PHYSICAL REVIEW E, VOLUME 63, 061806

Density functional theory of charged colloidal systems

Derek Y. C. Chan*
Particulate Fluids Processing Centre, Department of Mathematics and Statistics, The University of Melbourne,
Parkville, Victoria 3010, Australia

(Received 15 November 2000; published 23 May 2001)

The phase behavior of charged colloidal systems has been studied recently by the density functional theory formalism (DFT) [R. van Roij, M. Dijkstra, and J. P. Hansen, Phys. Rev. E **59**, 2010 (1999)]. A key feature of this approach is the appearance of a density and temperature-dependent effective Hamiltonian between the charged colloids. Under certain approximations, the effective Hamiltonian is made up only of a sum of position-independent one-body or volume terms and two-body colloid-separation dependent terms. In the limit of low colloidal densities, the DFT results do not reduce to the familiar Debye-Hückel limiting law nor do the results agree with previous work based on an identical approach but were developed using traditional statistical-mechanical methods [B. Beresford-Smith, D. Y. C. Chan, and D. J. Mitchell J. Colloid Interface Sci. **105**, 216 (1985)]. This paper provides a reconciliation of these differences and comments on the significance of the one-body volume terms in the effective Hamiltonian of a system of charged colloids in determining thermodynamics and phase behavior.

DOI: 10.1103/PhysRevE.63.061806 PACS number(s): 83.50.−v, 64.60.Cn

I. INTRODUCTION

The density functional theory (DFT) has been applied to study the phase behavior of a charged colloidal system [1,2] modeled as an asymmetric primitive model electrolyte in which the Coulombic interactions between the highly charged colloidal particles and the univalent counterions are treated explicitly, while the aqueous solvent is modeled as a dielectric continuum with a constant relative permittivity ε. For this model the configurational part of the Hamiltonian of the system is a sum of interactions between various ionic species:

$$H(\{\mathbf{R}_i\},\{\mathbf{r}_j\}) = H_{\text{colloid-colloid}} + H_{\text{colloid-ion}} + H_{\text{ion-ion}}. \tag{1}$$

Owing to the high charge asymmetry of the colloidal component, van Roij, Disjkstra, and Hansen (vRDH) [1,2] proposed to first fix the colloids at positions $\{\mathbf{R}_i\}$ and average over the coordinates $\{\mathbf{r}_j\}$ of the ions to give an effective colloid-colloid Hamiltonian

$$H^{\text{eff}}(\{\mathbf{R}_i\}) = H_{\text{colloid-colloid}} + F(\{\mathbf{R}_i\}), \tag{2}$$

where $F(\{\mathbf{R}_i\})$, defined by $(\beta = 1/kT)$

$$\exp[-\beta F(\{\mathbf{R}_i\})] \equiv \frac{1}{V^{N_1}} \int \exp[-\beta(H_{\text{colloid-ion}} + H_{\text{ion-ion}})]\, d\{\mathbf{r}_j\} \tag{3}$$

is the Helmholtz free energy of an inhomogeneous fluid of ions, obtained by averaging over the ion coordinates $\{\mathbf{r}_j\}$ $(j = 1,\ldots,N_1)$, in the external field due to the colloids fixed at positions $\{\mathbf{R}_i\}$ $(i = 1..N_0)$. As a consequence, the colloids can now be regarded as a one-component system characterized by the effective Hamiltonian, $H^{\text{eff}}(\{\mathbf{R}_i\})$ which is a sum of the term $H_{\text{colloid-colloid}}$ that contains the direct Coulomb and short-ranged interaction between colloids and the state dependent quantity $F(\{\mathbf{R}_i\})$. Thermodynamics of the colloidal system was then obtained for this one-component system of colloids governed by the effective Hamiltonian, $H^{\text{eff}}(\{\mathbf{R}_i\})$. The DFT, with certain approximations, was then use to calculate $F(\{\mathbf{R}_i\})$.

The DFT results of vRDH [1,2] have the following features:

(i) The expression for the effective Hamiltonian $H^{\text{eff}}(\{\mathbf{R}_i\})$ contains a position independent but temperature and density dependent constant or volume term that arises from $F(\{\mathbf{R}_i\})$ and this term has been regarded to have special significance in determining the phase behavior of Coulombic systems.

(ii) The colloid position dependent portion of $H^{\text{eff}}(\{\mathbf{R}_i\})$ is comprised of a sum of pairwise interactions between the colloids, which have the screened Coulomb form. The screening parameter has the familiar Debye form and depends only on the concentrations of counterions and added salt concentration.

(iii) In the low colloid density limit and in the absence of added salt, the Coulombic part of the free energy of the system has the characteristic (3/2)-power dependence on the concentration of all charged species but has a different dependence on the colloid valency [3] to the Debye-Hückel limiting law.

In an earlier study of the structure of colloidal systems, Beresford-Smith, Chan, and Mitchell (BCM) [4] followed an identical approach but used a traditional statistical-mechanical formulation to derive the effective Hamiltonian for the colloidal particles. While the results of BCM and that of vRDH should be identical because they studied essentially the same system under the same approximations, there are in fact a number of similarities and differences:

(i) The position independent but temperature and density dependent constant or volume term in the effective Hamiltonian obtained by BCM has one more term than that derived from the DFT. However, this volume term did not, in the

---

*Email address: D.Chan@ms.unimelb.edu.au final analysis, contribute to the system thermodynamics. Indeed, one can provide a very general argument to support this.

(ii) BCM and vRDH employed the same approximations in treating the model and therefore in both cases the colloid position dependent portion of $H^{\text{eff}}(\{\mathbf{R}_i\})$ contains the same sum of screened Coulomb terms for the pairwise interactions between the colloids.

(iii) BCM took a different route to calculate system thermodynamics from the effective Hamiltonian $H^{\text{eff}}(\{\mathbf{R}_i\})$ and recovered the Debye-Hückel limiting law behavior at low colloid densities and also revealed a delicate cancelation of contributions to system thermodynamics from the colloid position independent one-body volume term and from the position dependent interaction terms in $H^{\text{eff}}(\{\mathbf{R}_i\})$.

The aim of this paper is to provide a reconciliation between the more modern DFT formulation and the older formalism and also to offer some general remarks about the role of the volume term in the free energy and the effective Hamiltonian approach in charged systems.

For this purpose, we therefore consider a colloidal system modeled as a primitive model electrolyte in a volume V, which contains N_0 colloids at number density $n_0 = N_0/V$ and valence $Z(\gg 1)$, balanced by N_1 counterions of number density $n_1 = N_1/V$ and valence (-1). There is no added salt and the following bulk electroneutrality condition holds:

$$n_0 Z + n_1(-1) = 0. \tag{4}$$

The presence of added salt can be easily included but it does add to the algebraic complexity without altering the key physical conclusions. For pedagogic reasons we prefer to keep the system simple to bring out the key ideas that helps in identifying and reconciling the differences between the two treatments of the same model. To this end, we will consider the case of point ions and point colloids, which will facilitate the analytic demonstration of the contribution of various terms. Again, the inclusion of the colloid size can be incorporated as an extension but this does not alter the main conclusions—added salt and size effects will be discussed in the concluding section.

II. DENSITY FUNCTIONAL THEORY

The DFT involves the construction of the Helmholtz free-energy functional $\mathcal{F}[n^{(1)}(\mathbf{r})]$ which depends on the variational or trial number density profile, $n^{(1)}(\mathbf{r})$ of counterions for a given configuration of colloids at positions $\{\mathbf{R}_i\}$. The *equilbrium* density profile $n(\mathbf{r})$ is found by the Euler-Lagrange condition

$$\frac{\delta \mathcal{F}[n^{(1)}(\mathbf{r})]}{\delta n^{(1)}(\mathbf{r})} = \mu \quad \text{at} \quad n^{(1)}(\mathbf{r}) = n(\mathbf{r}), \tag{5}$$

where the Lagrange multiplier μ is chosen to satisfy the following normalization condition on the ion number density

$$\int n(\mathbf{r}) d\mathbf{r} = N_1 = n_1 V. \tag{6}$$

The ion-averaged Helmholtz free energy $F(\{\mathbf{R}_i\})$, defined earlier, is related to the equilibrium density profile $n(\mathbf{r})$ by

$$F(\{\mathbf{R}_i\}) = \mathcal{F}[n(\mathbf{r})]. \tag{7}$$

We now recapitulate the salient features of the vRDH formulation of the DFT [2]. The functional $\mathcal{F}$ is taken to have contributions from entropic terms of the mobile counterions treated as an ideal gas, $\mathcal{F}_{\text{id}}$, from the external field due to the colloids at fixed positions $\{\mathbf{R}_i\}, \mathcal{F}_{\text{ex}}$, from Coulomb interactions between the counterions, $\mathcal{F}_{\text{Coul}}$, and from counterion-counterion correlations, $\mathcal{F}_{\text{corr}}$:

$$\mathcal{F} = \mathcal{F}_{\text{id}} + \mathcal{F}_{\text{ext}} + \mathcal{F}_{\text{Coul}} + \mathcal{F}_{\text{corr}}, \tag{8}$$

These four terms are assumed to take the following forms [2]:

$$\begin{aligned}\mathcal{F}_{\text{id}} &= kT \int n^{(1)}(\mathbf{r})\{\ln[n^{(1)}(\mathbf{r})\Lambda^3] - 1\} d\mathbf{r} \\ &\simeq VkT[n_1 \ln(n_1\Lambda^3) - n_1] + \frac{kT}{2n_1}\int [n^{(1)}(\mathbf{r}) - n_1]^2 d\mathbf{r},\end{aligned} \tag{9}$$

$$\mathcal{F}_{\text{ext}} = \sum_{i=1}^{N_0} \int \frac{[Ze][-en^{(1)}(\mathbf{r})]}{\varepsilon|\mathbf{r} - \mathbf{R}_i|} d\mathbf{r}, \tag{10}$$

$$\mathcal{F}_{\text{Coul}} = \frac{1}{2}\int \frac{[-en^{(1)}(\mathbf{r})][-en^{(1)}(\mathbf{r}')]}{\varepsilon|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \tag{11}$$

$$\mathcal{F}_{\text{corr}} = 0, \tag{12}$$

where Λ is the counterion thermal wavelength and e the protonic charge.

The use of the ideal-gas expression in the first line of Eq. (9) places this DFT formulation at the same level as the mean-field nonlinear Poisson-Boltzmann theory and the expansion to quadratic order in local inhomogeneities in the second line of Eq. (9) is equivalent to linearizing the Poisson-Boltzmann equation. Similar approximations were also made in the BCM calculation. The Coulomb interaction terms in Eqs. (10) and (11) have exact analogues in the BCM treatment. So far, the assumptions in vRDH and BCM are identical.

The neglect of correlation effects, $\mathcal{F}_{\text{corr}} = 0$, in Eq. (12) is one of the differences between the vRDH approach and the BCM approach (see discussion that follows Eq. (45) below). This assumption is also equivalent to neglecting effects from the fluctuation potential, which is normally included in the family of Modified Poisson-Boltzmann theories [5] of Coulombic systems. The neglect of ion-ion correlation effects is one reason why the vRDH treatment will not reduce to the Debye-Hückel limiting law because the treatment of Coulombic interactions involving ions and colloids is no longer symmetric as it is in the Debye-Hückel theory.

The equation for the equilibrium counterion density $n(\mathbf{r})$ is obtained by taking the first variation

$$\frac{\delta\{\mathcal{F}[n^{(1)}(\mathbf{r})]-\mu[\int n^{(1)}(\mathbf{r})d\mathbf{r}-N_1]\}}{\delta n^{(1)}(\mathbf{r})}=0 \quad \text{at} \quad n^{(1)}(\mathbf{r})=n(\mathbf{r}), \tag{13}$$

which gives

$$\frac{n(\mathbf{r})}{n_1}=1+\beta e\psi(\mathbf{r})+\beta\mu, \tag{14}$$

where

$$\psi(\mathbf{r})\equiv\sum_{i=1}^{N_0}\frac{Ze}{\varepsilon|\mathbf{r}-\mathbf{R}_i|}+\int\frac{[-en(\mathbf{r}')]}{\varepsilon|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \tag{15}$$

can be interpreted as the mean electrostatic potential at **r**, due to the colloids being fixed at positions $\{\mathbf{R}_i\}$ and to the counterions at the equilibrium density profile $n(\mathbf{r})$.

What follows diverges slightly from vRDH who carried out their analysis in Fourier space. We shall not use this approach but the difference is only technical while the physical content remains unaffected. Using Eq. (14) we can see that Eq. (15) is equivalent to the differential equation

$$\nabla^2 n(\mathbf{r})-\kappa_1^2 n(\mathbf{r})=-\kappa_1^2 Z\sum_{i=1}^{N_0}\delta(\mathbf{r}-\mathbf{R}_i), \tag{16}$$

where

$$\kappa_1^2\equiv\frac{4\pi n_1\beta e^2}{\varepsilon} \tag{17}$$

is the inverse Debye screening length due only to the counterions. The bounded solution of Eq. (16) is

$$n(\mathbf{r})=\frac{\kappa_1^2 Z}{4\pi}\sum_{i=1}^{N_0}\frac{\exp[-\kappa_1(\mathbf{r}-\mathbf{R}_i)]}{|\mathbf{r}-\mathbf{R}_i|} \quad (\text{DFT}). \tag{18}$$

It is easy to verify that this result for the ion density satisfies the ion number normalization condition in Eq. (6) and therefore by integrating Eqs. (14) and (15) we can establish the result: $\mu=0$. To carry out the necessary algebra, vRDH suggested the standard technique of replacing the $(1/r)$ kernels in the integrals in Eq. (15) by $(\exp[-\alpha r]/r)$ to handle the apparent divergencies, and then take the limit $\alpha\to 0$ at the end of the calculation.

We can now use the result for the equilibrium ion density $n(\mathbf{r})$, Eq. (18), in Eqs. (9)–(11) to give $(R_{ij}\equiv|\mathbf{R}_i-\mathbf{R}_j|)$

$$\begin{aligned}\mathcal{F}_{\text{id}}&=VkT[n_1\ln(n_1\Lambda^3)-n_1]+\frac{kT}{2n_1}\int[n(\mathbf{r})-n_1]^2d\mathbf{r}\\&=VkT[n_1\ln(n_1\Lambda^3)-n_1]\\&\quad+\frac{Z^2e^2\kappa_1}{4\varepsilon}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\i\neq j}}^{N_0}\exp[-\kappa_1R_{ij}]\\&\quad+\frac{Z^2e^2\kappa_1}{4\varepsilon}N_0-\frac{1}{2}ZN_0kT,\end{aligned} \tag{19}$$

$$\begin{aligned}\mathcal{F}_{\text{ext}}&=\sum_{i=1}^{N_0}\int\frac{[Ze][-en(\mathbf{r})]}{\varepsilon|\mathbf{r}-\mathbf{R}_i|}d\mathbf{r}\\&=-\frac{Z^2e^2\kappa_1}{\varepsilon}N_0-\frac{Z^2e^2}{\varepsilon}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\i\neq j}}^{N_0}\frac{1-\exp[-\kappa_1R_{ij}]}{R_{ij}},\end{aligned} \tag{20}$$

$$\begin{aligned}\mathcal{F}_{\text{Coul}}&=\frac{1}{2}\int\frac{[-en(\mathbf{r})][-en(\mathbf{r}')]}{\varepsilon|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'\\&=\frac{Z^2e^2}{2\varepsilon}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\i\neq j}}^{N_0}\frac{1-\exp[-\kappa_1R_{ij}]}{R_{ij}}\\&\quad-\frac{Z^2e^2\kappa_1}{4\varepsilon}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\i\neq j}}^{N_0}\exp[-\kappa_1R_{ij}]+\frac{Z^2e^2\kappa_1}{4\varepsilon}N_0.\end{aligned} \tag{21}$$

Inserting the results in Eqs. (19)–(21) into Eqs. (7) and (8) gives

$$\begin{aligned}F(\{\mathbf{R}_i\})&=\mathcal{F}[n(\mathbf{r})]\\&=VkT[n_1\ln(n_1\Lambda^3)-n_1]\\&\quad-\left(\frac{Z^2e^2\kappa_1}{2\varepsilon}N_0+\frac{1}{2}ZN_0kT\right)\\&\quad+\frac{Z^2e^2}{2\varepsilon}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\i\neq j}}^{N_0}\frac{\exp[-\kappa_1R_{ij}]}{R_{ij}}-\frac{Z^2e^2}{2\varepsilon}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\i\neq j}}^{N_0}\frac{1}{R_{ij}}\end{aligned} \tag{22}$$

and from Eq. (2) with

$$H_{\text{colloid-colloid}}=\frac{1}{2}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\i\neq j}}^{N_0}\frac{Z^2e^2}{\varepsilon R_{ij}}, \tag{23}$$

we find for the effective Hamiltonian

$$\begin{aligned}H^{\text{eff}}(\{\mathbf{R}_i\})&=VkT[n_1\ln(n_1\Lambda^3)-n_1]\\&\quad-\left(\frac{Z^2e^2\kappa_1}{2\varepsilon}N_0+\frac{1}{2}ZN_0kT\right)\\&\quad+\frac{Z^2e^2}{2\varepsilon}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\i\neq j}}^{N_0}\frac{\exp[-\kappa_1R_{ij}]}{R_{ij}}\quad(\text{DFT}).\end{aligned} \tag{24}$$

The first term in Eq. (24) is the ideal-gas free energy. The terms in parenthesis

$$F_1\equiv-\left(\frac{Z^2e^2\kappa_1}{2\varepsilon}N_0+\frac{1}{2}ZN_0kT\right) \quad (\text{DFT}) \tag{25}$$

is the one-body or volume term of vRDH (for point ions and point colloids) which depends on density and temperature but not on colloid positions. This term is always negative and gives a cohesive contribution to the free energy. The final term is a sum of two-body screened Coulomb potentials of the form

$$u^{\text{eff}}(R_{ij}) \equiv \frac{Z^2 e^2 \exp[-\kappa_1 R_{ij}]}{\varepsilon R_{ij}} \tag{26}$$

between the colloids with the screening length $(1/\kappa_1)$ that depends only on the counterion concentration, Eq. (17). The effective two-body potential $u^{\text{eff}}(R_{ij})$ between colloids is a temperature or state dependent quantity through κ_1 and reflects its character as a free energy.

The next step is to calculate the free energy of the system from Eq. (24). In the vRDH paper, they used a variational method to estimate the free energy from $u^{\text{eff}}(R_{ij})$. In the low-density limit, they estimated this contribution to be [2]

$$\begin{aligned} F_2 &= \frac{1}{2} N_0 n_0 \int u^{\text{eff}}(r)\, d\mathbf{r} \\ &= \frac{1}{2} Z N_0 kT \quad \text{(DFT low-density limit)} \end{aligned} \tag{27}$$

and the total free energy in the low-density limit becomes [3]

$$\begin{aligned} F &= F_1 + F_2 \\ &= VkT[n_1 \ln(n_1\Lambda^3) - n_1] - \left(\frac{Z^2 e^2 \kappa_1}{2\varepsilon} N_0 + \frac{1}{2} Z N_0 kT \right) \\ &\quad + \frac{1}{2} Z N_0 kT \\ &= VkT[n_1 \ln(n_1\Lambda^3) - n_1] - \frac{Z^2 e^2 \kappa_1}{2\varepsilon} N_0 \\ &= VkT[n_1 \ln(n_1\Lambda^3) - n_1] - \frac{kT\kappa_0^2 \kappa_1}{8\pi} V \quad \text{(DFT)}, \end{aligned} \tag{28}$$

which is different to the Debye-Hückel limiting law result [6]

$$\begin{aligned} F &= VkT[n_1 \ln(n_1\Lambda^3) - n_1] \\ &\quad - \frac{kT\kappa_D^3}{12\pi} V \quad \text{(Debye-Hückel limiting law)} \end{aligned} \tag{29}$$

where

$$\kappa_D^2 = \frac{4\pi\beta e^2}{\varepsilon} n_0 Z^2 + \frac{4\pi\beta e^2}{\varepsilon} n_1 \equiv \kappa_0^2 + \kappa_1^2 \tag{30}$$

is the usual Debye screening parameter for the whole system that includes contributions from the charged colloids and the counterions. The difference between Eqs. (28) and (29) is significant, especially for $Z \gg 1$ and this may be important in determining phase equilibria.

III. STATISTICAL-MECHANICAL THEORY (SMT)

The starting point of the statistical-mechanical theory of BCM [4] is the formal expression of the effective Hamiltonian, $H^{\text{eff}}(\{\mathbf{R}_i\})$ expressed as an integral over the counterion coordinates $\{\mathbf{r}_i\}$

$$\begin{aligned} \exp[-\beta H^{\text{eff}}(\{\mathbf{R}_i\})] &= \frac{1}{V^{N_1}} \int \exp[-\beta H(\{\mathbf{R}_i\},\{\mathbf{r}_j\})] \; d\{\mathbf{r}_j\} \\ &\equiv \langle \exp[-\beta H(\{\mathbf{R}_i\},\{\mathbf{r}_j\})] \rangle, \end{aligned} \tag{31}$$

where $\langle \cdots \rangle$ denotes an average over the counterion coordinates. The strategy is to calculate $H^{\text{eff}}(\{\mathbf{R}_i\})$, which is a free energy, by a temperature integration of the corresponding internal energy. To do this we define the total charge-density operator $\hat{\rho}(\mathbf{r})$ for the colloids and the counterions by

$$\hat{\rho}(\mathbf{r}) = Ze \sum_{i=1}^{N_0} \delta(\mathbf{r} - \mathbf{R}_i) + (-e) \sum_{j=1}^{N_1} \delta(\mathbf{r} - \mathbf{r}_j) \equiv \hat{\rho}_0(\mathbf{r}) + \hat{\rho}_1(\mathbf{r}) \tag{32}$$

and the electrostatic potential operator $\hat{\psi}(\mathbf{r})$ by

$$\hat{\psi}(\mathbf{r}) = \sum_{i=1}^{N_0} \frac{Ze}{\varepsilon|\mathbf{r} - \mathbf{R}_i|} + \sum_{j=1}^{N_1} \frac{(-e)}{\varepsilon|\mathbf{r} - \mathbf{r}_j|} = \int \frac{\hat{\rho}(\mathbf{r})}{\varepsilon|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{33}$$

so that the Hamiltonian describing Coulombic interactions in the colloidal system is

$$\begin{aligned} H(\{\mathbf{R}_i\},\{\mathbf{r}_i\}) &= \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{(Ze)^2}{\varepsilon|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{\substack{i,j \\ i \neq j}} \frac{(Ze)(-e)}{\varepsilon|\mathbf{R}_i - \mathbf{r}_j|} \\ &\quad + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \frac{(-e^2)}{\varepsilon|\mathbf{R}_i - \mathbf{r}_j|} \\ &= \frac{1}{2} \int \hat{\rho}(\mathbf{r}) \hat{\psi}(\mathbf{r}) d\mathbf{r} - E_s, \end{aligned} \tag{34}$$

where E_s is the electrostatic self-energy of the ions and colloids that originates from the extra $i = j$ terms that have been included in the integral in the second line of Eq. (34). Differentiating Eq. (31) with respect to β, and using Eq. (34) we have the exact relation

$$\frac{\partial[\beta H^{\text{eff}}(\{\mathbf{R}_i\})]}{\partial\beta} = \frac{1}{2} \int \langle \hat{\rho}(\mathbf{r}) \hat{\psi}(\mathbf{r}) \rangle d\mathbf{r} - E_s. \tag{35}$$

The charge-potential correlation function $\langle \hat{\rho}(\mathbf{r}) \hat{\psi}(\mathbf{r}) \rangle$ can now be split formally into a sum of a mean-field term $\langle \hat{\rho}(\mathbf{r}) \rangle \langle \hat{\psi}(\mathbf{r}) \rangle$ and a correlation term using Eq (33):

$$\begin{aligned}\langle\hat{\rho}(\mathbf{r})\hat{\psi}(\mathbf{r})\rangle &\equiv \langle\hat{\rho}(\mathbf{r})\rangle\langle\hat{\psi}(\mathbf{r})\rangle\\ &\quad+\int\frac{\langle\hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}')\rangle-\langle\hat{\rho}(\mathbf{r})\rangle\langle\hat{\rho}(\mathbf{r}')\rangle}{\varepsilon|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\\ &=\langle\hat{\rho}(\mathbf{r})\rangle\langle\hat{\psi}(\mathbf{r})\rangle\\ &\quad+\int\frac{e^{2}n(\mathbf{r})[\delta(\mathbf{r}-\mathbf{r}')+h_{11}(\mathbf{r},\mathbf{r}')]n(\mathbf{r}')}{\varepsilon|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}',\end{aligned} \tag{36}$$

where the integral in the second line in Eq. (36) only depends on the counterion number density $n(\mathbf{r})$ and defines the counterion-counterion correlation function $h_{11}(\mathbf{r},\mathbf{r}')$ in the external field provided by the fixed colloidal particles [4]. So Eq. (35) becomes

$$\begin{aligned}\frac{\partial[\beta H^{\mathrm{eff}}\{\mathbf{R}_i\}]}{\partial\beta}&=\frac{1}{2}\int\langle\hat{\rho}(\mathbf{r})\rangle\langle\hat{\psi}(\mathbf{r})\rangle d\mathbf{r}-E_s\\ &\quad+\frac{1}{2}\int\frac{e^{2}n(\mathbf{r})[\delta(\mathbf{r}-\mathbf{r}')+h_{11}(\mathbf{r},\mathbf{r}')]n(\mathbf{r}')}{\varepsilon|\mathbf{r}-\mathbf{r}'|}\\ &\quad\times d\mathbf{r}\,d\mathbf{r}'. \quad (\mathrm{SMT})\end{aligned} \tag{37}$$

This is a completely general result. The next step is to determine the average charge density $\langle\hat{\rho}(\mathbf{r})\rangle$, the average electrostatic potential $\langle\hat{\psi}(\mathbf{r})\rangle$, the counterion number density $n(\mathbf{r})$, and the counterion-counterion correlation function $h_{11}(\mathbf{r},\mathbf{r}')$ in order to evaluate this expression.

The average total charge density $\langle\hat{\rho}(\mathbf{r})\rangle$ and electrostatic potential $\langle\hat{\psi}(\mathbf{r})\rangle$ and electrostatic potential are related by the Poisson equation

$$\nabla^{2}\langle\hat{\psi}(\mathbf{r})\rangle=-\frac{4\pi}{\varepsilon}\langle\hat{\rho}(\mathbf{r})\rangle \tag{38}$$

with average charge density

$$\langle\hat{\rho}(\mathbf{r})\rangle=Ze\sum_{i=1}^{N_0}\delta(\mathbf{r}-\mathbf{R}_i)+(-e)n(\mathbf{r}). \tag{39}$$

To close Eqs. (38) and (39) we assume the linearized Boltzmann distribution

$$\begin{aligned}n(\mathbf{r})&=n_1\exp[+\beta e\langle\hat{\psi}(\mathbf{r})\rangle-\overline{\psi})]\\ &\cong n_1\{1+\beta e(\langle\hat{\psi}(\mathbf{r})\rangle-\overline{\psi})\},\quad(\mathrm{SMT})\end{aligned} \tag{40}$$

where $\overline{\psi}$ is the (constant) potential at the position where $n(\mathbf{r})=n_1$. Combining Eqs. (38)–(40), we see that

$$\nabla^{2}n(\mathbf{r})-\kappa_1^{2}n(\mathbf{r})=-\kappa_1^{2}Z\sum_{i=1}^{N_0}\delta(\mathbf{r}-\mathbf{R}_i) \tag{41}$$

with the bounded solution

$$n(\mathbf{r})=\frac{\kappa_1^{2}Z}{4\pi}\sum_{i=1}^{N_0}\frac{\exp[-\kappa_1(\mathbf{r}-\mathbf{R}_i)]}{|\mathbf{r}-\mathbf{R}_i|}\quad(\mathrm{SMT}), \tag{42}$$

which is the same as the result in Eqs. (16)–(18) for the DFT.

To find the correlation function $h_{11}(\mathbf{r},\mathbf{r}')$, we consider the fluctuation potential $\varphi(\mathbf{r},\mathbf{r}')$ which is the potential at $\mathbf{r}$ given that the colloids are fixed at $\{\mathbf{R}_i\}$ and one counterion of charge (-1) is at $\mathbf{r}'$. The potential $\varphi(\mathbf{r},\mathbf{r}')$ therefore satisfies the following Poisson equation:

$$\begin{aligned}\nabla^{2}\varphi(\mathbf{r},\mathbf{r}')=-\frac{4\pi}{\varepsilon}\Bigg\{&Ze\sum_{i=1}^{N_0}\delta(\mathbf{r}-\mathbf{R}_i)+(-e)n(\mathbf{r})\\ &\times[1+h_{11}(\mathbf{r},\mathbf{r}')]+(-e)\delta(\mathbf{r}-\mathbf{r}')\Bigg\}.\end{aligned} \tag{43}$$

The mean-field closures

$$\begin{gathered}h_{11}(\mathbf{r},\mathbf{r}')\cong-\beta(-e)\varphi(\mathbf{r},\mathbf{r}'),\\ n(\mathbf{r})\cong n_1,\\ \sum_{i=1}^{N_0}\delta(\mathbf{r}-\mathbf{R}_i)\cong n_0\end{gathered} \tag{44}$$

provide the approximate solution

$$h_{11}(\mathbf{r},\mathbf{r}')\cong-\frac{\beta e^{2}}{\varepsilon}\frac{\exp[-\kappa_1(\mathbf{r}-\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}\quad(\mathrm{SMT}). \tag{45}$$

The key results for the counterion density $n(\mathbf{r})$ in Eqs. (40) and (42) and for the correlation function $h_{11}(\mathbf{r},\mathbf{r}')$ in Eq. (45), can now be inserted in Eq. (37) to give the effective Hamiltonian $H^{\mathrm{eff}}(\{\mathbf{R}_i\})$. The constant potential $\overline{\psi}$ drops out of the calculation because of the neutrality condition: $\int\langle\hat{\rho}(\mathbf{r})\rangle d\mathbf{r}=0$. After some algebra, see Ref. [4], and adding the ideal-gas reference term, we have the result for the effective Hamiltonian

$$\begin{aligned}H^{\mathrm{eff}}(\{\mathbf{R}_i\})&=VkT[n_1\ln(n_1\Lambda^{3})-n_1]\\ &\quad-\left(\frac{Z^{2}e^{2}\kappa_1}{2\varepsilon}N_0+\frac{Ze^{2}\kappa_1}{3\varepsilon}N_0+\frac{1}{2}ZN_0kT\right)\\ &\quad+\frac{Z^{2}e^{2}}{2\varepsilon}\sum_{i=1}^{N_0}\sum_{\substack{j=1\\ i\neq j}}^{N_0}\frac{\exp[-\kappa_1R_{ij}]}{R_{ij}}\quad(\mathrm{SMT}).\end{aligned} \tag{46}$$

This is almost identical to the DFT result in Eq. (24)—the separation dependent effective pair potential is the same in both theories. However, the one body or volume term, in the parenthesis in Eq. (46), obtained from the SMT, contains the extra term $\{Ze^{2}\kappa_1N_0/(3\varepsilon)\}$:

$$F_1 \equiv -\left(\frac{Z^2e^2\kappa_1}{2\varepsilon}N_0 + \frac{Ze^2\kappa_1}{3\varepsilon}N_0 + \frac{1}{2}ZN_0kT\right) \quad (\mathrm{SMT}). \tag{47}$$

This additional term originates from the second term on the right-hand side of Eq. (37) that depends on the correlation function $h_{11}(\mathbf{r},\mathbf{r}')$, and this is equivalent to the contribution from the correlation functional $\mathcal{F}_{\mathrm{corr}}$, Eq. (8), that has been neglected in the DFT treatment, Eq. (12).

IV. THE ONE-BODY VOLUME TERM

In the DFT treatment, the one-body volume term, F_1 has special significance because at low densities, the free energy of the system originates from this term, see Eq. (28), and therefore it appears to have a fundamental role in the study of phase behavior in Coulombic systems [2].

However, the formula in Eq. (27) for estimating the contribution of the effective pair potential $u^{\mathrm{eff}}(R_{ij})$ to the free energy is inadequate in this situation. For short-ranged temperature independent pair potentials, this formula does give the leading-order result in density. However, for long-ranged state dependent potentials such as $u^{\mathrm{eff}}(R_{ij})$, its use will lead to omission of terms of equal order in density. Instead, as is typical in Coulombic systems, we need to sum ring diagrams to ensure we collect all terms of the same order in density n_0. For a system with a pair potential $u^{\mathrm{eff}}(r)$, the two-body free energy F_2 can be calculated with the following formula that involves a coupling constant λ integration;

$$F_2 = \int_0^1 \left(\frac{1}{2}N_0 n_0 \int [\lambda u^{\mathrm{eff}}(r)][1+h_{00}(r,\lambda)]d\mathbf{r}\right) d\lambda/\lambda, \tag{48}$$

where $h_{00}(r,\lambda)$ is the total colloid-colloid correlation function of a one-component system of colloidal particles that interact with pair potential $[\lambda u^{\mathrm{eff}}(r)]$. We now sum simple ring diagrams by calculating $\tilde{h}_{00}(k,\lambda)$, the Fourier transform of $h_{00}(r,\lambda)$, which is a function of wave number k, via the Ornstein-Zernike equation:

$$\tilde{h}_{00}(k,\lambda) = \frac{\tilde{c}_{00}(k,\lambda)}{1-n_0\tilde{c}_{00}(k,\lambda)} \tag{49}$$

with

$$c_{00}(r,\lambda) = -\lambda\frac{u^{\mathrm{eff}}(r)}{kT} = -\lambda\frac{(Ze)^2}{\varepsilon kT}\frac{\exp[-\kappa_1 r]}{r}, \quad r>0. \tag{50}$$

Combining Eqs. (49) and (50) gives

$$h_{00}(r,\lambda) = \lambda\frac{(Ze)^2}{\varepsilon kT}\frac{\exp[-\kappa_D(\lambda)r]}{r}, \quad r>0, \tag{51}$$

where

$$\kappa_D(\lambda) = (\lambda\kappa_0^2 + \kappa_1^2)^{1/2}. \tag{52}$$

Using Eqs. (51) and (52) in Eq. (48), we obtain for the two-body free energy, F_2

$$F_2 = \left(\frac{Z^2e^2\kappa_1}{2\varepsilon}N_0 + \frac{Ze^2\kappa_1}{3\varepsilon}N_0 + \frac{1}{2}ZN_0kT\right) - \frac{kT\kappa_D^3}{12\pi}V. \tag{53}$$

Therefore from Eqs. (47) and (53) we have the final expression for the free energy

$$\begin{aligned} F = F_1 + F_2 = &\Bigg\{ VkT[n_1\ln(n_1\Lambda^3) - n_1] \\ &- \left(\frac{Z^2e^2\kappa_1}{2\varepsilon}N_0 + \frac{Ze^2\kappa_1}{3\varepsilon}N_0 + \frac{1}{2}ZN_0kT\right)\Bigg\} \\ &+ \left\{\left(\frac{Z^2e^2\kappa_1}{2\varepsilon}N_0 + \frac{Ze^2\kappa_1}{3\varepsilon}N_0 + \frac{1}{2}ZN_0kT\right) - \frac{kT\kappa_D^3}{12\pi}V\right\} \\ = &\, VkT[n_1\ln(n_1\Lambda^3) - n_1] - \frac{kT\kappa_D^3}{12\pi}V \quad (\mathrm{SMT}), \end{aligned} \tag{54}$$

which is in agreement with the Debye-Hückel limiting law.

We observe that the constant one-body volume term F_1 is canceled exactly by identical terms that form part of the free energy F_2 that has its origin in the effective pair potential $u^{\mathrm{eff}}(r)$. This cancelation is more that just a curiosity of the Debye-Hückel treatment. Indeed, Belloni has constructed a general and powerful argument regarding the one-body volume term by considering the compressibility equation that relates thermodynamics and correlations functions [10]. In the present context, this argument proceeds as follows.

The most general form of effective Hamiltonian can be written as

$$H^{\mathrm{eff}}(\{\mathbf{R}_i\}) = F_1 + W(\{\mathbf{R}_i\}), \tag{55}$$

where $W(\{\mathbf{R}_i\})$ may contain two-, three- and higher-body terms. It is clear that all ensemble averages of quantities that only depend on the colloid coordinates, such as the colloid-colloid pair-correlation function, $h_{00}(r)$ or its Fourier transform, $\tilde{h}_{00}(k)$ can only depend on $W(\{\mathbf{R}_i\})$ and not on the constant one-body volume term F_1. One route to thermodynamic properties is via the compressibility equation [6]

$$\begin{aligned} -\frac{kT}{V}\frac{\partial V}{\partial P} &= \frac{[1+n_1\tilde{h}_{11}(0)][1+n_0\tilde{h}_{00}(0)] - n_0n_1[\tilde{h}_{01}(0)]^2}{n_0[1+n_1\tilde{h}_{11}(0)] + n_1[1+n_0\tilde{h}_{00}(0)] - 2n_0n_1\tilde{h}_{01}(0)} \\ &= \frac{1}{n_0}[1+n_0\tilde{h}_{00}(0)] = \frac{1}{n_1}[1+n_1\tilde{h}_{11}(0)], \end{aligned} \tag{56}$$

where the local electroneutrality conditions about a single charged colloid or counterion

$$Z=-n_0Z\tilde{h}_{00}(0)+n_1\tilde{h}_{01}(0),$$

$$-1=-n_0Z\tilde{h}_{10}(0)+n_1\tilde{h}_{11}(0), \tag{57}$$

have been used to express the first line of Eq. (56) in terms of only the correlation function: $\tilde{h}_{00}(0)$ or $\tilde{h}_{11}(0)$ in subsequent lines. In particular, from the second equality of Eq. (56), we can see that for the salt free system, all thermodynamic quantities can be expressed only in terms of the colloid-colloid pair-correlation function $\tilde{h}_{00}(0)$, which in turn does not depend on the constant one-body volume term F_1. However, the constant one-body volume term will play a role in theoretical approaches that involves constructing the total free energy in successive stages such as with the DFT formulation, where the one- and two-body contributions to the free energy is formulated and calculated separately. In such an approach, the role of the one-body volume term will be to cancel out a corresponding contribution from the position dependent part of the effective Hamiltonian rather than being the source of the free-energy term that controls phase behavior as inferred earlier [2].

The third equality of Eq. (56) reveals the importance of including ion-ion correlations as well because the assumption $\mathcal{F}_{\mathrm{corr}}=0$ is equivalent to assuming the counterion-counterion correlation $\tilde{h}_{11}(0)=0$, and thereby violates one of the local electroneutrality conditions in Eq. (57).

V. CONCLUSIONS

Modern DFT has been brought to bear on the problem of phase behavior in colloidal systems whose properties are dominated by Coulombic interactions. While the DFT formalism has enjoyed much success in solid-state physics, its application to colloidal problems requires making the necessary theoretical connections with established approaches in the colloid literature and the clarification of its status with respect to other existing theories. While the discussion and pedagogic illustrations presented herein are only based on a point-ion and point-colloid model without added salt, it does serve to highlight the subtleties of the problem and the relations between different theoretical approaches. We have shown that the DFT formalism [2] is identical to the earlier statistical-mechanical theory [4] provided that

(i) ion correlations effects are included in the DFT, and

(ii) the calculation of the free energy from the effective pair potential $u^{\mathrm{eff}}(r)$ is consistent with the calculation of the one-body volume term in so far as obtaining consistent orders in the number density as typical in Coulombic systems.

Clearly a creditable model of colloidal systems, even within the primitive model, should allow for the colloids and counterions to have different hard-sphere radii R_0 and R_1. In this case, the excess internal energy due to Coulombic interactions has the general form ($\alpha, \beta=0,1$)

$$\begin{aligned}\frac{E^{\mathrm{coul}}}{V}&=\frac{e^2}{2\varepsilon}\sum_{\alpha,\beta} n_\alpha z_\alpha n_\beta z_\beta\int\frac{h_{\alpha\beta}(r)}{r}d\mathbf{r}\\&=\frac{2\pi e^2}{\varepsilon}\sum_{\alpha,\beta} n_\alpha z_\alpha n_\beta z_\beta\int_{R_\alpha+R_\beta}^{\infty} r h_{\alpha\beta}(r)\,dr\\&\quad-\frac{\pi e^2}{\varepsilon}\sum_{\alpha,\beta} n_\alpha z_\alpha n_\beta z_\beta (R_\alpha+R_\beta)^2.\end{aligned} \tag{58}$$

The first term in the second line depends on the (yet to be determined) pair-correlations functions $h_{\alpha\beta}(r)$ while the second term is exact and is a consequence of the straightforward coupling between Coulombic interactions and particle size differences that comes form the energy integral in the interval $0<r<(R_\alpha+R_\beta)$ where $h_{\alpha\beta}(r)=-1$. This second term is negligible for ionic size differences typical for ionic solutions. However, for size asymmetries that are characteristic of colloids and ions, this term can account for up to 50% of the internal energy when compared to Monte Carlo simulation studies [7]. Recent attempts at modeling phase behavior driven by Coulombic interactions in colloidal systems [1,2,8] all seem not to have fully accounted for this size-asymmetry contribution and its importance in determining Coulomb interaction driven phase behavior in colloidal systems has only just been considered [9]. Furthermore, the introduction of finite sizes for the ionic components will generate terms beyond just two-body effective potentials in the effective Hamiltonian and the importance of such higher body terms remain to be quantified [10].

In the salt-free case, the inclusion of size asymmetry between the colloid and the counterions is sufficient to give rise to a gas-liquid phase equilibrium [9]. The general physical reason for this equilibrium is easy to understand although the present linear Debye-Hückel treatment may not be accurate with the quantitative details of the phase boundary. With the addition of salt, the DFT theory predicts the existence of a upper as well as a lower critical salt concentration between which the system can exhibit gas-liquid phase equilibrium [2]. The physical reason for the existence of lower critical salt concentration is less obvious.

The role of Coulombic effects on phase separation in colloidal systems is a problem first studied by Langmuir [11] many years ago and the problem remains open today.

ACKNOWLEDGMENTS

This research was funded in part by the Australian Research Council and their support is gratefully acknowledged. It is also a pleasure to acknowledge the contributions of Luc Belloni (CEA/SACLAY) and Per Linse (Lund) who offered their time generously and patiently to discuss electrostatic matters.

[1] R. van Roij, M. Dijkstra, and J. P. Hansen, Phys. Rev. Lett. **79**, 3082 (1997).
[2] R. van Roij, M. Dijkstra, and J. P. Hansen, Phys. Rev. E **59**, 2010 (1999).
[3] R. van Roij and R. Evans, J. Phys.: Condens. Matter **11**, 10047 (1999).
[4] B. Beresford-Smith, D. Y. C. Chan, and D. J. Mitchell, J. Colloid Interface Sci. **105**, 216 (1985).
[5] C. W. Outhwaite, M. Molero, and L. B. Bhuryan, J. Chem. Soc., Faraday Trans. **87**, 3227 (1991).
[6] D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).
[7] P. Linse, J. Chem. Phys. **112**, 4359 (2000).
[8] P. B. Warren, J. Chem. Phys. **112**, 4683 (2000).
[9] D. Y. C. Chan, P. Linse, and S. N. Petris, Langmuir (to be published).
[10] L. Belloni, J. Phys.: Condens. Matter **12**, R549 (2000).
[11] I. Langmuir, J. Chem. Phys. **6**, 873 (1938).