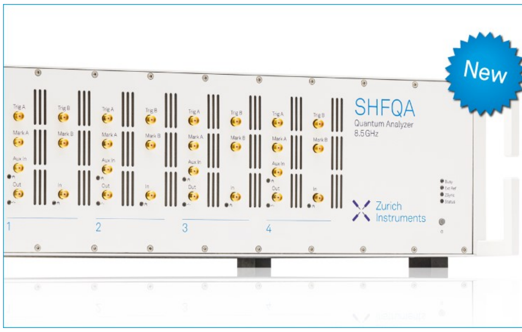
The Journal of Chemical Physics

Thermodynamics of strongly-coupled Yukawa systems near the one-component-plasma limit. I. Derivation of the excess energy

Cite as: J. Chem. Phys. **101**, 9876 (1994); https://doi.org/10.1063/1.467954
Submitted: 02 May 1994 . Accepted: 31 August 1994 . Published Online: 31 August 1998

S. Hamaguchi, and R. T. Farouki



Thermodynamics of strongly-coupled Yukawa systems near the one-component-plasma limit. I. Derivation of the excess energy

S. Hamaguchi and R. T. Farouki
IBM Thomas J. Watson Research Center, P. O. Box 218, Yorktown Heights, New York 10598

(Received 2 May 1994; accepted 31 August 1994)

The excess energy for a system of charged mesoscopic particles or "particulates" immersed in a neutralizing background medium is derived analytically, and is shown to approach that of the classical one-component plasma in the limit of high background temperatures. Examples of such systems, which are known as Yukawa systems due to the form of the interparticle pair potential, include dusty plasmas and colloidal suspensions. The expression for the excess energy allows thermodynamic properties of Yukawa systems to be determined from Monte Carlo or molecular-dynamics simulations. © *1994 American Institute of Physics.*

I. INTRODUCTION

Systems of charged "mesoscopic" particles (particles that are small on the macroscopic scale but significantly larger than molecular sizes) immersed in a smooth neutralizing medium are commonly observed in nature. One example of such systems is a suspension of dust grains in a plasma—charged "cosmic" or interstellar grains in space plasmas have long interested astrophysicists.[1–2] Recently, charged dust grains in process plasmas have been recognized as a major source of contamination in microelectronics fabrication systems.[3–7] Another example is the colloidal solution, which has been extensively studied on account of its wide-ranging technological uses.[8]

To investigate the behavior of such systems, we shall consider an idealized model comprising N identical point charges (representing the particulates) immersed in a "smooth" (i.e., statistically-averaged) neutralizing background medium. This background may be a mixture of different media, each assumed to be in thermal equilibrium at a given temperature.

The electric potential at position $\mathbf{r}$ in this system is given by the Yukawa (i.e., screened Coulomb) potential $\phi(\mathbf{r}) = -(Q/4\pi\varepsilon_0 r)\exp(-k_D r)$, where $r=|\mathbf{r}|$ and k_D^{-1} is the characteristic Debye length for the background medium, if a point charge $-Q$ is located at $\mathbf{r}=0$ and the effect of all other point charges is ignored. This represents a linearized solution (the Debye–Hückel approximation) of the Poisson–Boltzmann system. There have been several Monte Carlo (MC) and molecular-dynamics (MD) simulations of "Yukawa systems," i.e., systems of particles that interact through a pair potential given by the Yukawa form or some variant thereof (e.g., Refs. 9–13).

These earlier studies, however, do not take proper account of the energy due to the charged background medium in the analysis of simulation data. The contribution of the background to the total energy becomes particularly important when one evaluates thermodynamical quantities from MC or MD simulations in the case of weak screening. As will be explained in detail later, the total Yukawa-system potential energy diverges in the weak screening limit. To obtain physical quantities in such a case, one must therefore subtract the correct infinite energy due to the background charge from the total Yukawa potential energy.

In the companion paper,[14] we shall present MD simulations for Yukawa systems in the weak-screening regime. If the screening vanishes completely, the system is called the one-component plasma (OCP).[15–21] In the present paper, we derive an expression for the total excess energy of Yukawa systems that converges to that of the OCP system. This expression is used to calculate various thermodynamical quantities in the companion paper. In the derivation of the excess energy, we employ full periodic boundary conditions (which are also used in the MD simulations presented in the companion paper) and establish the correct relation between the Yukawa pair potential and the Ewald potential used for the OCP system.

In the dusty plasma system, the dust grains are negatively charged due to the high electron mobility, and surrounded by Debye sheaths of radius comparable to the Debye length k_D^{-1}. If the plasma consists of electrons and a single species of ions, the characteristic Debye length is related to the ion and electron Debye lengths λ_i and λ_e by $k_D^{-1} = (1/\lambda_i^2 + 1/\lambda_e^2)^{-1/2}$. In process plasmas, the electron temperature T_e is typically much higher than the ion temperature T_i, so that $\lambda_i \ll \lambda_e$ and $k_D \approx \lambda_i^{-1}$.

If the Yukawa particulate system is in thermodynamic equilibrium, it may be characterized in terms of two dimensionless parameters:[12,22] the ratio $\kappa = k_D a$ of the interparticulate distance $a = (3/4\pi n)^{1/3}$ (where n is the particulate density) to the screening length k_D^{-1}, and the normalized inverse temperature

$$\Gamma = \frac{Q^2}{4\pi\varepsilon_0 a k_B T}. \tag{1}$$

Γ represents the Coulomb energy of a pair of particulates measured in units $k_B T$, although the real pair potential energy is smaller by factor $\exp(-\kappa)$ due to the Debye shielding. [Note that in some earlier work, e.g., Refs. 12,13,22, the quantity

$$\Gamma^* = \frac{Q^2 \exp(-\kappa)}{4\pi\varepsilon_0 a k_B T}$$

is used instead of Eq. (1). In the companion paper, however,

Γ as defined by Eq. (1) is mainly used, since the particulate temperature—kinetic energy—and screening length are then conveniently represented by Γ^{-1} and κ^{-1}.]

For example, for ion density $n_i = 10^9\,\mathrm{cm}^{-3}$, temperature $T_i = 0.1\,\mathrm{eV}$ ($\ll T_e$), and charge $q = Z_i e = e$, and particulate density $n = 10^6\,\mathrm{cm}^{-3}$, temperature (i.e., kinetic energy) $T = 0.1\,\mathrm{eV}$, and charge $-Q = -Z_D e = -10^3 e$, we have $\kappa = 0.83$, $\Gamma = 232$, and $\Gamma^* = 101$. The system may be called "strongly coupled" since the ratio of the typical interparticle energy to the thermal energy ($\simeq \Gamma^*$) is sufficiently larger than 1. The free electron density is determined by charge neutrality: $n_e = Z_i n_i - Z_D n \approx 0$ in this case, i.e., all electrons are attached to dust grains. The example is typical of process plasmas, but κ and Γ may vary widely depending on the plasma state.

If the system is not in thermodynamic equilibrium, particulates may be subject to various forces, including drag forces[23] and polarization forces,[24,25] in addition to the interparticle forces. The collective behavior of such systems will be the subject of future studies.

II. DERIVATION OF THE FIELD POTENTIAL

We first derive the electrostatic potential generated by charged particulates and a neutralizing background medium confined to a cubical domain V of side length L ($V = L^3$). The potential satisfies periodic boundary conditions.

Consider a system of N identical, infinitesimally small dust grains of mass m and charge $-Q = -Z_D e$. The average density of dust grains is then given by $n = N/V$. The potential $\Psi(\mathbf{r})$ satisfies Poisson's equation

$$\Delta \Psi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\varepsilon_0}, \tag{2}$$

where the charge density $\rho(\mathbf{r})$ is given by

$$\rho(\mathbf{r}) = -Q \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) + q n_i(\mathbf{r}) - e n_e(\mathbf{r}) .$$

Here $q = Z_i e$ denotes the charge on each ion, and $n_i(\mathbf{r})$ and $n_e(\mathbf{r})$ are the ion and electron densities at position $\mathbf{r}$. The overall charge neutrality condition requires $\int_V \rho(\mathbf{r}) d\mathbf{r} = 0$. We shall assume ions of a single species; the extension to multiple species is straightforward.

Assuming that motion of charged particulates is sufficiently slow so that the background plasma may be considered in thermal equilibrium at each time instance, we may employ Boltzmann distributions for ions and electrons, i.e., $n_\alpha(\mathbf{r}) \propto \exp(-q_\alpha \beta_\alpha \Psi)$ for $\alpha = i,e$ where $q_i = q$, $q_e = -e$, and $\beta_\alpha = 1/k_B T_\alpha$.[26] The ion and electron temperatures, T_i and T_e, are assumed to be constant throughout V. Defining the mean ion and electron densities by

$$\bar{n}_\alpha = \frac{1}{V} \int_V n_\alpha(\mathbf{r})\, d\mathbf{r} \quad \text{for } \alpha = i,e ,$$

we have

$$n_\alpha(\mathbf{r}) = \frac{\bar{n}_\alpha \exp(-q_\alpha \beta_\alpha (\Psi(\mathbf{r}) - C))}{V^{-1} \int_V \exp(-q_\alpha \beta_\alpha (\Psi(\mathbf{r}) - C))\, d\mathbf{r}}, \tag{3}$$

where C is an arbitrary constant. If the constant C may be chosen in such a way that the conditions

$$|q_\alpha \beta_\alpha (\Psi(\mathbf{r}) - C)| \ll 1 \tag{4}$$

hold everywhere for $\alpha = i$ and e [i.e., the variation of $\Psi(\mathbf{r})$ over V is much smaller than the thermal energy $k_B T_\alpha$], Eq. (3) may be linearized to obtain

$$n_\alpha(\mathbf{r}) = q_\alpha \bar{n}_\alpha [1 - q_\alpha \beta_\alpha \varphi(\mathbf{r})] , \tag{5}$$

where

$$\varphi(\mathbf{r}) = \Psi(\mathbf{r}) - \bar{\Psi} \tag{6}$$

and

$$\bar{\Psi} = \frac{1}{V} \int_V \Psi(\mathbf{r})\, d\mathbf{r} .$$

Using Eq. (5), we rewrite the charge density as

$$\rho(\mathbf{r}) = -Q \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) + Qn - \varepsilon_0 k_D^2 \varphi(\mathbf{r}). \tag{7}$$

Here $k_D^2 = \Sigma_\alpha q_\alpha^2 \bar{n}_\alpha \beta_\alpha / \varepsilon_0 = 1/\lambda_i^2 + 1/\lambda_e^2$ (where λ_i and λ_e are the ion and electron Debye lengths) and we have used the condition of overall charge neutrality,

$$Qn = q\bar{n}_i - e\bar{n}_e .$$

The first term of Eq. (7)

$$\rho_D = -Q \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) \tag{8}$$

obviously represents the particulate charge density. The second term

$$\rho_0^{\mathrm{bg}} = Qn \tag{9}$$

represents the constant background charges that neutralize the particulate charges, and the third term

$$\delta\rho^{\mathrm{bg}} = -\varepsilon_0 k_D^2 \varphi(\mathbf{r}) \tag{10}$$

represents the background plasma density perturbation due to the electrostatic perturbation. Note that the space average of $\delta\rho^{\mathrm{bg}}$ vanishes; there is no net charge contribution from Eq. (10). Note also that the charge perturbation $\delta\rho^{\mathrm{bg}}$ vanishes in the high plasma temperature limit (i.e., $T_i, T_e \to \infty$ and therefore $k_D \to 0$) since the background plasma becomes so mobile in this limit that it can maintain a uniform density. As mentioned in the previous section, this is the OCP limit.

Under the linear response conditions (5), Eq. (2) may be rewritten as

$$(\Delta - k_D^2)\, \varphi(\mathbf{r}) = \frac{Q}{\varepsilon_0} \sum_{j=1}^{N} \left[\delta(\mathbf{r} - \mathbf{r}_j) - \frac{1}{V} \right]. \tag{11}$$

Periodic boundary conditions for a cube of side length L ($V = L^3$) require

$$\varphi(\mathbf{r} + \mathbf{n}L) = \varphi(\mathbf{r}) , \tag{12}$$

where $\mathbf{n} = (\ell, m, n)$ denotes an integer triplet. This periodic boundary condition may be used in MC or MD simulations to emulate an infinite system.

The Green's function $G(\mathbf{r},\mathbf{r}')$ for the operator $\Delta - k_D^2$ defined on the unit cell $D=\{(x,y,z) \mid 0 \leq x,y,z \leq L\}$ with periodic boundary conditions is given by

$$G(\mathbf{r},\mathbf{r}')=\frac{1}{4\pi}\sum_{\mathbf{n}}\frac{\exp(-k_D|\mathbf{r}-\mathbf{r}'-\mathbf{n}L|)}{|\mathbf{r}-\mathbf{r}'-\mathbf{n}L|} \quad (\mathbf{r},\mathbf{r}' \in D),$$

where $\Sigma_{\mathbf{n}}$ denotes the sum over all integer triplets $\mathbf{n}$. Using this Green's function, one may express the solution to Eq. (11) as

$$\varphi(\mathbf{r})=\frac{-Q}{4\pi\varepsilon_0}\sum_{j=1}^{N}\int_D\sum_{\mathbf{n}}\frac{\exp(-k_D|\mathbf{r}-\mathbf{r}'-\mathbf{n}L|)}{|\mathbf{r}-\mathbf{r}'-\mathbf{n}L|}\times\left[\delta(\mathbf{r}'-\mathbf{r}_j)-\frac{1}{L^3}\right]d\mathbf{r}'$$

$$=\frac{-Q}{4\pi\varepsilon_0}\sum_{j=1}^{N}\sum_{\mathbf{n}}\int_{D_{\mathbf{n}}}\frac{\exp(-k_D|\mathbf{r}-\boldsymbol{\rho}|)}{|\mathbf{r}-\boldsymbol{\rho}|}\times\left[\delta(\boldsymbol{\rho}-\mathbf{r}_j-\mathbf{n}L)-\frac{1}{L^3}\right]d\boldsymbol{\rho}, \tag{13}$$

where $\boldsymbol{\rho}=\mathbf{r}'+\mathbf{n}L$ and $D_{\mathbf{n}}=D+\mathbf{n}L=\{(x+\ell L,y+mL,z+nL) \mid (x,y,z) \in D\}$. Note that, for a given $\mathbf{n}$ and $\boldsymbol{\rho} \in D_{\mathbf{n}}$, the equation $\delta(\boldsymbol{\rho}-\mathbf{r}_j-\mathbf{n}'L)=0$ holds for all $\mathbf{n}' \neq \mathbf{n}$ since $\mathbf{r}_j \in D$. Thus we have

$$\delta(\mathbf{r}'-\mathbf{r}_j)=\delta(\boldsymbol{\rho}-\mathbf{r}_j-\mathbf{n}L)=\sum_{\mathbf{n}'}\delta(\boldsymbol{\rho}-\mathbf{r}_j-\mathbf{n}'L).$$

Using this relation and the fact that $\Sigma_{\mathbf{n}}\int_{D_{\mathbf{n}}}=\int_{V_\infty}$ with V_∞ being the entire space $\mathbf{R}^3$, we obtain from Eq. (13)

$$\varphi(\mathbf{r})=\frac{-Q}{4\pi\varepsilon_0}\int_{V_\infty}\frac{\exp(-k_D|\mathbf{r}-\boldsymbol{\rho}|)}{|\mathbf{r}-\boldsymbol{\rho}|}\sum_{j=1}^{N}\left[\sum_{\mathbf{n}}\delta(\boldsymbol{\rho}-(\mathbf{r}_j+\mathbf{n}L))-\frac{1}{L^3}\right]d\boldsymbol{\rho}$$

$$=-\frac{Q}{4\pi\varepsilon_0}\sum_{j=1}^{N}\sum_{\mathbf{n}}\frac{\exp(-k_D|\mathbf{r}-\mathbf{r}_j-\mathbf{n}L|)}{|\mathbf{r}-\mathbf{r}_j-\mathbf{n}L|}+\frac{Qn}{\varepsilon_0 k_D^2}. \tag{14}$$

From the above it is easy to verify that $\int_D\varphi(\mathbf{r})\,d\mathbf{r}=0$. From Eq. (6), we obtain

$$\Psi(\mathbf{r})=-\frac{Q}{4\pi\varepsilon_0}\sum_{j=1}^{N}\sum_{\mathbf{n}}\frac{\exp(-k_D|\mathbf{r}-\mathbf{r}_j-\mathbf{n}L|)}{|\mathbf{r}-\mathbf{r}_j-\mathbf{n}L|}, \tag{15}$$

and

$$\bar{\Psi}=-\frac{Qn}{\varepsilon_0 k_D^2}.$$

As might be expected, the potential $\Psi(\mathbf{r})$ given above comprises Yukawa potentials $\phi(|\mathbf{r}|)$ for all the particulates (at $\mathbf{r}_j$) in D and all their images (at $\mathbf{r}_j+\mathbf{n}L$) under periodic boundary conditions.

III. HAMILTONIAN FOR YUKAWA SYSTEMS

As shown in Appendix A, the Hamiltonian for the system of N particulates is given by

$$H=\sum_{j=1}^{N}\frac{|\mathbf{p}_j^2|}{2m}+U_{\text{ex}}, \tag{16}$$

where $\mathbf{p}_j$ is the momentum of the jth particulate and U_{ex} is the Helmholtz free energy of the particulates and background plasma. The term U_{ex} is also called the "excess energy" since it represents the energy in excess of the thermal (kinetic) energy of the particulates.

The excess energy has the form

$$U_{\text{ex}}=F_{\text{id}}^{\text{bg}}+F_{\text{int}}^{\text{bg}}, \tag{17}$$

where

$$F_{\text{id}}^{\text{bg}}=\sum_{\alpha=i,e}k_BT_\alpha\int_V n_\alpha(\mathbf{r})[\ln n_\alpha(\mathbf{r})\Lambda_{T\alpha}^3-1]\,d\mathbf{r} \tag{18}$$

denotes the ideal gas contribution to the background free energy and

$$F_{\text{int}}^{\text{bg}}=\frac{1}{2}\int_V\rho(\mathbf{r})\Psi(\mathbf{r})\,d\mathbf{r}-\frac{Q^2}{8\pi\varepsilon_0}\sum_{j=1}^{N}\int_V\frac{\delta(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|}d\mathbf{r} \tag{19}$$

represents the electrostatic potential energy of all the charged species. In Eq. (18), $\Lambda_{T\alpha}=(h^2/2\pi m_\alpha k_BT_\alpha)^{1/2}$ denotes the thermal de Broglie wavelength. The second term in Eq. (19) serves to subtract the infinite self-energy of each dust grain, which is formally included in the first term.

Substituting the linear response relation (5) into (18) and taking the terms up to the second order in $q_\alpha\beta\varphi(\mathbf{r})$, we obtain

$$F_{\text{id}}^{\text{bg}}=F_{\text{unif}}^{\text{bg}}+\frac{1}{2}\varepsilon_0k_D^2\int_{V_\infty}\varphi^2(\mathbf{r})\,d\mathbf{r}, \tag{20}$$

where

$$F_{\text{unif}}^{\text{bg}}=V\sum_\alpha k_BT_\alpha\bar{n}_\alpha(\ln\bar{n}_\alpha\Lambda_{T\alpha}^3-1) \tag{21}$$

is the free energy of the uniform (i.e., unperturbed) background plasma. Since $F_{\text{unif}}^{\text{bg}}$ only provides obvious thermodynamical information on the unperturbed (ideal gas) background plasma, we shall drop this term from the U_{ex} expression in the following argument for simplicity.

If the linear response relation (5) holds, we may write Eq. (20) (after ignoring the term $F_{\text{unif}}^{\text{bg}}$) as

$$F_{\text{id}}^{\text{bg}}=-\frac{1}{2}\int_V\delta\rho^{\text{bg}}(\mathbf{r})\Psi(\mathbf{r})\,d\mathbf{r}. \tag{22}$$

Clearly this free energy is equal in size but opposite in sign to the potential energy of background plasma perturbations. Note that $F_{\text{id}}^{\text{bg}}$ vanishes as $k_D\rightarrow 0$, i.e., in the OCP limit (see Appendix B).

Substituing Eqs. (8)–(10) into Eqs. (19) and (22), we obtain the excess energy of the Yukawa system as

$$U_{\rm ex}=-\frac{Q}{2}\int_V\sum_{j=1}^{N}\left[\delta(\mathbf{r}-\mathbf{r}_j)-\frac{1}{V}\right]\Psi(\mathbf{r})\,d\mathbf{r}$$
$$-\frac{Q^2}{8\pi\varepsilon_0}\sum_{j=1}^{N}\int_V\frac{\delta(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|}d\mathbf{r}. \tag{23}$$

From Eq. (15), it is straightforward to confirm that Eq. (23) may be written as

$$U_{\rm ex}=\frac{1}{2}\sum\sum_{i\neq j}\psi(\mathbf{r}_i-\mathbf{r}_j)+U_0, \tag{24}$$

with the pair potential

$$\psi(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\int_{V_\infty}\left[\sum_{\mathbf{n}}\delta(\boldsymbol{\rho}-\mathbf{n}L)-\frac{1}{L^3}\right]$$
$$\times\frac{\exp(-k_D|\boldsymbol{\rho}-\mathbf{R}|)}{|\boldsymbol{\rho}-\mathbf{R}|}d\boldsymbol{\rho}, \tag{25}$$

and the constant

$$U_0=\frac{1}{2}N\lim_{|\mathbf{R}|\to 0}\left(\psi(\mathbf{R})-\frac{Q^2}{4\pi\varepsilon_0|\mathbf{R}|}\right). \tag{26}$$

Carrying out the integration in Eq. (25), we obtain

$$\psi(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\sum_{\mathbf{n}}\frac{\exp(-k_D|\mathbf{R}-\mathbf{n}L|)}{|\mathbf{R}-\mathbf{n}L|}-\frac{Q^2}{\varepsilon_0k_D^2L^3} \tag{27}$$

and the energy constant

$$U_0=-\frac{Q^2n}{2\varepsilon_0k_D^2}-\frac{NQ^2k_D}{8\pi\varepsilon_0}+\frac{Q^2N}{8\pi\varepsilon_0}\sum_{\mathbf{n}\neq\mathbf{0}}\frac{\exp(-k_DL|\mathbf{n}|)}{|\mathbf{n}|L}. \tag{28}$$

It is easy to confirm that $\psi(\mathbf{R})=\psi(-\mathbf{R})$.

From Eqs. (24), (27), and (28), it is sometimes more convenient to express the excess energy in terms of the periodic Yukawa pair potential

$$\Phi(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\sum_{\mathbf{n}}\frac{\exp(-k_D|\mathbf{R}-\mathbf{n}L|)}{|\mathbf{R}-\mathbf{n}L|}$$

as

$$U_{\rm ex}=\frac{1}{2}\sum\sum_{i\neq j}\Phi(\mathbf{r}_i-\mathbf{r}_j)-\frac{NQ^2n}{2\varepsilon_0k_D^2}$$
$$-\frac{NQ^2k_D}{8\pi\varepsilon_0}+\frac{Q^2N}{8\pi\varepsilon_0}\sum_{\mathbf{n}\neq\mathbf{0}}\frac{\exp(-k_DL|\mathbf{n}|)}{|\mathbf{n}|L}. \tag{29}$$

In Eq. (29), the second term on the right-hand side represents the free energy (excluding the uniform ideal-gas free energy) of the background plasma that, on average, neutralizes the charge of the particulates. The third term represents the free energy of each sheath [see Eq. (17) of Ref. 24], and the fourth term represents the energy of interaction of every particulate and its own images under periodic boundary conditions.

The equation of motion of each particulate may be obtained directly from the Hamiltonian, i.e., Eqs. (16) and (29), as

$$\frac{d\mathbf{p}_i}{dt}=-\sum_{j(\neq i)=1}^{N}\frac{\partial}{\partial\mathbf{r}_i}\Phi(\mathbf{r}_i-\mathbf{r}_j).$$

This is the equation for the ith particulate that will be used in the MD simulations described in the companion paper.[14] Note that particulates interact with each other through the Yukawa potential.

The Yukawa pair potential may also be derived from the density functional approach[27] under the conditions that we have stated above; e.g., sufficiently high background-plasma temperatures Eq. (4), which allows the linearization of the density perturbation Eq. (5)—this is often referred to as small "inhomogeneity"—and weak coupling of the background-plasma, which allows us to neglect the correlation term discussed in Appendix A. Under more general conditions, of course, the true interparticle potential deviates from the Yukawa potential. To study such a general system, one may use *ab initio* numerical simulations.[28]

IV. CLASSICAL OCP LIMIT

If the background screening is sufficiently weak ($\kappa=k_Da\ll 1$), one expects the densities of the background species, $n_i(\mathbf{r})$ and $n_e(\mathbf{r})$, to become almost uniform due to the rapid thermal motions of these species, and thus the system will approach the classical one-component plasma. However, this is not immediately apparent from the pair potential expressions given in Eq. (27) since both the first and second terms diverge as $k_D\to 0$. We now show that the form (27) of the pair potential appropriate to periodic boundary conditions does in fact reduce to the standard Ewald potential [15,16,29,30] for the classical OCP in the limit $\kappa\to 0$.

The classical OCP consists of ions (which correspond to our dust grains) of charge Q and a uniform electron background giving overall charge neutrality. The ions interact with each other through the Coulomb potential, and thus the pair potential for the OCP is given by

$$\psi^{\rm OCP}(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\int_{V_\infty}\left[\sum_{\mathbf{n}}\delta(\boldsymbol{\rho}-\mathbf{n}L)-\frac{1}{L^3}\right]\frac{1}{|\boldsymbol{\rho}-\mathbf{R}|}d\boldsymbol{\rho}. \tag{30}$$

The second term in the square bracket is proportional to the charge due to the uniform background. The infinite lattice sum in this expression is only conditionally convergent, and the physically-meaningful convergent sum is given by the Ewald potential:

$$\psi^{\rm OCP}(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\left[\frac{\mathrm{erfc}(\sqrt{\pi}|\mathbf{R}|/L)}{|\mathbf{R}|}-\frac{1}{L}\right]$$
$$+\frac{Q^2}{4\pi\varepsilon_0}\sum_{\mathbf{n}\neq\mathbf{0}}\left[\frac{\mathrm{erfc}(\sqrt{\pi}|\mathbf{R}+\mathbf{n}L|/L)}{|\mathbf{R}+\mathbf{n}L|}\right.$$
$$\left.+\frac{\exp(-\pi|\mathbf{n}|^2)\cos(2\pi\mathbf{n}\cdot\mathbf{R}/L)}{\pi|\mathbf{n}|^2L}\right], \tag{31}$$

where erfc($\cdot$) is the complementary error function. The excess energy is then given by:[15,16]

$$U_{ex}^{OCP}=\frac{1}{2}\sum\sum_{i\neq j}\psi^{OCP}(\mathbf{r}_i-\mathbf{r}_j)+U_0^{OCP},$$

where, as in Eq. (26),

$$U_0^{OCP}=\frac{1}{2}N\lim_{|\mathbf{R}|\to 0}\left(\psi^{OCP}(\mathbf{R})-\frac{Q^2}{4\pi\varepsilon_0|\mathbf{R}|}\right) \quad (32)$$

$$\approx -1.4186487\frac{Q^2N}{4\pi\varepsilon_0 L}. \quad (33)$$

The pair potential for the Yukawa system is given by Eq. (25), or equivalently Eq. (27). It is evident from Eq. (25) and Eq. (30) that $\psi(\mathbf{R})\to\psi^{OCP}(\mathbf{R})$ as $k_D\to 0$. However, it is not clear how each term of the Ewald potential (31) corresponds to the terms of the Yukawa pair potential. To establish this correspondence, we now derive an alternative expression for the Yukawa pair potential $\psi(\mathbf{r})$.

Let us split $\psi(\mathbf{R})$ in Eq. (25) into the following two parts:

$$\psi(\mathbf{R})=\psi_1(\mathbf{R})+\psi_2(\mathbf{R}),$$

where

$$\psi_1(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\int_{V_\infty} w(\boldsymbol{\rho})\,\eta(|\boldsymbol{\rho}-\mathbf{R}|)\frac{\exp(-k_D|\boldsymbol{\rho}-\mathbf{R}|)}{|\boldsymbol{\rho}-\mathbf{R}|}d\boldsymbol{\rho}, \quad (34)$$

$$\psi_2(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\int_{V_\infty} w(\boldsymbol{\rho})[1-\eta(|\rho-\mathbf{R}|)]\times\frac{\exp(-k_D|\boldsymbol{\rho}-\mathbf{R}|)}{|\boldsymbol{\rho}-\mathbf{R}|}d\boldsymbol{\rho}. \quad (35)$$

In these expressions we have introduced the functions

$$w(\boldsymbol{\rho})=\sum_{\mathbf{n}}\delta(\boldsymbol{\rho}-\mathbf{n}L)-\frac{1}{L^3},$$

$$\eta(x)=A\int_x^\infty \exp(k_Dt-\gamma^2t^2)\,dt=B\,\mathrm{erfc}\left(\gamma x-\frac{k_D}{2\gamma}\right),$$

where

$$A=\frac{2\gamma B}{\sqrt{\pi}}\exp\left(-\frac{k_D^2}{4\gamma^2}\right) \quad \text{and} \quad B=\frac{1}{1+\mathrm{erf}(k_D/2\gamma)}.$$

Here γ is a positive constant (which will be set to be $\sqrt{\pi}/L$ later) and $\mathrm{erf}(\cdot)$ is the error function: $\mathrm{erf}(x)\equiv 1-\mathrm{erfc}(x)$. Note that

$$\eta(0)=A\int_0^\infty \exp(k_Dt-\gamma^2t^2)\,dt=1,$$

$$1-\eta(x)=A\int_0^x \exp(k_Dt-\gamma^2t^2)\,dt,$$

and

$$\lim_{k_D\to 0}\eta(x)=\mathrm{erfc}(\gamma x).$$

Evaluating the integral in Eq. (34) yields

$$\psi_1(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\left\{\frac{\eta(|\mathbf{R}|)}{|\mathbf{R}|}\exp(-k_D|\mathbf{R}|)-\frac{4\pi}{k_D^2L^3}\left[1-\frac{\exp(-k_D^2/4\gamma^2)}{1+\mathrm{erf}(k_D/2\gamma)}\left(1+\frac{k_D}{\sqrt{\pi}\gamma}\right)\right]\right\}+\frac{Q^2}{4\pi\varepsilon_0}\sum_{\mathbf{n}\neq\mathbf{0}}\frac{\eta(|\mathbf{R}-\mathbf{n}L|)}{|\mathbf{R}-\mathbf{n}L|}\exp(-k_D|\mathbf{R}-\mathbf{n}L|). \quad (36)$$

By setting $\gamma=\sqrt{\pi}/L$, one can readily confirm that the first term (i.e., all the terms in the brackets) of Eq. (36) corresponds to the first term of the Ewald potential (31) in the $k_D\to 0$ limit, and the second term corresponds to the first term in the second square bracket of Eq. (31):

$$\lim_{k_D\to 0}\psi_1(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\left[\frac{\mathrm{erfc}(\sqrt{\pi}|\mathbf{R}|/L)}{|\mathbf{R}|}-\frac{1}{L}\right]+\frac{Q^2}{4\pi\varepsilon_0}\sum_{\mathbf{n}\neq\mathbf{0}}\frac{\mathrm{erfc}(\sqrt{\pi}|\mathbf{R}+\mathbf{n}L|/L)}{|\mathbf{R}+\mathbf{n}L|}.$$

To evaluate $\psi_2(\mathbf{R})$ in Eq. (35) we use Parseval's identity. The Fourier transform of $w(\mathbf{R})$ is

$$\tilde{w}(\mathbf{k})=\sum_{\mathbf{n}}\exp(2\pi iL\mathbf{r}\cdot\mathbf{n})-\frac{1}{L^3}\delta(\mathbf{k}).$$

Since the Poisson sum formula yields

$$\sum_{\mathbf{n}}\exp(2\pi iL\mathbf{r}\cdot\mathbf{n})=\frac{1}{L^3}\sum_{\mathbf{n}}\delta\left(\mathbf{k}-\frac{\mathbf{n}}{L}\right),$$

we obtain

$$\tilde{w}_1(\mathbf{k})=\frac{1}{L^3}\sum_{\mathbf{n}\neq\mathbf{0}}\delta\left(\mathbf{k}-\frac{\mathbf{n}}{L}\right). \quad (37)$$

On the other hand, the Fourier transform of the term

$$[1-\eta(|\boldsymbol{\rho}-\mathbf{R}|)]\frac{\exp(-k_D|\boldsymbol{\rho}-\mathbf{R}|)}{|\boldsymbol{\rho}-\mathbf{R}|}$$

may be calculated by means of integration by parts:

$$F(\mathbf{k})=\frac{2A}{k}\exp(2\pi i\mathbf{k}\cdot\mathbf{R})\int_0^\infty dx\,\sin(2\pi kx)\times\exp(-k_Dx)\int_0^x dt\,\exp(k_Dt-\gamma^2t^2)$$

$$=\frac{2A}{k}\frac{\exp(2\pi i\mathbf{k}\cdot\mathbf{R})}{k_D^2+4\pi^2k^2}\int_0^\infty dx\,(k_D\sin 2\pi kx+2\pi k\cos 2\pi kx)\exp(-\gamma^2x^2)$$

$$=\frac{2A}{k}\frac{\exp(2\pi i\mathbf{k}\cdot\mathbf{R})}{k_D^2+4\pi k^2}\frac{\exp(-\pi^2k^2/\gamma^2)}{\gamma}\times\left[\pi\sqrt{\pi}k+k_D\int_0^{\pi k/\gamma}dt\,\exp(t^2)\right],$$

where $k=|\mathbf{k}|$. Therefore, from Parseval's identity, we obtain

$$\psi_2(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\frac{1}{L^3}\sum_{\mathbf{n}\neq\mathbf{0}}\delta\left(\mathbf{k}-\frac{\mathbf{n}}{L}\right)F(\mathbf{k})$$

$$=\frac{Q^2}{4\pi\varepsilon_0}\frac{2A}{\gamma L}\sum_{\mathbf{n}\neq\mathbf{0}}\exp\left(\frac{2\pi i\mathbf{n}\cdot\mathbf{R}}{L}\right)\exp\left(-\frac{\pi^2|\mathbf{n}|^2}{\gamma^2L^2}\right)$$

$$\times\left[\frac{\pi\sqrt{\pi}}{k_D^2L^2+4\pi^2|\mathbf{n}|^2}+\frac{k_DL}{(k_D^2{}^2+4\pi^2|\mathbf{n}|^2)|\mathbf{n}|}\int_0^{\pi|\mathbf{n}|/\gamma L}dt\,\exp(t^2)\right]. \quad (38)$$

Noting the asymptotic expansion

$$\exp(-x^2)\int_0^x\exp(t^2)dt \overset{\text{asymp}}{=} \sum_{m=0}^{\infty}\frac{(2m-1)!!}{2^{m+1}x^{2m+1}} \text{ as } x\to\infty$$

$$=\frac{1}{2x}+\frac{1}{4x^3}+\cdots$$

one can see that the infinite sum over $\mathbf{n}\neq\mathbf{0}$ of the second term in the square brackets of Eq. (38) converges algebraically. Therefore, with $\gamma=\sqrt{\pi}/L$, the potential $\psi_2(\mathbf{R})$ corresponds to the second term in the second square bracket of the Ewald potential (31), i.e,

$$\lim_{k_D\to0}\psi_2(\mathbf{R})=\frac{Q^2}{4\pi\varepsilon_0}\sum_{\mathbf{n}\neq\mathbf{0}}\frac{\exp(2\pi i\mathbf{n}\cdot\mathbf{R}/L)\exp(-\pi|\mathbf{n}|^2)}{\pi|\mathbf{n}|^2L}. \quad (39)$$

Note that the functions $\exp(2\pi i\mathbf{n}\cdot\mathbf{R}/L)$ in Eqs. (38) and (39) may be replaced by their real parts $\cos(2\pi\mathbf{n}\cdot\mathbf{R}/L)$, since the imaginary parts cancel when the summations are taken over $\mathbf{n}$.

It is evident that $U_0\to U_0^{\mathrm{OCP}}$ since Eqs. (26) and (32) hold and $\psi(\mathbf{R})\to\psi^{\mathrm{OCP}}(\mathbf{R})$. Although both the first and third terms of Eq. (28) diverge as $k_D\to0$, the difference of these terms converges to the constant given by Eq. (33).

V. CONCLUDING REMARKS

We have derived the excess energy U_{ex} [i.e., Eq. (29)] of the Yukawa system under periodic boundary conditions, taking into account the energy contributions from the background charges. It was also demonstrated that U_{ex} converges to the excess energy $U_{\mathrm{ex}}^{\mathrm{OCP}}$ of the OCP system in the weak screening limit (i.e., $\kappa=k_Da\to0$). The derived excess energy serves as a basis for calculating various thermodynamical quantities from simulation data, especially near the OCP limit, as demonstrated in the companion paper.[14] [Note that the obvious contributions from the unperturbed ideal-gas background to the excess energy, which is given by Eq. (21), is not included in U_{ex} of Eq. (29) for simplicity.]

It is interesting to note that the excess energy U_{ex} is the Helmholtz free energy of the system, rather than the internal energy $\langle H_{\mathrm{micro}}\rangle$, as shown in Appendix A. This is of course due to the fact that the background species are continuously exchanging energy with a heat bath so as to maintain constant temperature during the particulate motion. Historically, there was some confusion in this respect: at an early stage of the development of lyophobic colloid theory, erroneous pair potentials were derived from the total potential energy. The errors were later corrected when the use of Helmholtz free energy was suggested by Derjaguin[31] and Verwey and Overbeek.[32,33]

The pair potentials that may be derived from the total potential energy $\langle H_{\mathrm{micro}}\rangle$ exhibits an attractive potential superimposed on the Yukawa repulsive potential [see Eq. (B7) in Appendix B]. This fallacious attractive potential was once used to account for the experimentally observed attraction between colloid particles, which is now essentially explained by the van der Waals interactions. The attractive potential reflects the electrostatic potential between the space charge in the Debye sheath of one particulate and the opposite charge on another particulate.

This potential would incur an attractive force between particulates if the space charges were "attached" to the particulate and thus the particulate and its Debye sheath formed an inseparable single system. In reality, however, the sheath space charge is merely a perturbation of the background plasma induced by the charge on the particulate. If the particulate moves from position A to position B, the plasma will relax to the unperturbed state around A and a new perturbation will be formed around B. The Debye sheaths are thus not "attached" to the particulates at all.

The true behavior of the background charges is indeed thermodynamically expressed by the second term of Eq. (A4), i.e., the heat gain by the system from the heat bath. The ideal-gas contribution to the Helmholtz free energy $F_{\mathrm{id}}^{\mathrm{bg}}$ of Eq. (22)—which is essentially the heat term of Eq. (A4)—exactly cancels the attractive potential energy included in $\langle H_{\mathrm{micro}}\rangle$. The resulting true pair potential then becomes the Yukawa potential.

In the OCP limit, the ideal-gas Helmholtz free energy $F_{\mathrm{id}}^{\mathrm{bg}}$ vanishes, as demonstrated in Appendix B. Consequently, for the OCP system, the excess energy $U_{\mathrm{ex}}^{\mathrm{OCP}}$ indeed agrees with its total potential energy. Therefore, in most studies of the OCP system, the excess energy $U_{\mathrm{ex}}^{\mathrm{OCP}}$ is simply derived from the total potential energy (e.g., Ref. 15) although its physical meaning should be the Helmholtz free energy, as has been discussed in this paper.

ACKNOWLEDGMENTS

The authors wish to thank H. E. DeWitt, E. E. Salpeter, and Y. Rosenfeld for helpful discussions.

APPENDIX A: INTERMEDIATE-SCALE HAMILTONIAN

In this Appendix, we show under what conditions the Hamiltonian (16) adequately describes the motion of charged mesoscopic particles immersed in a charge-neutralizing background. In such systems there are three distinct length scales: the microscopic scale, in which particulates and background charges are all regarded as individual particles; the intermediate scale, in which the particulates act as individual particles whereas the background species are statistically averaged and treated as a smooth field; and the macroscopic scale, in which all particles—the particulates and background species—may be statistically averaged.

The Hamiltonian relevant to the intermediate length scale may therefore be obtained from a statistical average over a more detailed microscopic Hamiltonian. In the averaging process, however, we assume that the background species are in contact with a large heat bath, so that the background temperatures (T_i and T_e in the plasma-dust system) remain uniform in space and constant in time. The microscopic Hamiltonian—i.e., the sum of the total kinetic energy and electrostatic potential energy for all the particles—is therefore not a constant of motion on the microscopic scale. The heat exchanged by the system and the heat bath during the particulate motion must be taken into account in the averaging process.

On the intermediate scale, therefore, the work done by the system to displace particulates through the electrostatic interactions is given by the change of its Helmholtz free energy F, rather than its electrostatic potential energy. If the motions of heavy particulates and light background charges may be separated (i.e., the adiabatic approximation), then the change of the free energy is all used for the change of particulates' kinetic energies. Therefore the intermediate-scale Hamiltonian H for particulates may be written as the sum of the particulate kinetic energy and the Helmholtz free energy F, as Eq. (16), where $U_{\rm ex}=F$. The Hamiltonian H *is* a constant of motion if the background temperatures, particle numbers, and volume are held constant.

As in Sec. II, we again consider a system of N identical negatively-charged dust grains of charge $-Q$ and mass m, and a neutralizing background of N_b charged particles. The background is assumed to consist of N_i ions of a single species with charge q and mass m_i, and N_e electrons with charge $-e$ and mass m_e ($N_i+N_e=N_b$), which are confined in volume V. The extension to systems with multiple ion species is straightforward.

On the microscopic scale, the state of the jth particulate may be represented by a point $(\mathbf{p}_j,\mathbf{r}_j)$ $(1\leq j\leq N)$ in phase space, where $\mathbf{p}_j$ and $\mathbf{r}_j$ denote its momentum and position. Likewise, the microscopic state of the jth background particle of species $\alpha(\alpha=i$ and e for ions and electrons), whose mass and charge are m_α and $q_\alpha(q_i=q$ and $q_e=-e)$ is defined by the phase-space point $(\mathbf{p}_j^{(\alpha)},\mathbf{r}_j^{(\alpha)})$ $(1\leq j\leq N_\alpha)$.

The N_α-particle joint-probability distribution function of the background species α may be written as

$$f_\alpha^{(N_\alpha)}(\mathbf{p}_\alpha^{N_b},\mathbf{r}_\alpha^{N_b};\mathbf{r}^N), \tag{A1}$$

where $\mathbf{p}_\alpha^{N_\alpha}$ and $\mathbf{r}_\alpha^{N_\alpha}$ denote the sets of momenta and positions of all background particles, i.e., $\mathbf{p}_\alpha^{N_\alpha}=(\mathbf{p}_1^{(\alpha)},\mathbf{p}_2^{(\alpha)},\ldots,\mathbf{p}_{N_b}^{(\alpha)})$, etc. In writing Eq. (A1), we have assumed that motions of dust grains are sufficiently slow compared to the motion of background species, and therefore the probability function $f_\alpha^{(N_\alpha)}$ explicitly depends on the instantaneous dust-grain positions $\mathbf{r}^N$, but not their momenta $\mathbf{p}^N$. Note that the N_b-particle joint-probability distribution function for all the background particles $f^{(N_b)}(\mathbf{X}_i^{N_i},\mathbf{X}_e^{N_e};\mathbf{r}^N)$ is related to $f_\alpha^{(N_\alpha)}$ as, e.g.,

$$f_i^{(N_i)}(\mathbf{X}_i^{N_i};\mathbf{r}^N)=\int\cdots\int f^{(N_b)}(\mathbf{X}_i^{N_i},\mathbf{X}_e^{N_e};\mathbf{r}^N)d\mathbf{X}_e^{N_e},$$

where we have used the abbreviated notations $\mathbf{X}^N=(\mathbf{p}^N,\mathbf{r}^N)$ and $\mathbf{X}_\alpha^{(N_\alpha)}=(\mathbf{p}_\alpha^{N_\alpha},\mathbf{r}_\alpha^{N_\alpha})$.

The 2-ion joint-probability distribution function is also defined in the usual manner by

$$f^{(i,i)}(\mathbf{X}_1^{(i)},\mathbf{X}_2^{(i)}\mathbf{r}^N)=\int\cdots\int f_i^{(N_i)}(\mathbf{X}_i^{N_i};\mathbf{r}^N)d\mathbf{X}_3^{(i)}\times d\mathbf{X}_4^{(i)}\cdots d\mathbf{X}_{N_i}^{(i)}.$$

Here $\mathbf{X}_j^{(i)}=(\mathbf{p}_j^{(i)},\mathbf{r}_j^{(i)})$. The ion-electron and two-electron joint-probability distribution functions $f^{(i,e)}$ and $f^{(e,e)}$ are defined similarly.

On the microscopic scale, the Hamiltonian for the background ions and electrons is given by

$$H_{\rm micro}=\sum_\alpha\sum_{j=1}^{N_\alpha}\frac{|\mathbf{p}_j^{(\alpha)}|^2}{2m_j}+U_{\rm micro},$$

where Σ_α denotes the sum over all the species α (i.e., $\alpha=i$ and e) and $U_{\rm micro}$ is the potential energy

$$U_{\rm micro}=\frac{1}{2}\int_V\rho_{\rm micro}(\mathbf{r})\Psi_{\rm micro}(\mathbf{r})\,d\mathbf{r}-\frac{Q^2}{8\pi\varepsilon_0}\sum_{j=1}^N\int_V\frac{\delta(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|}d\mathbf{r}-\frac{1}{8\pi\varepsilon_0}\sum_\alpha\sum_{j=1}^{N_\alpha}\int_V\frac{q_\alpha^2\delta(\mathbf{r}-\mathbf{r}_j^{(\alpha)})}{|\mathbf{r}-\mathbf{r}_j^{(\alpha)}|}d\mathbf{r}. \tag{A2}$$

Here

$$\rho_{\rm micro}(\mathbf{r})=-Q\sum_{j=1}^N\delta(\mathbf{r}-\mathbf{r}_j)+\sum_\alpha\sum_{j=1}^{N_\alpha}q_\alpha\delta(\mathbf{r}-\mathbf{r}_j^{(\alpha)})$$

and

$$\Psi_{\rm micro}(\mathbf{r})=\frac{1}{4\pi\varepsilon_0}\int_V\frac{\rho_{\rm micro}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

denote the charge distribution and its electrostatic potential. The last two terms on the right-hand side of Eq. (A2) subtract the infinite self-energies of particulates and background charges, which are formally included in the first term.

The statistical average $\langle\cdot\rangle$ of the Hamiltonian $H_{\rm micro}$ over the probability distribution function yields the the internal energy of the background plasma:

$$\langle H_{\rm micro}\rangle=\int\cdots\int H_{\rm micro}(\mathbf{X}^{N_b};\mathbf{r}^N)f^{(N_b)}(\mathbf{X}^{N_b};\mathbf{r}^N)\,d\mathbf{X}^{N_b}. \tag{A3}$$

If the correlation between ions and electrons is assumed negligible, we have $f^{(N_b)}=f_i^{(N_i)}f_e^{(N_e)}$. The Helmholtz free energy is then given by

$$F=\langle H_{\rm micro}\rangle+\sum_\alpha T_\alpha S_\alpha^{\rm bg}, \tag{A4}$$

where

$$S_\alpha^{\mathrm{bg}} = -k_B \langle \ln f_\alpha^{(N_\alpha)}(\mathbf{X}_\alpha^{N_\alpha l};\mathbf{r}^N) \rangle$$

denotes the entropy of the background species α.

We now further assume that (i) each of the background species is in local thermal equilibrium, and (ii) pair correlations of the background species are negligible. Then the two-particle joint probability function $f^{(\alpha,\alpha)}$ becomes

$$f^{(\alpha,\alpha)}(\mathbf{X}_1^{(\alpha)},\mathbf{X}_2^{(\alpha)};\mathbf{r}^N) = \frac{n_\alpha(\mathbf{r}_1)n_\alpha(\mathbf{r}_2)}{N_\alpha(N_\alpha-1)}\left[\frac{\beta_\alpha}{2m_\alpha\pi}\right]^{3/2} \times \exp\left(-\frac{\beta_\alpha}{2m_\alpha}p^2\right), \quad \text{(A5)}$$

where $n_\alpha(\mathbf{r})$ denotes the density of background species α at position $\mathbf{r}$ and $\beta_\alpha = 1/k_B T_\alpha$, as before. Here the dependence of $n_\alpha(\mathbf{r})$ on the particulate positions $\mathbf{r}^N$ is suppressed for brevity.

Carrying out the integral (A3) using Eq. (A5), we obtain the expressions for the internal energy as

$$\langle H_{\mathrm{micro}} \rangle = \sum_\alpha K_\alpha + \frac{1}{2}\int_V \rho(\mathbf{r})\Psi(\mathbf{r})\,d\mathbf{r} - \frac{Q^2}{8\pi\varepsilon_0}\sum_{j=1}^{N}\int_V \frac{\delta(\mathbf{r}-\mathbf{r}_j)}{|\mathbf{r}-\mathbf{r}_j|}\,d\mathbf{r}, \quad \text{(A6)}$$

where

$$\rho(\mathbf{r}) = -Q\sum_{j=1}^{N}\delta(\mathbf{r}-\mathbf{r}_j) + qn_i(\mathbf{r}) - en_e(\mathbf{r}), \quad \text{(A7)}$$

$$\Psi(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0}\int_V \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}', \quad \text{(A8)}$$

and the entropy of the background species α is given by

$$S_\alpha^{\mathrm{bg}} = -\frac{1}{T_\alpha}K_\alpha - k_B\int_V n_\alpha(\mathbf{r})[\ln n_\alpha(\mathbf{r})\Lambda_{T\alpha} - 1]\,d\mathbf{r}. \quad \text{(A9)}$$

In the equations above, $K_\alpha = \frac{3}{2}N_\alpha k_B T_\alpha$ denotes the kinetic energy for the species α.

From Eqs. (A4), (A6)–(A9), we obtain Eq. (17). (Recall that the free energy F is denoted by U_{ex} in the main text.) Thus the intermediate-scale Hamiltonian H is given by Eq. (16) with Eq. (23) if correlations among background charges are negligible. Note that the entropy of the background plasma is approximated by the local entropy (the Thomas–Fermi approximation), as shown in the second term of Eq. (A9).

APPENDIX B: THE OCP LIMIT OF THE IDEAL-GAS FREE ENERGY

In this appendix, we shall show that the ideal-gas contribution to the free energy $F_{\mathrm{id}}^{\mathrm{bg}}$ of Eq. (22) vanishes in the limit $k_D \to 0$. As is readily seen from Eqs. (10) and (15), $\delta\rho^{\mathrm{bg}} \to 0$ and $\Psi(\mathbf{r}) \to \infty$ in this limit. Therefore it is not immediately evident from Eq. (22) that $F_{\mathrm{id}}^{\mathrm{bg}} \to 0$ in the OCP limit.

It is straightforward to rewrite Eq. (22) as

$$F_{\mathrm{id}}^{\mathrm{bg}} = \frac{1}{2}\sum_{i\neq j}\sum \psi_3(\mathbf{r}_i-\mathbf{r}_j) + \frac{1}{2}N\lim_{|\mathbf{R}|\to 0}\psi_3(\mathbf{R}). \quad \text{(B1)}$$

Here the pair potential $\psi_3(\mathbf{R})$ is given by

$$\psi_3(\mathbf{R}) = \frac{Q^2}{4\pi\varepsilon_0}\int_{V_\infty} w_2(\boldsymbol{\rho})\frac{\exp(-k_D|\boldsymbol{\rho}-\mathbf{R}|)}{|\boldsymbol{\rho}-\mathbf{R}|}\,d\boldsymbol{\rho}, \quad \text{(B2)}$$

with

$$w_2(\boldsymbol{\rho}) = \frac{k_D^2}{4\pi}\sum_{\mathbf{n}}\frac{-k_D|\boldsymbol{\rho}-\mathbf{n}L|}{|\rho-\mathbf{n}L|} - \frac{1}{L^3}.$$

To evaluate $\psi_3(\mathbf{R})$, we again appeal to Parseval's identity. The Fourier transform of $w_2(\boldsymbol{\rho})$ may be calculated in a manner similar to that used to obtain Eq. (37):

$$\tilde{w}_2(\mathbf{k}) = \frac{1}{L^3}\left[\frac{k_D^2}{k_D^2+4\pi k^2}\sum_{\mathbf{n}}\delta\left(\mathbf{k}-\frac{\mathbf{n}}{L}\right) - \delta(\mathbf{k})\right] = \frac{k_D^2}{L^3(k_D^2+4\pi^2k^2)}\sum_{\mathbf{n}\neq 0}\delta\left(\mathbf{k}-\frac{\mathbf{n}}{L}\right). \quad \text{(B3)}$$

Similarly the Fourier transform of

$$\frac{\exp(-k_D|\mathbf{r}-\mathbf{a}|)}{|\mathbf{r}-\mathbf{a}|}$$

is given by

$$\frac{4\pi\exp(2\pi i\mathbf{k}\cdot\mathbf{r})}{4\pi^2k^2+k_D^2}. \quad \text{(B4)}$$

Using Eqs. (B3) and (B4), we obtain

$$\psi_3(\mathbf{R}) = \frac{Q^2}{4\pi\varepsilon_0}\frac{1}{L^3}\int_{V_\infty}^{k}\sum_{\mathbf{n}\neq 0}\delta\left(\mathbf{k}-\frac{\mathbf{n}}{L}\right)\exp(2\pi i\mathbf{k}\cdot\mathbf{R}) \times \frac{4\pi k_D^2}{(k_D^2+4\pi k^2)^2}\,d\mathbf{k} = \frac{Q^2}{4\pi\varepsilon_0}\frac{4\pi k_D^2}{L^3}\sum_{\mathbf{n}\neq 0}\frac{\exp(2\pi i\mathbf{n}\cdot\mathbf{R}/L)}{(k_D^2+4\pi^2|\mathbf{n}|^2/L^2)^2}. \quad \text{(B5)}$$

From the following inequality, it is easy to see that the sum in Eq. (B5) converges even in the case $k_D = 0$:

$$\sum_{\mathbf{n}\neq 0}\left|\frac{\exp(2\pi i\mathbf{n}\cdot\mathbf{R}/L)}{(k_D^2+4\pi^2|\mathbf{n}|^2/L^2)^2}\right| \leq \frac{L^4}{16\pi^4}\sum_{\mathbf{n}\neq 0}\frac{1}{|\mathbf{n}|^4},$$

where the sum $\Sigma_{\mathbf{n}\neq 0}|\mathbf{n}|^{-4}$ is clearly convergent. Therefore, we have

$$\lim_{k_D\to 0}\psi_3(\mathbf{R}) = 0. \quad \text{(B6)}$$

From Eqs. (B1) and (B6), we thus readily obtain

$$F_{\mathrm{id}}^{\mathrm{bg}} \to 0 \quad \text{as} \quad k_D \to 0.$$

Using the identity

$$\int_{V_\infty} \frac{\exp(-k_D|\mathbf{r}-\mathbf{a}|-k_D|\mathbf{r}-\mathbf{b}|)}{|\mathbf{r}-\mathbf{a}||\mathbf{r}-\mathbf{b}|} d\mathbf{r}$$

$$= \frac{2\pi}{k_D} \exp(-k_D|\mathbf{a}-\mathbf{b}|),$$

we may evaluate $\psi_3(\mathbf{r})$ as

$$\psi_3(\mathbf{R}) = \frac{Q^2 k_D}{8\pi\varepsilon_0} \sum_{\mathbf{n}} \exp(-k_D|\mathbf{R}-\mathbf{n}L|) - \frac{Q^2}{\varepsilon_0 k_D^2 L^3}.$$

It then follows from Eq. (B1) that

$$F_{\mathrm{id}}^{\mathrm{bg}} = \frac{Q^2 k_D}{16\pi\varepsilon_0} \sum_{i\neq j}\sum \sum_{\mathbf{n}} \exp(-k_D|\mathbf{R}-\mathbf{n}L|)$$

$$-\frac{NQ^2 n}{2\varepsilon_0 k_D^2} + \frac{NQ^2 k_D}{8\pi\varepsilon_0} \sum_{\mathbf{n}} \exp(-k_D|\mathbf{n}|L).$$

Since $\langle H_{\mathrm{micro}}\rangle = U_{\mathrm{ex}} - F_{\mathrm{id}}^{\mathrm{bg}}$, the "pair-potential" form of the internal energy $\langle H_{\mathrm{micro}}\rangle$ becomes

$$\langle H_{\mathrm{micro}}\rangle = \frac{1}{2} \sum_{i\neq j}\sum \left(\frac{1}{|\mathbf{R}_{ij}-\mathbf{n}L|} - \frac{k_D}{2}\right) \exp(-k_D|\mathbf{n}|L)$$

$$-\frac{3NQ^2 k_D}{16\pi\varepsilon_0} + \frac{Q^2 N}{8\pi\varepsilon_0} \sum_{\mathbf{n}\neq\mathbf{0}} \left(\frac{1}{|\mathbf{n}|L} - \frac{k_D}{2}\right)$$

$$\times \exp(-k_D L|\mathbf{n}|), \tag{B7}$$

where $\mathbf{R}_{ij} = \mathbf{r}_i - \mathbf{r}_j$.

[1] F. Hoyle and N. C. Wickramasinghe, *The Theory of Cosmic Grains* (Kluwer Academic, London, 1991).
[2] T. G. Northrop, Phys. Scr. **45**, 475 (1992).
[3] K. G. Spears, T. J. Robinson, and R. M. Roth, IEEE Trans. Plasma Sci. **14**, 179 (1986).
[4] G. S. Selwyn, J. Singh, and R. S. Bennett, J. Vac. Sci. Technol. A **7**, 2758 (1989).
[5] R. N. Carlile, S. Geha, J. F. O'Hanlon, and J. C. Stewart, Appl. Phys. Lett. **59**, 1167 (1991).
[6] B. Ganguly, A. Garscadden, J. Williams, and P. Haaland, J. Vac. Sci. Technol. A **11**, 1119 (1993).
[7] H. Thomas, G. E. Morfill, V. Demmel, J. Goree, B. Feuerbacher, and D. Möhlmann, Phys. Rev. Lett. (submitted).
[8] See, for example, D. H. Everett, *Basic Principles of Colloid Science* (The Royal Society of Chemistry, London, 1988).
[9] R. O. Rosenberg and D. Thirumalai, Phys. Rev. A **36**, 5690 (1987).
[10] M. O. Robbins, K. Kremer, and G. S. Grest, J. Chem. Phys. **88**, 3286 (1988).
[11] E. J. Meijer and D. Frenkel, J. Chem. Phys. **94**, 2269 (1991).
[12] R. T. Farouki and S. Hamaguchi, Appl. Phys. Lett. **61**, 2973 (1992).
[13] R. T. Farouki and S. Hamaguchi, J. Comp. Phys. (in press).
[14] R. T. Farouki and S. Hamaguchi, J. Chem. Phys. **101**, 9885 (1994).
[15] S. G. Brush, H. L. Sahlin, and E. Teller, J. Chem. Phys. **45**, 2102 (1966).
[16] J.-P. Hansen, Phys. Rev. A **8**, 3096 (1973).
[17] H. E. DeWitt, Phys. Rev. A **14**, 1290 (1976).
[18] M. Baus and J.-P. Hansen, Phys. Rep. **59**, 1 (1980).
[19] G. S. Stringfellow, H. E. DeWitt, and W. L. Slattery, Phys. Rev. A **41**, 1105 (1990).
[20] *Strongly Coupled Plasma Physics*, edited by F. J. Rogers, and H. E. DeWitt (Plenum, New York, 1986).
[21] R. T. Farouki and S. Hamaguchi, Phys. Rev. E **47**, 4330 (1993).
[22] H. Ikezi, Phys. Fluids **29**, 1764 (1986).
[23] T. G. Northrop and T. J. Birmingham, Planet. Space Sci. **38**, 319 (1990).
[24] S. Hamaguchi and R. T. Farouki, Phys. Rev. E **49**, 4430 (1994).
[25] S. Hamaguchi and R. T. Farouki, Phys. Plasmas **1**, 2110 (1994).
[26] E. C. Whipple, T. G. Northrop, and D. A. Mendis, J. Geophys. Res. **90**, 7405 (1985).
[27] Y. Rosenfeld, Phys. Rev. E **49**, 4425 (1994).
[28] H. Löwen, P. A. Madden, and J.-P. Hansen, Phys. Rev. Lett. **68**, 1081 (1992).
[29] P. P. Ewald, Ann. Phys. **64**, 253 (1921).
[30] B. R. A. Nijboer and F. W. De Wette, Physica **23**, 309 (1957).
[31] B. Derjaguin, Trans. Faraday Soc. **36**, 203 (1940).
[32] E. J. Verwey and J. Th. G. Overbeek, Discuss. Faraday Soc. B **42**, 117 (1946).
[33] E. J. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).