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Adiabatic pair potential for charged particulates in plasmas and electrolytes

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A treatment of the linear screening approximation for the adiabatic interaction between charged "heavy" particles (particulates, macroions) is presented, which highlights the common points and the different points in its application to disparate physical systems such as plasmas and colloidal suspensions.

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I. INTRODUCTION

Equilibrium many body systems composed of charged "heavy" particles (particulates, macroions) coupled to charged "light" particles (microions), e.g., liquid metals, plasmas of ions and electrons, colloidal suspensions, or dust "particulates" in microelectronic process plasmas, are commonly treated in the adiabatic approximation [1,2]. The microions are assumed to adiabatically follow the motion of the macroions, and the traditional Born-Oppenheimer formalism [3] is invoked to derive the screened, effective Hamiltonian for the motion of the macroions while the coordinates of the microions are integrated out. In the linear-screening approximation a simple Debye-like (Yukawa) effective pair potential is obtained, as e.g., the electrostatic component in the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) potential between the macroions in a colloidal suspension [4], or the Poisson-Boltzmann-Thomas-Fermi screened-Coulomb potential between the ions in plasmas [5] or between dust grains in plasmas [6].

According to the prevailing wisdom [1,2,7,8], the Born-Oppenheimer adiabatic separation of the motions of "heavy" and "light" charged particles leads to an effective interaction between the macroions (particulates) which is derived from the *Helmholtz free energy* of the nonuniform microion system in the external field created by the macroions at their instantaneous locations. Yet, the basis of this result and the details of its formal derivation are not generally known, leading to conflicting results in the literature. For example, attractive regions for the effective interaction potential between like macroions were obtained, within the linear-screening approximation, from the potential energy or from the Gibbs free energy of the nonuniform light particles [9]. This result was criticized [10] and further discussed [11], and can be shown (see below) to follow from an incomplete treatment of the kinetic contributions of the microions. The analogy between the calculation of effective interactions for colloid dispersions and the linear-response treatment of electron screening in liquid metals was fruitfully exploited [8], invoking the pseudopotential theory and linear-response formalism for liquids [7].

The purpose of this short article is (1) to show that the effective adiabatic interaction between the macroions (particulates) is *necessarily* derived from the *Helmholtz free energy* of the nonuniform microion system in the external field created by the macroions at their instantaneous locations, and (2) to present a particularly simple and general treatment of the linear-screening approximation which highlights the common and the different points in its application to quite disparate physical systems like plasmas and colloidal suspensions.

II. ADIABATIC INTERACTION

Let $\mathcal{M}\equiv\{M_s\}$, $\mathcal{R}\equiv\{\mathbf{R}_s\}$, $\mathcal{Q}\equiv\{Q_s\}$ and $\mathscr{m}\equiv\{m_i\}$, $\mathscr{r}\equiv\{\mathbf{r}_i\}$, $\mathscr{q}\equiv\{q_i\}$ denote the masses, coordinates, and quantum state labels of the heavy and light particles, respectively. The Hamiltonian of the system is

$$\hat{H}=\hat{T}_{\mathcal{R}}+\hat{V}_{\mathcal{R},\mathcal{R}}+\hat{T}_{\mathscr{r}}+\hat{V}_{\mathscr{r}\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}}. \tag{1}$$

$\hat{T}_{\mathcal{R}}$ and $\hat{T}_{\mathscr{r}}$ denote the kinetic-energy operators for the heavy and light particles, respectively. $\hat{V}_{\mathcal{R},\mathcal{R}}$ denotes the interactions between the heavy particles, $\hat{V}_{\mathscr{r},\mathscr{r}}$ denotes the interactions between the light particles, while $\hat{V}_{\mathcal{R},\mathscr{r}}$ denotes the interactions between the heavy and light particles.

The adiabatic approximation [3], which is valid for small ratios of the microion mass to the macroion mass, assumes that the Hamiltonian of the system can be separated by integrating out the motion of the light particles, and consists of the ansatz that the total wave function of the system $|\Psi_{\mathcal{Q},\mathscr{q}}(\mathcal{R},\mathscr{r})\rangle$ can be written as a product of the wave functions for the separated Hamiltonians,

$$|\Psi_{\mathcal{Q},\mathscr{q}}(\mathcal{R},\mathscr{r})\rangle=|\Psi_{\mathcal{Q},\mathscr{q}}(\mathcal{R})\rangle|\Psi_{\mathcal{R},\mathscr{q}}(\mathscr{r})\rangle\ , \tag{2}$$

where $|\Psi_{\mathcal{R},\mathscr{q}}(\mathscr{r})\rangle$ obeys

$$(\hat{T}_{\mathscr{r}}+\hat{V}_{\mathscr{r}\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}})|\Psi_{\mathcal{R},\mathscr{q}}(\mathscr{r})\rangle=E_q(\mathcal{R})|\Psi_{\mathcal{R},\mathscr{q}}(\mathscr{r})\rangle\ , \tag{3}$$

while $|\Psi_{\mathcal{Q},\mathscr{q}}(\mathcal{R})\rangle$ is obtained from

$$\hat{H}^{\text{eff}}_{\mathcal{R},\mathscr{q}}|\Psi_{\mathcal{Q},\mathscr{q}}(\mathcal{R})\rangle\equiv[\hat{T}_{\mathcal{R}}+\hat{V}_{\mathcal{R},\mathcal{R}}+E_{\mathscr{q}}(\mathcal{R})]|\Psi_{\mathcal{Q},\mathscr{q}}(\mathcal{R})\rangle$$
$$=E_{\mathcal{Q},\mathscr{q}}|\Psi_{\mathcal{Q},\mathscr{q}}(\mathcal{R})\rangle\ . \tag{4}$$

The "effective" Hamiltonian for the heavy particles is

$$\hat{H}^{\text{eff}}_{\mathcal{R},\mathscr{q}}=\hat{T}_{\mathcal{R}}+\hat{V}^{\text{eff}}_{\mathcal{R},\mathscr{q}}\ , \tag{5}$$

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where the effective potential is given by the standard textbook result [3]

$$\hat{V}^{\text{eff}}_{\mathcal{R},\mathscr{q}}=\hat{V}_{\mathcal{R},\mathcal{R}}+\langle\Psi_{\mathcal{R},\mathscr{q}}(\mathscr{r})|\hat{T}_{\mathscr{r}}+\hat{V}_{\mathscr{r}\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}}|\Psi_{\mathcal{R},\mathscr{q}}(\mathscr{r})\rangle\ . \tag{6}$$

The first step beyond the standard textbook treatment is to apply the coupling-constant integration trick [12], to obtain

$$\langle\Psi_{\mathcal{R},\mathscr{q}}(\mathscr{r})|\hat{T}_{\mathscr{r}}+\hat{V}_{\mathscr{r},\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}}|\Psi_{\mathcal{R},\mathscr{q}}(\mathscr{r})\rangle=E^{(0)}_{\mathscr{q}}+\int_0^1\frac{d\lambda}{\lambda}\langle\Psi_{\mathcal{R},\mathscr{q},\lambda}(\mathscr{r})|\lambda(\hat{V}_{\mathscr{r},\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}})|\Psi_{\mathcal{R},\mathscr{q},\lambda}(\mathscr{r})\rangle \tag{7}$$

where

$$[\hat{T}_{\mathscr{r}}+\lambda(\hat{V}_{\mathscr{r},\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}})]|\Psi_{\mathcal{R},\mathscr{q},\lambda}(\mathscr{r})\rangle=E^{(\lambda)}_{\mathscr{q}}|\Psi_{\mathcal{R},\mathscr{q},\lambda}(\mathscr{r})\rangle \tag{8}$$

so that the effective potential takes the following form

$$\hat{V}^{\text{eff}}_{\mathcal{R},\mathscr{q}}=E^{(0)}_{\mathscr{q}}+\hat{V}_{\mathcal{R},\mathcal{R}}+\int_0^1\frac{d\lambda}{\lambda}\langle\Psi_{\mathcal{R},\mathscr{q},\lambda}(\mathscr{r})|\lambda(\hat{V}_{\mathscr{r},\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}})|\Psi_{\mathcal{R},\mathscr{q},\lambda}(\mathscr{r})\rangle\ . \tag{9}$$

The next step is the observation that in the case when the interactions are electrostatic, all interaction terms are proportional to the coupling parameter e^2 where e is the electron charge, so that

$$\hat{V}^{\text{eff}}_{\mathcal{R},\mathscr{q}}=E^{(0)}_{\mathscr{q}}+\int_0^{e^2}\frac{de^2}{e^2}\langle\Psi_{\mathcal{R},\mathscr{q},e}(\mathscr{r})|\hat{V}_{\mathcal{R},\mathcal{R}}+\hat{V}_{\mathscr{r},\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}}|\Psi_{\mathcal{R},\mathscr{q},e}(\mathscr{r})\rangle\ . \tag{10}$$

The expectation value on the right-hand side is the total electrostatic energy of the system as function of the positions of the heavy particles

$$U_{\mathscr{q},e}(\mathcal{R})=\langle\Psi_{\mathcal{R},\mathscr{q},e}(\mathscr{r})|\hat{V}_{\mathcal{R},\mathcal{R}}+\hat{V}_{\mathscr{r},\mathscr{r}}+\hat{V}_{\mathcal{R},\mathscr{r}}|\Psi_{\mathcal{R},\mathscr{q},e}(\mathscr{r})\rangle\ . \tag{11}$$

Thus, up to a constant kinetic energy of the reference system of noninteracting light particles in state $\mathscr{q},E^{(0)}_{\mathscr{q}}$, the effective potential is related to $U_{\mathscr{q},e}(\mathcal{R})$ by

$$\hat{V}^{\text{eff}}_{\mathcal{R},\mathscr{q}}=E^{(0)}_{\mathscr{q}}+F_{\mathscr{q},e}(\mathcal{R})\ , \tag{12}$$

where

$$F_{\mathscr{q},e}(\mathcal{R})=\int_0^{e^2}\frac{de^2}{e^2}U_{\mathscr{q},e}(\mathcal{R})\ . \tag{13}$$

Finally, for a thermodynamic system of light particles, e.g., a fluid, when the light particles adiabatically follow the heavy particles, we should replace the $\mathscr{q}$-dependent effective potential by its statistical average; i.e., the state label $\mathscr{q}$ in (13) should be replaced by the thermodynamic characterizations of the system, like the temperature T and the mean densities of the light particles $\{n_{i,0}\}$:

$$\hat{V}^{\text{eff}}_{\mathcal{R},T}=E^{(0)}_{T}+F_e(T,\{n_{i,0}\};\mathcal{R})\ , \tag{14}$$

where

$$F_e(T,\{n_{i,0}\};\mathcal{R})=\int_0^{e^2}\frac{de^2}{e^2}U_e(T,\{n_{i,0}\};\mathcal{R})\ . \tag{15}$$

Here $U_e(T,\{n_{i,0}\};\mathcal{R})$ is the potential energy of the system composed of the *inhomogeneous fluid* of light particles and of the heavy particles at static positions $\mathcal{R}$, and $F_e(T,\{n_{i,o}\};\mathcal{R})$ is the corresponding electrostatic contribution to the excess free energy as obtained by the standard relation [13,14] between the *energy* and *Helmholtz free energy* via the charging process.

III. LINEARIZED THOMAS-FERMI-DEBYE-HUCKEL FREE ENERGY FUNCTIONAL

The free energy of the nonuniform system of microions is a functional of the instantaneous density profiles, $\{n_i(\mathbf{r})\}$, and depends parametrically on the macroion configuration $\mathcal{R}\equiv\{\mathbf{R}_s\}$. It is usually separated [1,2] into the ideal (F_{id}, noninteracting), Coulombic (F_C, interaction Coulomb potential energy between the microions), external (F_{ext}, interaction with the external field of the macroions at positions $\{\mathbf{R}_s\}$), and correlation (F_{corr}, accounting for microion correlations and non-Coulombic, e.g., hard-core, contributions) parts:

$$F=F_{\text{id}}+F_C+F_{\text{ext}}+F_{\text{corr}}\ , \tag{16}$$

where

$$F_C=\frac{e^2}{2}\sum_{i,j}z_iz_j\int\int\frac{n_i(\mathbf{r})n_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3r\,d^3r'\ , \tag{17}$$

$$F_{\text{ext}}=e^2\sum_i\int z_in_i(\mathbf{r})\left[\sum_s\int Z_s\frac{\rho_s(\mathbf{r}'-\mathbf{R}_s)}{|\mathbf{r}-\mathbf{r}'|}d^3r'\right]d^3r\ . \tag{18}$$

$\rho_s(\mathbf{r}'-\mathbf{R}_s)$ is the normalized charge distribution of the macroion, and Z_s is its total charge. In the Thomas-Fermi-Debye-Huckel (TFDH) approximation, for example [13], F_{corr} is ignored, while the ideal term is approximated by the local density form, using the bulk (noninteracting) free-energy density, $f(T;n_i)$,

$$F_{\text{id}}=\sum_i\int n_i(\mathbf{r})f(T;n_i(\mathbf{r}))d^3r\ . \tag{19}$$

The density profiles of the particles, $n_i(\mathbf{r})$, are obtained from the minimization of the free-energy subject to normalization constraints, i.e., one considers the grand potential

$$\Omega = F - \sum_i \mu_i \int n_i(\mathbf{r}) d^3r \tag{20}$$

and the density-profile equations

$$\frac{\delta\Omega[\{n_i(\mathbf{r})\}]}{\delta n_i(\mathbf{r})} = 0 \; . \tag{21}$$

The nonuniform fluid is assumed to be connected with a reservoir of the uniform fluid at large distances from the macroions, and thus $\mu_i = \mu_{i,0}(T, \{n_{i,0}\})$ is equal to the ideal uniform chemical potential.

Under conditions of weak coupling, namely, when the potential energy is much smaller than the kinetic energy, for the microions subsystem, and when the inhomogeneity is small, then one is justified in neglecting F_{corr}, and in expanding F_{id} to second order in the inhomogeneity, so that the density profile equations can be *linearized.* Denote

$$n_i(\mathbf{r}) = n_{i,0} + \Delta n_i(\mathbf{r}) \; , \tag{22}$$

where it assumed that $\Delta n_i(\mathbf{r}) \ll n_{i,0}$, then expand the solution to leading orders in the particles' density deviations from the uniform (average) densities $\Delta n_i(\mathbf{r})$. Define the functions $g_1(T;n) = \partial[nf(T;n)]/\partial n$, $g_2(T;n) = \partial[g_1(T;n)]/\partial n$ and the total electrostatic potential at the point $\mathbf{r}$ in the system

$$\Phi(\mathcal{R};\mathbf{r}) = e\sum_j z_j \int \frac{n_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + \sum_s Z_s \int \frac{\rho_s(\mathbf{r}'-\mathbf{R}_s)}{|\mathbf{r}-\mathbf{r}'|} d^3r' \tag{23}$$

and recall the standard relation between the free energy density and chemical potential for the uniform system at the reservoir average density $n_{i,0}$, namely, $\mu_{i,0} = g_1(T;n_{i,0})$. To the leading order in the density deviations, the solution for the density-profile equations is the well-known linearized TFDH result

$$\Delta n_i(\mathbf{r}) = \frac{z_i e}{g_2(T;n_{i,0})} \Phi(\mathcal{R};\mathbf{r}) \; , \tag{24}$$

which is inconsistent with (22) near points of singularity for the potential, where $\Delta n_i(\mathbf{r})$ also diverges. Expand the ideal free energy to second order in the density deviations, and make use of the extremum property (21) of the solution of the density profile equations, to obtain

$$\begin{aligned} F_e(T,\{n_{i,0}\};\mathcal{R}) &= \Omega - \Omega_0 = F - F_0 \\ &= \frac{1}{8\pi} \int \left[|\nabla_r \Phi(\mathcal{R};\mathbf{r})|^2 \right. \\ &\qquad \left. + \kappa^2 \Phi^2(\mathcal{R};\mathbf{r}) \right] d^3r \; , \end{aligned} \tag{25}$$

where

$$\kappa^2 = \sum_i \frac{4\pi z_i^2 e^2}{g_2(T;n_{i,0})} \tag{26}$$

is the TFDH inverse-screening length, and Ω_0, F_0 are the grand potential and Helmholtz free energy of the uniform system. Specifically, for classical particles

$$f(T;n) = k_B T(3\ln\Lambda - 1 + \ln n) \; , \tag{27}$$

where Λ is the deBroglie thermal wavelength, so that

$$g_2(T;n_{i,0}) = \frac{k_B T}{n_{i,0}} \; , \tag{28}$$

while for degenerate electrons

$$f(n) = \frac{3}{5} a n^{2/3} \; , \tag{29}$$

where the constant a is related to the chemical potential by $\mu_0 = a n_0^{5/3}$, so that

$$g_2(n_0) = \frac{2}{3} a n_0^{2/3} \equiv \frac{2}{3} \frac{\mu_0}{n_0} \; . \tag{30}$$

The potential energy

$$U_e(T,\{n_{i,0}\};\mathcal{R}) = \frac{1}{8\pi} \int |\nabla_r \Phi(\mathcal{R};\mathbf{r})|^2 d^3r \tag{31}$$

now includes the (possibly infinite) electrostatic self-energy of the heavy particles. The electrostatic contribution to the ideal, kinetic term, in the linearized TFDH approximation is given by

$$K_e(T,\{n_{i,0}\};\mathcal{R}) = \frac{1}{8\pi} \int \kappa^2 \Phi^2(\mathcal{R};\mathbf{r}) d^3r \; , \tag{32}$$

so that

$$F_e(T,\{n_{i,0}\};\mathcal{R}) = U_e(T,\{n_{i,0}\};\mathcal{R}) + K_e(T,\{n_{i,0}\};\mathcal{R}) \; . \tag{33}$$

For the degenerate electrons considered above, $K_e(n_0;\mathcal{R})$ is the electrostatic contribution to the kinetic energy.

IV. YUKAWA PAIR POTENTIAL

The Euler-Lagrange equation corresponding to the optimization of the electrostatic contribution to the free energy (i.e., the new form for the density profile equations) subject to the appropriate boundary conditions, takes the form

$$(\nabla^2 - \kappa^2)\Phi(\mathcal{R};\mathbf{r}) = -4\pi e \left[\sum_s Z_s \rho_s(\mathbf{r}-\mathbf{R}_s) + \sum_i n_{i,0} z_i \right] . \tag{34}$$

The Green's function for this Debye form for the Poisson-Botzmann–Thomas-Fermi equation is the *Yukawa* potential

$$\phi(r) = \frac{e^{-\kappa r}}{r}; \quad \tilde{\phi}(k) = \frac{4\pi}{k^2+\kappa^2} \; . \tag{35}$$

Consider, at first, the case when the microions can interpenetrate the macroions charge distributions, or when the macroions are point charges. Then, the formal solution for the Fourier transform of Φ is

$$\tilde{\Phi}(\mathcal{R};\mathbf{k})=\sum_s Z_s e\tilde{\rho}_s(\mathbf{k})\tilde{\phi}(k)+\left[\frac{4\pi e}{\kappa^2}\sum_i n_{i,0}z_i\right]\delta(\mathbf{k}) . \qquad (36)$$

The excess free energy (33) takes the form of the total potential energy of a collection of Yukawa charges:

$$F_e(T,\{n_{i,0}\};\mathcal{R})=\frac{1}{2}\sum_{s\neq t}u_{st}(\mathbf{R}_s-\mathbf{R}_t)+\sum_t u_{tt}(0) , \qquad (37)$$

so that the effective interaction between the macroions is *pairwise additive* where the *pair potential*

$$u_{st}(\mathbf{r})=\frac{1}{(2\pi)^3}\int u_{st}(\mathbf{k})e^{-i\mathbf{k}\cdot\mathbf{r}}d^3r , \qquad (38)$$

with Fourier transform

$$\tilde{u}_{st}(\mathbf{k})=Z_sZ_te^2\tilde{\phi}(k)\tilde{\rho}_s(\mathbf{k})\tilde{\rho}_t(\mathbf{k}) \qquad (39)$$

is the interaction between two Yukawa charge distributions $Z_s\rho_s(\mathbf{x})$, $Z_t\rho_t(\mathbf{x})$ of total charge Z_s,Z_t, respectively, and separation $\mathbf{r}$. The zero-separation value $u_{tt}(0)$ is the self-energy of the Yukawa-charge distribution $Z_t\rho_t(\mathbf{x})$ of Fourier transform $Z_t\tilde{\rho}_t(\mathbf{k})$.

Thus within linear-screening theory, when the microions are treated in the semiclassical linearized Thomas-Fermi approximation (as, e.g., in a plasma of electrons and ions), or the classical linearized Poisson-Boltzmann-Debye-Huckel approximation (as, e.g., in charged colloidal suspensions), and the microions are allowed to interpenetrate the macroions (or for point macroions) the adiabatic approximation amounts *exactly* to transforming the Coulomb charges on the particulates (macroions) into Yukawa charges. The Yukawa intermolecular potential [15] has the special property that it gives rise to the same functional form for the potential outside a spherically symmetric distribution of Yukawa charge, which thus appears as a renormalized point charge [16]. Specifically, the potential outside a single confined Yukawa-charge distribution, $\rho_s(x\geq R_s)=0$, at the origin of coordinates, is given by

$$\varphi(r\geq R_s)=\frac{1}{q_s(\kappa,R_s)}\frac{e^{-\kappa r}}{r} , \qquad (40)$$

where

$$\frac{1}{q_s(\kappa,R_s)}=\left[\frac{4\pi}{\kappa}\right]\int_0^{R_s}\rho_s(x)x\sinh(\kappa x)dx , \qquad (41)$$

so that the effective point-Yukawa charge for each macroion is

$$Z_s^{\text{eff}}=\frac{Z_s}{q_s(\kappa,R_s)} . \qquad (42)$$

In particular, for a uniform surface distribution

$$\frac{1}{q_s(\kappa,R_s)}=\frac{\sinh(\kappa R_s)}{\kappa R_s}\geq 1 \qquad (43)$$

and the pair potential takes the form

$$u_{st}(r\geq R_s+R_t)=\left[Z_se\frac{\sinh(\kappa R_s)}{\kappa R_s}\right]\times\left[Z_te\frac{\sinh(\kappa R_t)}{\kappa R_t}\right]\frac{e^{-\kappa r}}{r} . \qquad (44)$$

Finally, consider the case where the microions are excluded from the interior of the microions's charge distribution. This applies, for example, to colloidal suspensions, with the macroions assumed to behave like hard spheres with a uniform surface charge density $\sigma_s=Z_se/4\pi R_s^2$. The solution of Eq. (34) subject to the charge exclusion condition, now leads to the following result for the electrostatic potential outside a single sphere at the origin of coordinates [17]:

$$\varphi(r\geq R_s)=Z_se\frac{e^{\kappa R_s}}{1+\kappa R_s}\frac{e^{-\kappa r}}{r} , \qquad (45)$$

so that, up to an additive constant, the effective pair potential between the macroions takes the form

$$u_{st}(r\geq R_s+R_t)=\left[Z_se\frac{e^{\kappa R_s}}{1+\kappa R_s}\right]\left[Z_te\frac{e^{\kappa R_t}}{1+\kappa R_t}\right]\frac{e^{-\kappa r}}{r} . \qquad (46)$$

This effective pair potential but with renormalized charges Z_s^* and screening factors κ^* can still be used [18] for colloidal suspensions even when the linearization of the Poisson-Boltzmann equation is not strictly valid. Equations (44) and (46) become identical, of course, for point macroions ($R_s=0$), but in that case, however, the self-consistency condition for the validity of the linearization, namely $|\varphi(R_s)z_ie|<k_BT$, cannot be satisfied.

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