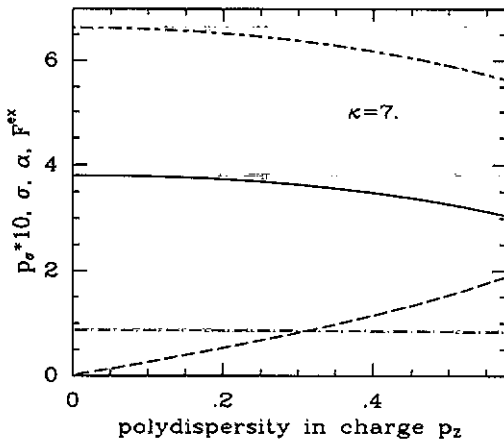
Figure 1. The excess free energy F_{ex} in units of U_0 (— – —) of the charge poly-disperse system obtained by hard-sphere mapping theory as well as the size poly-dispersity p_σ (– – –), $\bar\sigma$ in units of a (— · —), α (——) of the HS reference system versus polydispersity in charge p_Z. We choose $\rho a^3 = k_B T/U_0 = 1$, $\kappa = 7$.
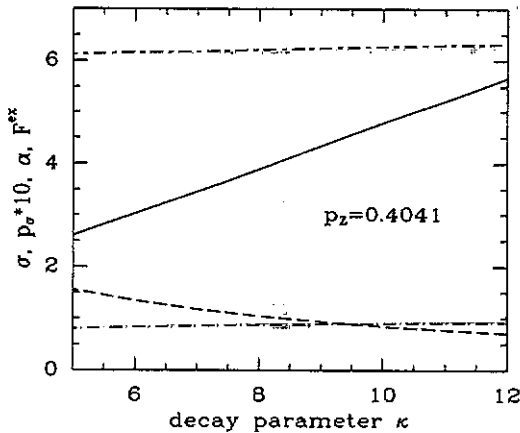

Figure 2. The excess free energy F_{ex} in units of U_0 versus κ ($p_Z = 0.4041$, $\rho a^3 = k_B T/U_0 = 1$). Curves labelled as in figure 1.

polydispersity. As shown in figure 2, the ratio α increases practically linearly with the screening parameter κ. As $\kappa \to \infty$, the system is mapped onto a *monodisperse* HS system with diameter a, i.e. $\alpha \to \infty, \bar\sigma \to a$. As is apparent from figure 1 and table 1, the excess free energy and the pressure of the Yukawa fluid decrease with increasing charge polydispersity p_Z. This behaviour contrasts with that of a poly-disperse HS system where these quantities increase with increasing size polydispersity (if $\bar\sigma$ is kept constant). A possible explanation is that, whereas in a HS system the ex-cluded volume increases with increasing polydispersity, leading thus to an increase of the excess thermodynamic properties, in charge polydisperse systems the more highly charged particles keep apart by surrounding themselves with lower charged particles; this 'charge ordering' favours a lowering of the pressure and of the free energy.

The pressure obtained by differentiating the variational estimate of the free energy

Table 1. Pressure of a dense charge polydisperse Yukawa fluid ($\rho a^3 = k_B T/U_0 = 1$, $\kappa = 7$) for three different charge polydispersities p_Z: MD data and HS mapping results are compared and, just for completeness, the values of p, $\bar{\sigma}$, α for the corresponding polydisperse HS system are given. The theoretical data for the pressure are obtained by differentiating the equation of state.

	$p/\rho k_B T$				
p_Z	Simulation	Theory	HS	$\bar{\sigma}/a$	α
0.0000	11.3	12.2	5.2	0.87	—
0.2887	10.9	11.8	5.1	0.86	3.65
0.5774	9.34	10.4	4.6	0.83	3.05

is compared with the 'exact' simulation results in table 1. The variational results lie about 10% above the MD data: part of this discrepancy may be traced back to the PY approximation for the polydisperse HS properties.
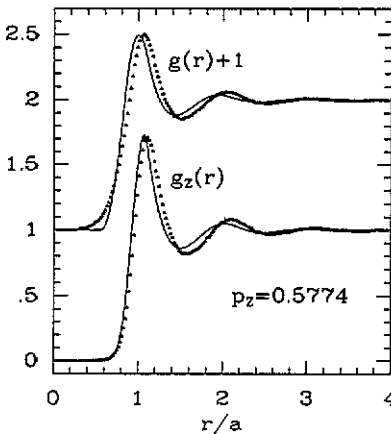

Figure 3. Comparison of $g(r)$ and $g_Z(r)$ for a charge polydispersity $p_Z = 0.5774$. Simulation results (▲) versus pair correlations of the HS system $g_0(r)$, $g_{Z0}(r)$ (——). As in figure 1, we choose $\rho a^3 = k_B T/U_0 = 1$, $\kappa = 7$.

The PY expression for the partial pair distribution functions $g_{\sigma\sigma'}(r)$ may be used to calculate the average and charge-averaged pair distribution functions of the HS reference system, according to

$$g_0(r) = \int_0^\infty \mathrm{d}\sigma \int_0^\infty \mathrm{d}\sigma' \, P_0(\sigma) P_0(\sigma') g_{\sigma\sigma'}(r) \tag{10a}$$

$$g_{Z0}(r) = \frac{1}{\bar{Z}^2} \int_0^\infty \mathrm{d}\sigma \int_0^\infty \mathrm{d}\sigma' \, P_0(\sigma) P_0(\sigma') Z(\sigma) Z(\sigma') g_{\sigma\sigma'}(r) \,. \tag{10b}$$

These estimates of the corresponding pair distribution functions of the polydisperse Yukawa fluid are compared with the 'exact' MD data in figure 3, for a charge polydispersity $p_Z = 0.5774$. Although the two sets of distribution functions oscillate slightly out of phase, the agreement between MD and variational results is reasonably good, thus confirming that the pair structure of the reference HS system, with

parameters $\bar{\sigma}$ and p_Z determined from the Gibbs–Bogoliubov variational principle, yields a reasonably accurate representation of the pair distribution functions of the polydisperse Yukawa model for charge stabilized colloidal suspensions.

In summary, we have shown that the Gibbs–Bogoliubov mapping of a charge-polydisperse system, modelled by the pair potentials (2), onto a polydisperse HS fluid yields a reasonably accurate description of the former. Hence, this mapping can be of great practical importance in view of the availability of analytic expressions for the pair structure of the HS reference system, within the PY approximation which is generally accepted to yield reliable results for HS systems. One of the main results is that the effective size polydispersity of the HS reference fluid is considerably reduced compared with the charge polydispersity of the charged colloidal system, except in the weak screening limit.

The polydisperse Yukawa fluid provides a simple model for charge-stabilized colloidal suspensions. For high polydispersity, freezing into a colloidal crystal is suppressed in favour of a colloidal glass [8, 9]. We have also investigated the glass transition of the polydisperse model system defined by equation (2) by Brownian dynamics simulations; these results will be published elsewhere.

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