Mean spherical model for the D-dimensional ν-component classical plasma

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The mean spherical model with continuous pair functions is solved exactly, in the limit of strong coupling, for a ν-component classical plasma with the D-dimensional Coulomb interaction. Exact lower bounds for the one-component plasma correlation energy, which are very effective for arbitrary coupling, are derived.

In this report the relation between the structure and the equation of state of strongly coupled D-dimensional ν-component classical plasmas (with the D-dimensional Coulomb potential) is discussed, and an exact solution of the mean spherical model (MSM) with continuous pair functions is presented. The explicit solution (for arbitrary D and ν) in the limit of infinitely strong coupling also provides a formal exact solution for arbitrary coupling. The function describing the interaction energy between two uniformly charged D-dimensional spheres at distance r plays a key role for strongly coupled plasmas (similar to that of the Debye-Hückel screened Coulomb potential for weak coupling) and provides the correct analytic form for the MSM direct correlation functions. When utilized in the Ewald hybrid expression, in conjunction with Mermin's inequality for the structure factor, it provides an exact lower bound for the one-component-plasma (OCP) correlation energy that interpolates between the Debye and ionsphere bounds and is very effective for arbitrary coupling.

Consider a D-dimensional ν-component system of charges $Q_i e$, with concentrations x_i, total number density $n = N/V$, at a given temperature $\beta = (k_B T)^{-1}$, imbedded in a uniform neutralizing background of charge density $-\rho_b = -ne\langle Q\rangle$ (the notation is $\langle Q^s\rangle = \sum_i x_i Q_i^s$), and interacting via the Coulomb potentials $u_{ij}(r) = Q_i Q_j e^2 \phi_D(r)$, where

$$\phi_D(r) = \begin{cases} \operatorname{sgn}(D-2) r^{2-D}, & D \neq 2 \\ -\ln(r), & D = 2 \end{cases} \tag{1}$$

is the solution of the D-dimensional Poisson equation

$$\Delta \phi_D(r) = (|D-2| + \delta_{D,2})\omega_D \delta_D(\vec{r}),$$

$$\tilde{\phi}_D(k) = \omega_D(|D-2| + \delta_{D,2})/k^2,$$

and

$$\omega_D = 2\pi^{D/2}/\Gamma(D/2)$$

is the surface of a D-dimensional unit sphere. Unified approaches to such plasmas have been given by several authors.[1-3] The thermodynamic state of the OCP is characterized by the coupling parameter $\gamma_D = \beta e^2 a_{WS}^{2-D}$, $a_{WS} = [D/(\omega_D n)]^{1/D}$ being the "ion-sphere" (Wigner-Seitz) radius. The correlation energy U, given in general by

$$\frac{U}{N} = \tfrac{1}{2} n \sum_{i,j} x_i x_j \int h_{ij}(\vec{r})[e^2 Q_i Q_j \phi_D(r)] d\vec{r} \tag{2}$$

is governed, in the strong-coupling regime ($\gamma_D \gg 1$), by a Madelung behavior $\beta U/N = \alpha_D^0 \gamma_D$, where α_D^0 is some structure-dependent constant. Here, $h_{ij}(\vec{r}) = g_{ij}(\vec{r}) - 1$ are the total correlation functions related to the structure factors by

$$S_{ij}(k) = \delta_{ij} + n(x_i x_j)^{1/2} \tilde{h}_{ij}(\vec{k}),$$

and the tilde denotes Fourier transforms.

Exact lower bounds for $\beta U/N$ that will be effective in the strong coupling regime (in the sense of being close to the energy of the most stable Wigner lattice) have been sought by essentially two closely related approaches. The formal approach[3] is based on the Ewald hybrid expression valid for any auxiliary function $\theta_{ij}(r)$ for which $\tilde{\theta}_{ij}(k)$ exists:

$$\beta U/N = B[\theta] + W_1(g,\theta) + W_2(S,\theta), \tag{3}$$

$$B[\theta] = -\tfrac{1}{2} n \sum_{ij} x_i x_j \int [\theta_{ij}(r) + \beta e^2 Q_i Q_j \phi_D(r)] d\vec{r} + \tfrac{1}{2}(2\pi)^{-D} \sum_i x_i \int \tilde{\theta}_{ii}(k) d\vec{k}, \tag{4}$$

$$W_1(g,\theta) = \tfrac{1}{2} n \sum_{ij} x_i x_j \int g_{ij}(\vec{r})[\theta_{ij}(r) + \beta e^2 Q_i Q_j \phi_D(r)] d\vec{r}, \tag{5}$$

$$W_2(S,\theta) = \tfrac{1}{2}(2\pi)^{-D} \sum_{ij} (x_i x_j)^{1/2} \int S_{ij}(\vec{k})[-\tilde{\theta}_{ij}(k)] d\vec{k}. \tag{6}$$

A judicious choice of the functions $\theta_{ij}(r)$ for which $W_1(g,\theta) \geq 0$ and $W_2(S,\theta) \geq 0$ will provide a lower bound via the structure independent term, $\beta U/N \geq B[\theta]$. A more physical approach[1,4-6] is based on Onsager's idea to replace the point charges with "smeared" charge distributions, $\rho_i(|\vec{r}|)$, of total charge $Q_i e$, confined within D-dimensional "balls" of radii α_i [$b(\alpha_i)$ denoted the type i ball].

For strongly coupled plasmas we expect that $\beta U/N \cong B[c]$ [the generalized MSM (Ref. 7)], where $c_{ij}(r)$ denotes the Ornstein-Zernike (OZ) direct correlation functions. Those Ewald auxiliary functions, $\theta_{ij}(r)$, that provide an exact bound which is effective in the strong coupling regime should have many features in common with the $c_{ij}(r)$'s, providing a link between the thermodynamics and structure of strongly coupled plasmas. A special role is played by the auxiliary functions that correspond to the approach by Onsager.

Let $\psi_{ij}^{(D)}(r)$ be the electrostatic interaction energy between the i and j balls with center to center distance r:

$$\psi_{ij}^{(D)}(r) = \int_{b(\alpha_i)} d\vec{x} \int_{b(\alpha_j)} d\vec{y}\, \rho_i(|\vec{x}|)\rho_j(|\vec{y}-\vec{r}|) \times \phi_D(|\vec{x}-\vec{y}|)\,. \tag{7}$$

Observe[8] that with the choice $\theta_{ij}(r) = -\beta\psi_{ij}^{(D)}(r)$, the Ewald hybrid expression (3) becomes identical, *term by term*, with the expression resulting from the Onsager scheme: $(N/\beta)W_1(g, -\beta\psi^{(D)})$ is the interaction energy between the point charges minus that between the smeared charges; the first term in Eq. (4) for $(N/\beta)B[-\beta\psi^{(D)}]$ is the interaction between the point charges and the background minus that between the smeared charges and the background, while the second term in Eq. (4) corresponds to the self energy of the smeared charges. In particular, $(N/\beta)W_2(S, -\beta\psi^{(D)}) \geq 0$ since it is the total electrostatic energy of the smeared charges plus the background. The desired bound now has the following *decoupled* form:

$$B[-\beta\psi^{(D)}] = \rho_b\beta \sum_i x_i B_i\{\rho_i\}\,,$$

where

$$B_i\{\rho_i\} = \int_{b(\alpha_i)} d\vec{x} \int_{b(\alpha_i)} d\vec{y} \left[\rho_i(|\vec{x}|)\left(1 - \frac{1}{2}\frac{\rho_i(|\vec{y}|)}{\rho_b}\right)\phi_D(|\vec{x}-\vec{y}|) - Q_i e\,\delta(\vec{x}-\vec{y})\phi_D(\vec{x})\right]\,. \tag{8}$$

The "best" smearing $\bar{\rho}_i(|\vec{x}|)$ is found by variation

$$\frac{\delta B_i\{\rho_i\}}{\delta\rho_i(|\vec{x}|)} = 0 \tag{9}$$

to be constant, $\bar{\rho}_i(|\vec{x}|) = \rho_b$. With the overbar denoting the best quantities we thus obtain that $\bar{\psi}_{ij}^{(D)}(r)$ is the interaction energy between two uniformly charged D-dimensional balls of charge density ρ_b and radii a_i and a_j, where $a_m = a_{\rm WS}(Q_m/\langle Q\rangle)^{1-2/D}$. Since[1] $W_1(g, -\beta\bar{\psi}^{(D)}) \geq 0$, an exact lower bound for the correlation energy is given by[9]

$$\beta U/N \geq \bar{B} \equiv -\alpha_D\gamma_D\langle Q\rangle^{1-2/D}\langle Q^{1+2/D}\rangle \tag{10}$$

corresponding to a one-fluid model with both the charge averaging and Madelung constant of the ion-sphere model.[9]

The unification of the Ewald and Onsager schemes above enables us (i) to obtain an exact lower bound for the OCP's which is very effective for *all values* of the coupling parameter, and (ii) to uncover basic relations between the pair structure and the thermodynamics of dense plasmas as featured by the MSM.

Consider the OCP's and let $\psi_{\rm OCP}^{(D)}(r,d)$ be the interaction energy between two identical uniformly charged D-dimensional balls of radius d and unit total charge. Using the Ewald hybrid scheme and a generalization[3,10] of Mermin's inequality,[11]

$$S(\vec{k}) \geq S_{\rm RPA}(k) = [1 + n\phi_D(k)]^{-1}\,, \tag{11}$$

one obtains the following exact lower bound:

$$(\beta U/N)_{\rm OCP} \geq B_{\rm op}(\gamma_D, d) \equiv B[-\beta\psi_{\rm OCP}^{(D)}(r,d)] + W_1(S_{\rm RPA}, -\beta\psi_{\rm OCP}^{(D)}(r,d))\,, \tag{12}$$

which can be optimized via $\partial B_{\rm op}/\partial d = 0$ to obtain $d_{\rm best}(\gamma_D)$. $\psi_{\rm OCP}^{(D)}(r,d)$ has the scaled form[12] $d^{2-D}\psi_0^{(D)}(r/d)$ for $D \neq 2$, and $\ln d + \psi_0^{(D)}(r/d)$ for $D = 2$. The leading asymptotic large γ_D behavior is

$$B_{\rm op}(\gamma_D, d_{\rm best}) = -\alpha_D\gamma_D + \tfrac{1}{2} + \cdots\,.$$

$B_{\rm op}(\gamma_D, d_{\rm best})$ interpolates between the Debye-Hückel (i.e., RPA) bound to which it equals for $\gamma_D \ll 1$ and the ion-sphere bound for $\gamma_D \gg 1$, providing an exact and very effective lower bound for the OCP energies (it improves upon the bounds given in Ref. 3 also due to the formal reason given in Ref. 12) that will be particularly useful as a check on other approximations.

Using the RPA free-energy functional

$$\mathfrak{F}[c] = B[c] + \tfrac{1}{2}(2\pi)^{-D}\int d\vec{k}\,\ln\{\det[\underline{1} - \underline{c}(k)]\}\,, \tag{13}$$

the MSM can be formulated variationally by the following equations[13]:

$$c_{ij}(r) = -\beta e^2 Q_i Q_j\phi_D(r)\,,\quad r > d_{ij} \tag{14}$$

$$\frac{\delta\mathfrak{F}[c]}{\delta c_{ij}(r)} = 0\,,\quad r < d_{ij}\,. \tag{15}$$

The matrix $(\underline{c})_{ij} = n(x_i x_j)^{1/2}c_{ij}(k)$ is related to the matrix of structure factors $(\underline{S})_{ij} = S_{ij}(k)$ by the OZ relations, $\underline{S} = (\underline{1} - \underline{c})^{-1}$, where $(\underline{1})_{ij} = \delta_{ij}$ is the unit matrix and det denotes the determinant. The MSM as modified[14] to treat soft (without hard-core) potentials, by the additional requirement that the pair functions be continuous (which fixes the otherwise free parameters d_{ij}), has been discussed[15] and termed "SMSA". If there is a solution to the SMSA equations for the plasma, which is continuous in γ_D for $\gamma_D \geq 0$, then $\mathcal{F}[c]$ is precisely the excess free energy per particle via the energy equation of state.[15] To solve the SMSA we may either impose[16] $\partial B[c]/\partial d_{ij}=0$ on the solution of Eqs. (14) and (15), or consider continuous functions $c_{ij}(r)$ that satisfy (14) and solve (15).

A physically acceptable solution of the SMSA in the strong coupling limit should feature a Madelung-type correlation energy

$$(\beta U/N)_{\text{SMSA}} \equiv B[c_{\text{SMSA}}]+\tfrac{1}{2} \xrightarrow[\gamma_D\to\infty]{} \alpha'_D \gamma_D .$$

This can be obtained if the c_{ij}'s *saturate* in the sense that $\lim_{\gamma_D\to\infty} c_{ij}(r)=c_{ij}^{(\infty)}(r)$ becomes proportional to γ_D and thus also $\lim_{\gamma_D\to\infty}\mathcal{F}[c^{(\infty)}]$. To solve the SMSA in this asymptotic limit we replace Eq. (15) by the following equations:

$$\delta B[c^{(\infty)}]/\delta c_{ij}^{(\infty)}(r)=0, \quad r<d_{ij}^{(\infty)} \tag{16}$$

$$\det(\underline{1}-\underline{c}^{(\infty)}) \geq 0. \tag{17}$$

A general way to write a continous function $c_{ij}(r)$ that has the saturation property and satisfies Eqs. (14) and (17) is[17] $c_{ij}(r)=-\beta\psi_{ij}^{(D)}(r)$, which sets $d_{ij}^{(\infty)}=\alpha_i+\alpha_j$. Equation (16) then becomes equivalent to Eq. (9), and the asymptotic SMSA problem is *mapped* on the "best bound" problem considered above. We thus immediately obtain the limiting behavior of the SMSA for plasmas:

$$\lim_{\gamma_D\to\infty} c_{ij}(r)=-\beta\overline{\psi}_{ij}^{(D)}(r), \tag{18a}$$

$$\lim_{\gamma_D\to\infty} (\beta U/N)=\overline{B}, \tag{18b}$$

$$\lim_{\gamma_D\to\infty} d_{ij}=a_i+a_j. \tag{18c}$$

The MSM was solved exactly for the 3D one- and two-component plasmas[18,19] ($\nu=1,2$). The resulting SMSA solution obtained by imposing directly the continuity of the pair functions, when taken in the limit $\gamma_D\to\infty$, is identical to our results given by Eqs. (18). The explicit exact solution for the asymptotic ($\gamma_D\to\infty$) behavior of the SMSA also provides a formal exact solution for decreasing values of γ_D, as long as there is no change in the analytic form of $c_{ij}(r<d_{ij})$. Equations (15) then provides a set of algebraic equations for the unknown coefficients. Indeed, the explicit analytic solution available in 3D maintains the same form (fifth-degree polynomials, as $\overline{\psi}_{ij}^{(3)}$) for all values of γ_3, and the same pattern is expected for all D.

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[8]Note the equality

$$\tfrac{1}{2}n\sum_{ij} x_i x_j \int_{b(\alpha_i)} [\psi_{ij}^{(D)}(r)-Q_iQ_je^2\phi_D(r)]d\vec{r}$$
$$=\rho_b \sum_i x_i \int_{b(\alpha_i)} [\varphi_i(r)-Q_ie\phi_D(r)]d\vec{r},$$

where $\varphi_i(r)$ is the electrostatic potential of the i ball.

[9]From Ref. 3 above we find that $\overline{B}_i=-[(D/2)E^{(D)}(a_i)+\frac{1}{4}\delta_{D,2}](Q_ie)^2$, where $E^{(D)}(a)$ is the self-energy of a uniformly charged ball of radius a and unit total charge, $E^{(D)}(a)=[(2/D)\alpha_D-\frac{1}{4}\delta_{D,2}]/a^{1-2/D}$. Thus,

$$\alpha_D=\tfrac{1}{2}[\,|D-2|\,(D+1)/(D+2)+\text{sgn}(D-2)]$$

for $D\neq 2$, and $\alpha_D=\frac{3}{8}-\frac{1}{2}\ln a_{\text{WS}}$ for $D=2$.

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[12]Direct correlation functions that scale like $\psi_{r,d}^{(3)}$ provided a starting point for analyzing D-dimensional plasmas with the 3D Coulomb interaction [Y. Rosenfeld, J. Phys. C 13, 3227 (1980) and Ref. (7) above]. $\psi_0^{(3)}(x/2)=\frac{12}{5}(1/x)\int_0^x f(z)dz$, where $f(z>1)=0$ and $f(z\leq 1)=1-5z^2+5z^3-z^5$. The function $f(z)$ is much more efficient than the customary Ewald auxiliary functions, e^{-z} or e^{-z^2}, for calculating inverse power, r^{-s}, lattice sums, with $\theta_s \propto x^{-s}\int_0^x f(z)z^{s-1}dz$. In particular, the following exact lower bound is obtained for the 2D OCP with the r^{-1} potential: $\beta U/N > -\frac{12}{5}(\frac{3}{14})^{1/2}\Gamma = -1.111\,098\,4\Gamma$, a significant improvement upon the result of Totsuji [(Phys. Rev. A 19, 1712 (1979)].

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[16]Given a solution of the MSM for any potential, the SMSA limit of continuous pair functions is equivalent to the additional requirement $\partial\mathcal{F}[c]/\partial d_{ij}=0$, which for potentials possessing Fourier transforms (e.g., r^{-1} and Yukawa in 3D) can be further replaced by $\partial B[c]/\partial d_{ij}=0$ (Y. Rosenfeld, unpublished). This is a general result. It was observed by R. G. Palmer, J. Chem. Phys. 73, 2009 (1980), for the r^{-1} potential, and can be readily checked for the Yukawa potential by using the results of C. Pastore *et al.*, Phys. Lett. 78A, 75 (1980).

[17]With the choice $\underline{c}=-\beta\underline{\psi}$ we have

$$\det(\underline{1}-\underline{c})=1-\text{tr}(\underline{c})=1+\beta n\sum_i x_i\widetilde{\psi}_{ii}^{(D)}(k)$$
$$=1+\beta n\sum_i x_i[\widetilde{\rho}_i(k)]^2\widetilde{\phi}_D(k)\geq 0.$$

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