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Onsager molecules: New theory for interacting charge clusters and screening potentials in plasmas

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The high-density solution of the hypernetted-chain equations for charge-cluster plasmas, as mapped on the Onsager charge-smearing optimization, defines "Onsager molecules." These are natural generalizations of the ion-sphere (Thomas-Fermi) "atom." The self-energy of these molecules and their dissociation properties provide the key for the first accurate calculation of the screening potentials in fluid classical plasmas.

Following Widom,[1] the m-body correlation function $g^{(m)}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_m)$ of a fluid can be expressed through the free-energy change upon fixing the positions of m fluid particles in the appropriate configuration to form an m-interaction-site molecule. As a special case, the zero-separation theorem[2] relates the $r=0$ value of the plasma pair-screening potential

$$H(r)=\ln[g(r)\exp(\beta\phi(r))]$$

to the thermodynamics of plasma mixtures.[3] This relation is the starting point for calculating enhancement factors of nuclear reaction rates.[4] It played a key role in the study of the short-range behavior of the bridge functions, notably their universal characteristics.[5] The application of Widom's relation for calculating the complete pair correlation function $g(r)$, not to mention higher-order correlation functions, has been out of reach of existing theories[6] for the thermodynamics of molecular fluids. A new theory for the statistical thermodynamics of interacting charged particles[7–10] is, however, of the required accuracy and simplicity to enable such a calculation. This theory is applied here to a molecular fluid composed of clusters of positive ions in a uniform neutralizing background charge density. We calculate the m-particle screening potentials in classical plasmas. The results reported below represent the first accurate calculation of fluid many-body correlation functions from a theory for the thermodynamics of molecular fluids.

To simplify the presentation we consider specifically the three-dimensional (3D) one-component plasma (OCP),[4,11,12] containing N positive point ions of charge Qe, at temperature $k_BT=\beta^{-1}$, in a uniform neutralizing background of volume V (eventually $N,V\rightarrow\infty$, $n=N/V$), characterized by the coupling parameter $\Gamma=\beta(Qe)^2/a$. The Wigner-Seitz radius $a=(3/4\pi n)^{2/3}$ serves as the unit of length in this paper, $\beta\phi(r)=\Gamma/r$.

For pair correlations, the OCP potential of mean force $w(r)=-\ln[g(r)]$ is given by[13]

$$w(r)=-\beta[F_0^{\mathrm{ex}}(N\cdot)-F_1^{\mathrm{ex}}(\cdot\underset{r}{\rule{1.5em}{0.4pt}}\cdot\;,N-2\cdot)]\;. \tag{1}$$

$F_0^{\mathrm{ex}}(N\cdot)$ is the excess free energy of the OCP containing N point ions. F_1^{ex} is the excess free energy of a OCP in which one pair of ions is kept at fixed separation r. That is, F_1^{ex} corresponds to an infinitely dilute solution of the two-site point-charge molecule $(\cdot\underset{r}{\rule{1.5em}{0.4pt}}\cdot)$ in a fluid of one-site point-charge ions, altogether in a uniform background. F_1^{ex} contains the electrostatic interaction between different point charges in the molecule, i.e., $(Qe)^2/r$, so that the screening potential $H(r)=-w(r)+\Gamma/r$ is finite for $r=0$.

From the exact diagrammatic expression one obtains[4,5] $H(r)=h(r)-c(r)-B(r)$, where $h(r)=g(r)-1$. The direct correlation function $c(r)$ is related to $h(r)$ by the Ornstein-Zernike (OZ) equation, which in k space takes the form $\tilde{c}(k)=\tilde{h}(k)/[1+n\tilde{c}(k)]$. $B(r)$, the bridge function, is expressed in terms of graphs with $h(r)$ bonds and at least triply connected field points. $B(r)=0$ defines the hypernetted-chain (HNC) approximation. The modified-HNC theory corrects this approximation by employing, e.g., the hard-sphere bridge functions and the ansatz of universality. The HNC integral equation,[4,5,11,14] obtained from the HNC closure $H(r)=h(r)-c(r)$ and the OZ relation, can also be derived variationally from a free-energy functional. This HNC free energy is of about 1% accuracy for one- and multiple-component plasmas in two and three dimensions, and it is much more accurate than the (short-range) HNC $g(r)$.

Our apporach is to iterate on the HNC approximation by using it not via its closure relation, but rather via its prediction for the free energies F_0^{ex}, F_1^{ex}, which approach is relatively more accurate. Yet exact solutions of the HNC equation for complex charge clusters, associated with high-order correlations, are not within our reach. We need more insight in order to perform the calculations.

Our theory implements[7–10] the Onsager charge-smearing optimization[15,16] into the variational free-energy functional of the HNC theory or the closely related[14] mean-spherical approximation (MSA). This leads to an approximate physically intuitive solution of the HNC integral equation for the structure. It yields, however, very accurate results for the HNC free energy for all $0<\Gamma<\infty$. Moreover, the leading $\Gamma\rightarrow\infty$ results for $c(r)$ and the free energy in our theory are the exact $\Gamma\rightarrow\infty$ HNC results. These are calculated as interactions between smeared charges at distance r, and as self-energies of the Onsager "atoms" and "molecules," respectively. These self-energies give an exact lower bound to the true potential energy of the system, which is a very tight bound when $\Gamma\gg 1$.

In the strong-coupling region $(\Gamma\gg 1)$ the free energies F_0^{ex}, F_1^{ex} are dominated by the corresponding Madelung potential-energy terms, for which the HNC-Onsager results are[10,17]

$$F_0^{\mathrm{ex}}(N\cdot)\xrightarrow[\Gamma\to\infty]{\mathrm{HNC}} NU_1(\odot)\ , \tag{2}$$

$$F_1^{\mathrm{ex}}(\cdot\underset{r}{\text{—}}\cdot, N-2\cdot)\xrightarrow[\Gamma\to\infty]{\mathrm{HNC}}(N-2)U_1(\odot)+U_2\left[\left(\,\cdot\underset{r}{\text{———}}\cdot\,\right)\right]. \tag{3}$$

U_1 denotes the self-energy of an "Onsager atom" (the ion-sphere Thomas-Fermi "atom") consisting of a point charge at the center of a neutralizing sphere (of radius a, for the OCP) having the background charge density. $\beta U_1=-0.9\Gamma$ provides a tight bound to the bcc lattice energy -0.895929Γ. U_2 denotes the self-energy of the "Onsager molecule" composed of a pair of ions at a distance r, and a uniform neutralizing charge cloud of the background charge density. The shape of the molecule is determined by the ("isolation") condition that the electrostatic potential and field vanish on its surface, i.e., there are no induced surface charges on the molecule if placed in an infinite neutral conductor. Denoting by HNC-F^{ex} the results obtained from the HNC predictions for the free energy, then from (1)–(3) we obtain

$$w(r)\xrightarrow[\Gamma\to\infty]{\mathrm{HNC}\text{-}F^{\mathrm{ex}}}\beta U_2\left[\left(\,\cdot\underset{r}{\text{———}}\cdot\,\right)\right]-2\beta U_1(\odot)\ . \tag{4}$$

The Onsager-molecule concept is readily extended for higher-order correlation functions. For example, for the triplet correlations

$$w^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=-\ln[g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)]\ ,$$

we get

$$w^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\xrightarrow[\Gamma\to\infty]{\mathrm{HNC}\text{-}F^{\mathrm{ex}}}\beta U_3\left[\left(\cdot 1\quad \overset{\cdot}{2}\quad 3\cdot\right)\right]-3\beta U_2(\odot)\ . \tag{5a}$$

The triplet screening potentials

$$H^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=-w^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+\Gamma(r_{12}^{-1}+r_{13}^{-1}+r_{23}^{-1}) \tag{5b}$$

are finite for r_{32} and/or r_{13} and/or $r_{23}=0$.

A most important property of the Onsager molecules, as defined above, is their "dissociation" whenever any molecular point charge is of distance larger than $2a$ from all others; e.g.,

$$U_3\left[\left(\cdot 1\quad \overset{\cdot}{2}\quad 3\cdot\right);r_{13},r_{23}\geq 2a\right]=U_2\left[\left(\,\underset{1}{\cdot}\underset{r_{12}}{\text{———}}\underset{2}{\cdot}\,\right)\right]+U_1(\textcircled{\scriptsize 3\cdot})\ . \tag{6}$$

In order to calculate the self-energies for complex geometries we seek a simple and accurate approximation that has the dissociation property (6). It is given via the "convolution-ball smearing" by which every molecular point charge is uniformly smeared within a sphere of some radius d_i. The number of such independent parameters d_i depends on the symmetry of the molecule, e.g., we need only one parameter for a symmetric polytop. Note, however, that with this "ball smearing" the resulting Onsager lower bound for the energy approximates well the self-energy of the Onsager molecule, but it is not the self-energy of the resulting dumbbell configuration. This energy bound, denoted by u_d, is equal to the difference between the smeared-charge–uniform-background and the point-charge–uniform-background interactions, minus the self-energy of the smeared charges, plus the self-energy of the point charges (relative to the sum of all individual self-energies of the point charges in the "molcule"). For the "diatomic" two-charge molecule we obtain[18]

$$U_2\left[\left(\,\cdot\underset{r}{\text{———}}\cdot\,\right)\right]\cong-[2\tfrac{3}{10}d^2+2\tfrac{3}{5}d^{-1}+\Psi_d(r)]+\Gamma/r\equiv\beta u_d \tag{7}$$

subject to $\partial u_d/\partial d=0$ which gives $d(r)$. $\Psi_d(r)=d^{-1}\Psi_1(r/d)$ is the electrostatic interaction between two uniformly charged spheres of radius d, unit total charge, and separation r, given for $d=1$ by[10]

$$\Psi_1(r)=\begin{cases}\frac{6}{5}-\frac{1}{2}r^2+\frac{3}{16}r^3-\frac{1}{160}r^5, & r\leq 2\\ r^{-1}, & r\geq 2\end{cases}$$
$$=-\lim_{\Gamma\to\infty}c_{\mathrm{HNC}}(r)/\Gamma\ . \tag{8}$$

It is useful[10] to define the "Ewald function"

$$f(z)=[\Psi_1(2z)+2z\Psi_1'(2z)]/\Psi_1(0)\ ,$$

i.e., $f(z\geq 1)=0$, $f(z\leq 1)=1-5z^2+5z^3-z^5$. Using the optimized $d(r)$ from (7), and defining $z=r/2d$, we obtain the following parametric expression for the screening potential representing the HNC result for the free-energy difference:

$$\lim_{\substack{\Gamma\to\infty\\ \mathrm{HNC}\text{-}F^{\mathrm{ex}}}}H(r)/\Gamma\cong H_{d(r)}(z)/\Gamma=\tfrac{9}{5}\{[1+\tfrac{1}{3}f(z)+\tfrac{5}{9}\Psi_1(2z)]/[1+f(z)]^{1/3}-1\}\ , \tag{9a}$$

$$r=2z[1+f(z)]^{1/3}\ . \tag{9b}$$

Note that $d/a=[1+f(z)]^{1/3}$ ranges from 1 at $r\geq 2a$ (dissociation) to 2 at $r=0$. Without optimization, namely, using

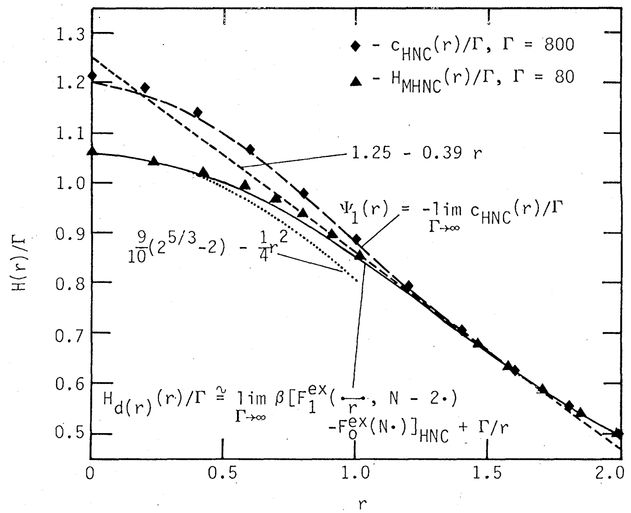

FIG. 1. Pair-screening potential $H(r)$ of the strongly coupled OCP. The line $1.25-0.39r$ fits well the simulation results in the range $0.5 < r < 1.8$ for all $\Gamma \gtrsim 5$ (Fig. 7 in Ref. 4). The symbols represent the HNC $\Gamma=800$ results (Ref. 20) for $c(r)/\Gamma$ and the $\Gamma=80$ results for $H(r)/\Gamma$ as obtained by the Modified-HNC (MHNC) equation (Ref. 5). The theoretical predictions $\Psi_1(r)$ and $H_{d(r)}(r)$ are described in the text.

$d(r)=1$, we obtain the HNC-closure (HNC-cl) result

$$H_{d=1}(r)/\Gamma = \Psi_1(r) = \lim_{\substack{\Gamma\to\infty \\ \text{HNC-cl}}} H(r)/\Gamma$$

$$= \lim_{\Gamma\to\infty} [h_{\mathrm{HNC}}(r) - c_{\mathrm{HNC}}(r)]/\Gamma \ . \qquad (10)$$

$H_{d(r)}(r)$ is in excellent agreement with both the simulations and modified-HNC calculations for the strongly coupled fluid OCP (see Fig. 1). Comparison of (9) and (10) with the modified-HNC results shows clearly that the bridge-diagram contributions (i.e., those missing in the HNC closure) are provided by the Onsager-molecule concept.

Note that $H_{d(r)}(r) = H_{d=1}(r) = \Gamma/r$ for $r \geq 2$ (the dissociation property), and that both functions are continuous with three continuous derivatives. That is why both functions are already nearly the same for $r \gtrsim 1$. This feature explains why the available simulation data, unguided by a suitable theory, led to different interpretations of the scaling properties of the screening potentials for multicomponent plasmas, and of their "linear" behavior for $0.5 < r < 1.5$.[19] Note also that for small r,

$$H_{d(r)}(r) = \Gamma \tfrac{9}{10}(2^{5/3}-2) - \frac{\Gamma}{4}r^2 + \cdots \ ,$$

in agreement with the well-known ion-sphere result, and Jancovici's[3] leading r^2 term, for small r. It should be emphasized that our method does not give any direct procedure for also obtaining $c(r)$ in close agreement with the modified-HNC results. Our short-range $H(r)$ should supplement the simulation results for $g(r)$, together providing the data to be fitted by an appropriate bridge function in the modified-HNC scheme. Within this context, our Fig. 1 just supplements the discussion in Ref. 5.

The dissociation property plays a key role for all values of Γ. The convolution-ball smearing that leads to (7) and (9), when incorporated into the Debye-Huckel (DH) or MSA free-energy functional, provides an effective interpolation between the weak- ($\Gamma \ll 1$) and strong- ($\Gamma \gg 1$) coupling regions which are well represented by the DH ($d_i \sim 0$) and Onsager ($d_i \sim 1$) lower bounds,[7,8] respectively. The OCP excess free energy is thus characterized by one smearing parameter $d_0(\Gamma)$, which varies from $d_0=1$ for $\Gamma \to \infty$ to $d=0$ for $\Gamma \to 0$, and represents the size of the effective hard-core radius. The molecular smearing radius $d_1(\Gamma, d_0(\Gamma))$ is obtained by optimizing the free-energy functional approximating F_1^{ex}. Careful analysis of the resulting expression for $H(r)$ reveals the following: For either $\Gamma \lesssim 1$ or $r \gtrsim 2d_0(\Gamma)$, the full HNC closure is obtained,

$$H(r)_{\mathrm{HNC}\text{-}F^{\mathrm{ex}}} \cong h_{\mathrm{HNC}}(r) - c_{\mathrm{HNC}}(r); \qquad (11)$$

$$\Gamma \lesssim 1 \text{ or } r \gtrsim 2d_0(\Gamma) \ .$$

Comparison with (8) and (10) shows that the $h(r)$ part in (11) is an entropic contribution for F_1^{ex} at large Γ. Indeed, numerical solutions[20] of the HNC equation for the OCP gives

$$h_{\mathrm{HNC}}(r) \propto S^{\mathrm{ex}}/Nk_B \propto \Gamma^{1/2} \ .$$

The same analysis leads to the following results for higher-order screening potentials:

$$H^{(m)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m; r_{ij} \gtrsim 2d_0(\Gamma) \text{ or } \Gamma \lesssim 1)_{\mathrm{HNC}\text{-}F^{\mathrm{ex}}}$$

$$\cong \sum_{\substack{j=1 \\ i>j}} [h_{\mathrm{HNC}}(r_{ij}) - c_{\mathrm{HNC}}(r_{ij})] \ . \qquad (12)$$

This is the Kirkwood superposition approximation[21] (KSA) combined with the HNC closure for the OCP. The short-range behavior of the bridge functions and the crossover to KSA-HNC are natural consequences of the Onsager molecules and their dissociation property.

Our results provide the rational for solving the Thomas-Fermi confined-molecule problem in order to calculate enhancement factors for nuclear reaction rates, and other short-range correlation effects in dense matter. Our method, concepts, and qualitative results are valid for a general D-dimensional multicomponent plasma, in which the charges may be associated with any Green's function potentials, the Coulomb and screened-Coulomb (Yukawa) potentials being the most important cases. Detailed analysis and calculations for multicomponent plasmas, along with a discussion of possible extensions of the method to other classical fluids, will be presented separately.

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[18] Direct application of Sec. IIIA in Ref. 8 above: Use Eq. (3.3) with (3.8) representing two-point charges of distance r apart, and (2.9) for the smearing function.

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