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Where the linearized Poisson-Boltzmann cell model fails: spurious phase separation in charged colloidal suspensions, by M. N. Tamashiro and H. Schiessel

A   Definition of the model

In this Appendix we give a detailed presentation and discussion of the mean-field PB WS-cell model briefly introduced in Section 2. In particular, we derive the nonlinear PB equation from the functional minimization of a free-energy density functional.

As presented in Section 1, one of the simplest theoretical descriptions of charged colloidal suspensions is the PM, that neglects the molecular nature of the solvent and dielectric discontinuities — even though its rigorous solution is highly nontrivial. A mean-field approach to the PM, although not thermodynamically consistent,[1–3] is represented by the PB approximation.[4–7] This treatment gives a reasonable description in the weak-coupling (high temperature or small charge densities) limit, when the microionic correlations that are neglected at the mean-field level are unimportant. But even the mean-field PB approximation for a suspension of charged polyions is a formidable task[8] due to the large asymmetry in size, mass and charge between the polyions and the small mobile microions. To circumvent this problem, the cell model has been introduced — originally for the cylindrical geometry[9, 10] — which reduces the many-body problem to the study of a (fixed) single polyion inside a WS cell, whose volume is related to the polyion density. In the WS-cell model the single polyion plays only the role of a *boundary condition.* Note that this represents a dramatic simplification to the original PM formulation, where polyions and microions are treated at the same level. Even though the applicability of the WS-cell model appears at first sight to be only justified for an ordered crystalline phase, it has also been used to describe the fluid phase,[11, 12] neglecting thus the polyion translational entropy, the polyion-polyion interactions and *intercell* (both microion-polyion and microion-microion) correlations — *intracell* microion-microion correlations are neglected because of the mean-field approximation, which computes only the *intracell* microion-polyion correlations. To simplify further, the geometry of the WS cell is usually taken as to match the boundary condition on the polyion charged surface. For example, for colloidal particles a spherical charged polyion is considered inside a concentric spherical WS cell. This reduces the problem to the solution of a second-order ordinary (rather than partial) differential equation. For the spherical geometry this requires the numerical solution of the nonlinear PB equation, contrary to the planar[13–15] and cylindrical[9, 10, 16] cases, when an exact analytical solution to this nonlinear equation is possible.

Although the derivation of the nonlinear PB equation from a free-energy density functional can be found elsewhere,[6, 7, 17] to introduce the notation and to stress the advantages of an explicitly gauge-invariant approach, it is helpful to rederive it in the following. For simplicity, we present here only the salt-free case (in the presence of neutralizing counterions only). Generalization of the model including monovalent salt is straightforward and briefly described in Appendices D and E for the canonical and semi-grand-canonical cases, respectively. The system to be considered is a hard charged sphere — a spherical polyion that, without loss of generality, is chosen to be a polyanion — of radius a and total charge $-Zq$ distributed uniformly on its surface inside a concentric spherical WS cell of radius $R > a$, where $q > 0$ is the elementary charge and $Z \gg 1$ is the polyion valence. The radius R of the WS cell is related to the polyion density n_{p} such that the total volume of the suspension is equally distributed between the polyions, i.e. $n_{\mathrm{p}} \equiv \left(4\pi R^3/3\right)^{-1}$, whose hard cores occupy a fraction $\phi \equiv (a/R)^3$ of the total volume. To ensure the overall WS-cell charge neutrality, there are Z mobile (positive) point-like counterions, each carrying a charge $+q$, that are allowed to move in the spherical shell $a < |\boldsymbol{r}| \leq R$, whose volume reads $V = (4\pi/3)\left(R^3 - a^3\right)$. Henceforth, to simplify the notation, it will be implicit that all integrations are performed over the free volume V unoccupied by the polyion core — but also including the polyion charged surface at $|\boldsymbol{r}| = a$ — unless otherwise stated. At the mean-field PB level the counterions are treated as an inhomogeneous ideal gas and are described by their (continuous) average local number density $n_+(\boldsymbol{r}) \equiv \left\langle\!\!\left\langle \sum_{i=1}^{Z} \delta^3 \left(\boldsymbol{r} - \boldsymbol{r}_i\right) \right\rangle\!\!\right\rangle$, where δ^3 is the three-dimensional Dirac delta function and the double brackets denote an ensemble (Boltzmann-weighted) average over all positions $\{\boldsymbol{r}_i\}$ of the counterions. The total charge number density (counterions plus the negative surface

charge on the polyion),

$$\rho(\boldsymbol{r}) = n_+(\boldsymbol{r}) - \frac{Z}{4\pi a^2}\delta^3(|\boldsymbol{r}| - a), \tag{A1}$$

is related to the reduced electrostatic potential $\psi(\boldsymbol{r}) \equiv \beta q \Psi(\boldsymbol{r})$ by the (exact) Poisson equation,

$$\nabla^2 \psi(\boldsymbol{r}) = -4\pi \ell_B \rho(\boldsymbol{r}), \tag{A2}$$

where $\ell_B = \beta q^2/\epsilon$ is the Bjerrum length and $\beta^{-1} = k_B T$ is the thermal energy at temperature T. It is implicitly assumed that the solvent dielectric constant ϵ remains the same inside the sphere, so image-charge effects due to dielectric contrast are absent. The formal solution to the Poisson equation (A2) may be written in terms of the Green function $G_3(\boldsymbol{r}, \boldsymbol{r}')$ in three dimensions,

$$\psi(\boldsymbol{r}) = \ell_B \int \mathrm{d}^3\boldsymbol{r}'\, G_3(\boldsymbol{r}, \boldsymbol{r}')\, \rho(\boldsymbol{r}'), \qquad \nabla^2 G_3(\boldsymbol{r}, \boldsymbol{r}') = -4\pi\delta^3(\boldsymbol{r} - \boldsymbol{r}'), \tag{A3}$$

which in turn allows us to express the mean-field Helmholtz free-energy functional $\mathscr{F}[n_+(\boldsymbol{r})]$ of a single WS cell as

$$\beta\mathscr{F}[n_+(\boldsymbol{r})] = \int \mathrm{d}^3\boldsymbol{r}\, n_+(\boldsymbol{r}) \left\{ \ln\left[n_+(\boldsymbol{r})\zeta_+^3 \right] - 1 \right\} + \frac{\ell_B}{2} \int \mathrm{d}^3\boldsymbol{r}\, \mathrm{d}^3\boldsymbol{r}'\, \rho(\boldsymbol{r})\, G_3(\boldsymbol{r}, \boldsymbol{r}')\, \rho(\boldsymbol{r}'), \tag{A4}$$

where ζ_+ is the thermal de Broglie wavelength of the counterions. It should be remarked that the mean-field Helmholtz free-energy functional (A4) can be derived from the underlying PM Hamiltonian in different ways: as the saddle point of the action in a field-theoretic approach,[6] from a Gibbs-Bogoljubov inequality applied to a trial product state that decouples the original Hamiltonian[7] or from a first-cumulant expansion of the density-functional reformulation of the associated partition function.[18] The first term of (A4) represents the configurational entropy of the inhomogeneous ideal gas of counterions, while the second term corresponds to the electrostatic energy, $\beta U = \frac{1}{2}\int \mathrm{d}^3\boldsymbol{r}\, \psi(\boldsymbol{r})\rho(\boldsymbol{r})$, which may be rewritten as

$$\beta U = \frac{1}{8\pi\ell_B} \int \mathrm{d}^3\boldsymbol{r}\, \left[\nabla\psi(\boldsymbol{r})\right]^2 - \frac{1}{8\pi\ell_B} \oint_{\partial V} \psi(\boldsymbol{r})\, \nabla\psi(\boldsymbol{r}) \cdot \mathrm{d}\boldsymbol{S}. \tag{A5}$$

The surface contributions to the electrostatic energy — the last term of the right-hand side of (A5), performed over the boundary ∂V of the free volume V, which *does not* include the polyion charged surface at $|\boldsymbol{r}| = a$, because it is already incorporated into the free volume V — vanish due to Gauss' law and the overall WS-cell charge neutrality,

$$\int \mathrm{d}^3\boldsymbol{r}\, \rho(\boldsymbol{r}) = 0, \qquad \text{or} \qquad \int \mathrm{d}^3\boldsymbol{r}\, n_+(\boldsymbol{r}) = Z. \tag{A6}$$

The equilibrium counterion-density profile is obtained by minimizing the mean-field functional $\mathscr{F}[n_+(\boldsymbol{r})]$ with respect to $n_+(\boldsymbol{r})$ under the constraint of overall WS-cell charge neutrality (A6). For this purpose it is convenient to introduce a translationally invariant (independent of $\boldsymbol{r}$) *virtual* Lagrange multiplier $\beta\mu_{\mathrm{el}}$ and to define the extended Helmholtz free-energy functional $\tilde{\mathscr{F}}[n_+(\boldsymbol{r})]$ including an additional Lagrange-multiplier term,

$$\tilde{\mathscr{F}}[n_+(\boldsymbol{r})] \equiv \mathscr{F}[n_+(\boldsymbol{r})] - \mu_{\mathrm{el}} \int \mathrm{d}^3\boldsymbol{r}\, \rho(\boldsymbol{r}) = \mathscr{F}[n_+(\boldsymbol{r})] - \mu_{\mathrm{el}} \left[\int \mathrm{d}^3\boldsymbol{r}\, n_+(\boldsymbol{r}) - Z \right]. \tag{A7}$$

We should remark that the extended Helmholtz free-energy functional $\tilde{\mathscr{F}}[n_+(\boldsymbol{r})]$ *does not correspond* to the conjugated semi-grand-canonical functional $\Omega[n_+(\boldsymbol{r})]$ in the (hypothetical) case of fixed chemical potential of counterions μ_+ (but fixed number of polyions),

$$\Omega[n_+(\boldsymbol{r})] \equiv \mathscr{F}[n_+(\boldsymbol{r})] - \mu_+ \int \mathrm{d}^3\boldsymbol{r}\, n_+(\boldsymbol{r}), \qquad \int \mathrm{d}^3\boldsymbol{r}\, n_+(\boldsymbol{r}) \not\equiv Z. \tag{A8}$$

In fact, for the salt-free case, it is not even possible to define the semi-grand-canonical functional $\Omega[n_+(\boldsymbol{r})]$, because it violates the *global* charge-neutrality of the system. Even by modeling the salt-free colloidal suspension by locally nonneutral cells — whose volume *are not* directly related to the polyion density — in electrochemical equilibrium with outer free counterions, as considered in Ref. [19], it is still not possible to define a true semi-grand-canonical functional $\Omega[n_+(\boldsymbol{r})]$, because the (pseudo-)chemical potential μ_+ of the

free counterions is fixed by the *global* charge-neutrality of the system. We refer the reader to the treatment of the Donnan-equilibrium problem — the system in electrochemical equilibrium with an infinite salt reservoir, considered in Appendices E and F — for an extended discussion about the differences between the virtual Lagrange multiplier μ_{el} and the true chemical potentials of microions $\mu_{\pm}$. We anticipated that, although this distinction may seem to be rather academic, it is important to stress that overall charge neutrality (ensured by the Lagrange multiplier μ_{el}) and electrochemical equilibrium (imposed by fixed chemical potentials of microions $\mu_{\pm}$) are *independent* constraints. This prevents misinterpretations when treating the Donnan equilibrium, when both constraints must be simultaneously satisfied.

Functional minimization of $\beta\tilde{\mathscr{F}}$ with respect to $n_+(\boldsymbol{r})$ leads to the Euler-Lagrange or stationary condition,[20]

$$\left.\frac{\delta\beta\tilde{\mathscr{F}}}{\delta n_+(\boldsymbol{r})}\right|_{n_+(\boldsymbol{r})=\bar{n}_+(\boldsymbol{r})} = \bar{\psi}(\boldsymbol{r}) + \ln\left[\bar{n}_+(\boldsymbol{r})\zeta_+^3\right] - \beta\bar{\mu}_{\mathrm{el}} = 0, \tag{A9}$$

which yields the equilibrium counterion profile, $\bar{n}_+(\boldsymbol{r}) = \mathrm{e}^{\beta\bar{\mu}_{\mathrm{el}}-\bar{\psi}(\boldsymbol{r})}/\zeta_+^3$. In the above formulas the equilibrium electrostatic potential, $\bar{\psi}(\boldsymbol{r})$, is obtained by inserting the equilibrium counterion profile $\bar{n}_+(\boldsymbol{r})$ into $\psi(\boldsymbol{r})$, Eq. (A3). The equilibrium Lagrange multiplier is obtained by imposing the charge neutrality constraint (A6),

$$\beta\bar{\mu}_{\mathrm{el}} = \ln\left(n_{\mathrm{c}}\zeta_+^3\right) - \ln\left\langle\mathrm{e}^{-\bar{\psi}(\boldsymbol{r})}\right\rangle, \tag{A10}$$

the brackets denoting unweighted spatial averages over V,

$$\langle\mathcal{X}(\boldsymbol{r})\rangle \equiv \frac{\int\mathrm{d}^3\boldsymbol{r}\,\mathcal{X}(\boldsymbol{r})}{\int\mathrm{d}^3\boldsymbol{r}}. \tag{A11}$$

We introduced the *effective* average density of counterions in the free volume V unoccupied by the polyion core,

$$n_{\mathrm{c}} \equiv \langle\bar{n}_+(\boldsymbol{r})\rangle = \frac{Z}{V}, \tag{A12}$$

in contrast to their *nominal* mean density in the suspension, $\tilde{n}_{\mathrm{c}} \equiv n_{\mathrm{c}}\,(1-\phi)$, which does not take into account the polyion hard cores. Note that the Lagrange multiplier (A10) may be decomposed into two terms, a chemical potential corresponding to an ideal gas of uniform density n_{c} and an electrostatic contribution due to the counterion-cloud polarization, which may be written in terms of an average related to the equilibrium electrostatic potential, $-\ln\left\langle\mathrm{e}^{-\bar{\psi}(\boldsymbol{r})}\right\rangle$.

We note that the presence of the Lagrange multiplier $\bar{\mu}_{\mathrm{el}}$ ensures *explicitly* the gauge invariance of the equations, that is, physical observables, like the equilibrium counterion-density profile,

$$\bar{n}_+(\boldsymbol{r}) = \frac{Z\mathrm{e}^{-\bar{\psi}(\boldsymbol{r})}}{\int\mathrm{d}^3\boldsymbol{r}\,\mathrm{e}^{-\bar{\psi}(\boldsymbol{r})}} = \frac{n_{\mathrm{c}}\exp\left[\langle\bar{\psi}\rangle - \bar{\psi}(\boldsymbol{r})\right]}{\left\langle\exp\left[\langle\bar{\psi}\rangle - \bar{\psi}(\boldsymbol{r})\right]\right\rangle}, \tag{A13}$$

and the electric field, $\boldsymbol{E}(\boldsymbol{r}) = -\nabla\Psi(\boldsymbol{r}) = -(\beta q)^{-1}\nabla\bar{\psi}(\boldsymbol{r})$, *clearly* do not depend on a particular choice of the zero of the electrostatic potential $\bar{\psi}(\boldsymbol{r})$, since observables can always be written in terms of the gauge-invariant difference $\beta\bar{\mu}_{\mathrm{el}} - \bar{\psi}(\boldsymbol{r})$. In particular, explicitly gauge-invariant forms of the density profiles will be *useful* to establish a connection between the nonlinear and the linearized osmotic pressures (cf. Appendices C to E) and to derive the self-consistent linearized averaged densities for the semi-grand-canonical ensemble (cf. Appendix F). We should remark that — because consistent theories should always be gauge invariant — the use of *explicitly* gauge-invariant forms constitutes just a technical convenience, it does not represent an essential requirement. However, we believe that it provides a systematic and more transparent way to perform the calculations and later, the linearization. Henceforth *gauge-invariant* will be a short-writing for *explicitly gauge-invariant,* unless otherwise stated.

The Boltzmann-weighted equilibrium counterion profile, Eq. (A13), together with the Poisson equation (A2), yields the nonlinear PB equation,

$$\nabla^2\bar{\psi}(\boldsymbol{r}) = -\frac{\kappa_{\mathrm{c}}^2\mathrm{e}^{-\bar{\psi}(\boldsymbol{r})}}{\left\langle\mathrm{e}^{-\bar{\psi}(\boldsymbol{r})}\right\rangle} + \frac{Z\ell_B}{a^2}\delta^3(|\boldsymbol{r}| - a), \tag{A14}$$

where we introduced the Debye screening length κ_c^{-1} associated with the *uniform counterion density* n_c,

$$\kappa_c \equiv \sqrt{4\pi\ell_B n_c}. \tag{A15}$$

The mean-field Helmholtz free energy (of a single WS cell) F is obtained by inserting the equilibrium density profile $\bar{n}_+(\boldsymbol{r})$, Eq. (A13), into the mean-field functional $\mathscr{F}$, Eq. (A4),

$$\beta F \equiv \beta\mathscr{F}[\bar{n}_+(\boldsymbol{r})] = Z\left[\ln\left(n_c\zeta_+^3\right) - 1\right] - \frac{Z}{2}\left[\bar{\psi}(r=a) + 2\ln\left\langle e^{-\bar{\psi}(\boldsymbol{r})}\right\rangle + \frac{\left\langle\bar{\psi}(\boldsymbol{r})\,e^{-\bar{\psi}(\boldsymbol{r})}\right\rangle}{\left\langle e^{-\bar{\psi}(\boldsymbol{r})}\right\rangle}\right], \tag{A16}$$

with $r \equiv |\boldsymbol{r}|$. In Section 3 of Ref. [7] it is shown[21] that the nonlinear osmotic pressure P (over pure solvent), defined as the negative *total derivative* of the Helmholtz free energy F, Eq. (A16), with respect to the WS-cell free volume[22] V, is simply given by

$$\beta P \equiv -\frac{\mathrm{d}\beta F}{\mathrm{d}V} = \bar{n}_+(R), \tag{A17}$$

which is the well-know WS-cell mean-field result that the salt-free osmotic pressure is related to the counterion density at the WS-cell boundary[11] $r = R$. This simple functional form still remains valid at the PM (beyond mean-field) level for WS cells of various geometries,[23] although the mean-field prediction for the equilibrium boundary density $\bar{n}_+(R)$ will (in general) disagree with the corresponding rigorous PM result due to the neglect of *intracell* microion-microion correlations and finite ionic sizes. Henceforth, to simplify the notation — except in Appendix C, where its use is necessary in order to avoid confusion — we will omit the bar to denote equilibrium properties.

B   Salt-free linearized equations

In this Appendix we present explicit expressions for the salt-free linearized equations, as well as we discuss the differences between alternative linearized schemes.

In the same way as for the salt-free nonlinear equations derived in Appendix A, in order to ensure the charge-neutrality constraint (A6), one needs to introduce a Lagrange multiplier μ_{el} and to define the extended Helmholtz free-energy functional $\tilde{\mathscr{F}}_{DH} = \mathscr{F}_{DH} - \mu_{el}\int\mathrm{d}^3\boldsymbol{r}\,\rho(\boldsymbol{r})$. Functional minimization of $\tilde{\mathscr{F}}_{DH}$ with respect to $n_+(\boldsymbol{r})$ leads to the linearized equilibrium counterion profile,

$$n_+(\boldsymbol{r}) = n_c\left[1 + \beta\mu_{el} - \ln\left(n_c\zeta_+^3\right) - \psi(\boldsymbol{r})\right]. \tag{B1}$$

It follows from Eqs. (A12) and (B1) that the linearized equilibrium Lagrange multiplier $\beta\mu_{el}$ is obtained by adding the uniform counterion-density chemical potential to the average electrostatic potential inside the WS cell,

$$\beta\mu_{el} = \ln\left(n_c\zeta_+^3\right) + \langle\psi(\boldsymbol{r})\rangle. \tag{B2}$$

Inserting the linearized equilibrium counterion-density profile (B1) into the Poisson equation (A2), leads to the linearized DH-like Eq. (7). It should be remarked that this DH-like equation leads to a *gauge-invariant* linearized solution for $\psi(\boldsymbol{r})$, i.e., independent of the choice of the zero of the potential, because it depends explicitly only on the difference $\langle\psi(\boldsymbol{r})\rangle - \psi(\boldsymbol{r})$. While the linearized DH-like Eq. (7) may be obtained by a functional minimization of the linearized free-energy functional (5), this is not the case for the standard linearized-PB solution,[12] when it is disputable how to construct a self-consistent associated functional, from which the linearized equations may be obtained by a functional minimization — see also discussion in the last paragraph of this Appendix. Such a functional in the Donnan-equilibrium problem has been proposed in Ref. [24] for arbitrary expansion densities.

The solution of the linearized DH-like Eq. (7) for *an arbitrary* WS-cell boundary potential $\psi(R)$ and under the appropriate boundary conditions,

$$\left.\frac{\mathrm{d}\psi(r)}{\mathrm{d}r}\right|_{r=a} = \frac{Z\ell_B}{a^2}, \qquad \text{and} \qquad \left.\frac{\mathrm{d}\psi(r)}{\mathrm{d}r}\right|_{r=R} = 0, \tag{B3}$$

reads

$$\psi(r) = \psi(R) + \frac{2Z\kappa\ell_B}{\Delta_2(\kappa R, \kappa a)} - \frac{Z\ell_B}{r}\frac{\Delta_1(\kappa R, \kappa r)}{\Delta_2(\kappa R, \kappa a)}, \tag{B4}$$

$$\Delta_1(u,v) = \Delta_+(u)\mathrm{e}^v - \Delta_-(u)\mathrm{e}^{-v}, \tag{B5}$$

$$\Delta_2(u,v) = \Delta_+(u)\Delta_-(v) - \Delta_-(u)\Delta_+(v), \tag{B6}$$

$$\Delta_\pm(u) = (1 \pm u)\mathrm{e}^{\mp u}, \tag{B7}$$

with the average electrostatic potential inside the WS cell given by

$$\langle\psi(\boldsymbol{r})\rangle = \psi(R) + \frac{2Z\kappa\ell_B}{\Delta_2(\kappa R, \kappa a)} - 1. \tag{B8}$$

Inserting the DH-like solution for the electrostatic potential (B4) into the linearized Helmholtz free-energy functional (5) leads, after some algebra, to the linearized Helmholtz free energy, $F_{\mathrm{DH}} = \mathscr{F}_{\mathrm{DH}}[n_+(\boldsymbol{r})]_{\mathrm{equil}}$,

$$\beta F_{\mathrm{DH}} = Z\left[\ln\left(n_{\mathrm{c}}\zeta_+^3\right) - 1\right] + \frac{Z}{2}\left[\langle\psi(\boldsymbol{r})\rangle - \psi(r=a)\right] = Z\left[\ln\left(n_{\mathrm{c}}\zeta_+^3\right) - \frac{3}{2}\right] + \frac{Z^2\ell_B}{2a}\frac{\Delta_1(\kappa R, \kappa a)}{\Delta_2(\kappa R, \kappa a)}. \tag{B9}$$

It is possible to show that the linearized Helmholtz *excess* free energy over the ideal-gas entropy of the uniform reference state, $\beta\Delta F_{\mathrm{DH}} \equiv \beta F_{\mathrm{DH}} - Z\left[\ln\left(n_{\mathrm{c}}\zeta_+^3\right) - 1\right]$, can also be obtained by a Debye charging process,[25] $\Delta F_{\mathrm{DH}} = 2\int_0^1 \mathrm{d}\lambda\, U(\lambda\kappa, \lambda^2\ell_B)/\lambda$, of the linearized electrostatic energy $U(\kappa, \ell_B)$, obtained by inserting the DH-like solution (B4) into $\beta U = 1/(8\pi\ell_B)\int \mathrm{d}^3\boldsymbol{r}\,\left[\nabla\psi(r)\right]^2$. This is a nontrivial result and confirms thus the thermodynamic self-consistency of the linearized Helmholtz free energy F_{DH}, Eq. (B9).

In the standard linearized-PB treatment of the spherical WS cell[12] the linearization is not performed at the level of the free-energy functional, but rather by expanding the nonlinear equilibrium profile (A13) about the WS-cell boundary at $r = R$, $n_+(\boldsymbol{r}) = n_+(R)\left[1 - \psi(\boldsymbol{r}) + \psi(R)\right]$, where the normalization constant $n_+(R)$ is fixed by the charge-neutrality constraint (A6), $n_+^{-1}(R) = \int \mathrm{d}^3\boldsymbol{r}\,\left[1 - \psi(\boldsymbol{r}) + \psi(R)\right]/Z$. More generally, by expanding in this approach the nonlinear equilibrium profile about an arbitrary distance $a \le b \le R$, the associated linearized solution to the electrostatic potential *is not* given by Eq. (B4), but rather by $\psi(r) = \psi(b) + 1 - (Z\ell_B/r)\Delta_1(\kappa R, \kappa r)/\Delta_2(\kappa R, \kappa a)$, and the effective Debye screening length κ^{-1} satisfies the eigenvalue equation $Z\ell_B\Delta_1(\kappa R, \kappa b) = b\Delta_2(\kappa R, \kappa a)$. In other words, in the standard treatment the screening length κ^{-1} depends on the arbitrary distance b about which the nonlinear equilibrium profile is expanded, contrary to the linearization scheme reported in Subsection 3.1, which is *independent* on the expansion point b. While in the standard approach the nonlinear equilibrium profile (A13) is *halfway* linearized as $n_+(\boldsymbol{r}) = n_{\mathrm{c}}\left[1 - \psi(\boldsymbol{r}) + \psi(b)\right]/\langle 1 - \psi(\boldsymbol{r}) + \psi(b)\rangle$, in the scheme here proposed the denominator is further expanded and the expansion-point dependence on $\psi(b)$ is cancelled, leading to Eq. (6), $n_+(\boldsymbol{r}) = n_{\mathrm{c}}\left[1 + \langle\psi(\boldsymbol{r})\rangle - \psi(\boldsymbol{r})\right]$. One should not confuse the choice of the expansion point with the freedom to choose the gauge. These two degrees of freedom were coupled in the analysis of Ref. [26], which leads to an incorrect interpretation of the gauge invariance. Whereas both linearization schemes are gauge invariant, distinct choices of the expansion point b in the standard approach yield different linearized equations, while here they remain invariant. We should also remark that the standard linearization procedure is based on an attempt to describe the asymptotic behaviour of the electrostatic potential in the vicinity of the expansion point at $r = b$ — being thus a *local* approach to the linearization — while in the scheme presented in the main text the linearization is based on a *global* description of the system, at the level of the whole free energy of the WS cell.

C   Formal derivation of the salt-free linearized osmotic pressure

In this Appendix it will be shown that the salt-free linearized osmotic pressure, Eq. (9), is given by a quadratic expansion of the nonlinear counterion density, Eq. (A13), at the WS-cell boundary,

$$\beta P_{\mathrm{DH}} = -\frac{\mathrm{d}\beta F_{\mathrm{DH}}}{\mathrm{d}V} = n_{\mathrm{c}}\left\{1 + \langle\bar\psi\rangle - \bar\psi(R) + \frac{1}{2}\left[\langle\bar\psi\rangle - \bar\psi(R)\right]^2 - \frac{1}{2}\left\langle\left[\langle\bar\psi\rangle - \bar\psi\right]^2\right\rangle\right\}, \tag{C1}$$

which may be obtained by truncating the expansion of the salt-free nonlinear PB osmotic pressure (4) to the quadratic terms,

$$\beta P = \frac{n_c \exp\left[\langle\bar{\psi}\rangle - \bar{\psi}(R)\right]}{\langle\exp\left[\langle\bar{\psi}\rangle - \bar{\psi}(r)\right]\rangle} = \beta P_{\mathrm{DH}} + \mathscr{O}\left(\left[\langle\bar{\psi}\rangle - \bar{\psi}(R)\right]^3, \left\langle\left[\langle\bar{\psi}\rangle - \bar{\psi}\right]^3\right\rangle\right), \tag{C2}$$

where the bar denotes equilibrium properties. One route to check that the salt-free linearized osmotic pressure (9) may be cast in the form (C1) is by using the linearized DH-like solution to the electrostatic potential (B4) and computing explicitly the spatial averages $\langle\Delta_1(\kappa R, \kappa r)/r\rangle$ and $\langle\Delta_1^2(\kappa R, \kappa r)/r^2\rangle$.

   Alternatively, Eq. (C1) may be checked by taking a *formal* functional derivative with respect to the WS-cell free volume V — analogously as performed in Section 3 of Ref. [7] for the nonlinear treatment; see also footnote [21] — of the salt-free linearized Helmholtz free energy functional (5), which is recast in the form

$$\beta\mathscr{F}_{\mathrm{DH}}[n_+(\boldsymbol{r})] = \int \mathrm{d}^3\boldsymbol{r}\, f[n_+(\boldsymbol{r})] + Z\left[\ln\left(n_c\zeta_+^3\right) - 1\right], \tag{C3}$$

$$f[n_+(\boldsymbol{r})] = \frac{1}{2}\,\psi(\boldsymbol{r})\rho(\boldsymbol{r}) + n_c\ln\left(n_c\zeta_+^3\right)\left[\frac{n_+(\boldsymbol{r})}{n_c} - 1\right] + \frac{1}{2}n_c\left[\frac{n_+(\boldsymbol{r})}{n_c} - 1\right]^2, \tag{C4}$$

where $\rho(\boldsymbol{r})$ and $\psi(\boldsymbol{r})$ are defined in Appendix A by Eqs. (A1) and (A3), respectively. The equilibrium counterion profile $\bar{n}_+(\boldsymbol{r})$ that minimizes the linearized version of the extended Helmholtz free-energy functional $\tilde{\mathscr{F}}_{\mathrm{DH}} = \mathscr{F}_{\mathrm{DH}} - \mu_{\mathrm{el}}\int \mathrm{d}^3\boldsymbol{r}\,\rho(\boldsymbol{r})$, with $\beta\bar{\mu}_{\mathrm{el}} = \ln\left(n_c\zeta_+^3\right) + \langle\bar{\psi}\rangle$, is given by

$$\bar{n}_+(\boldsymbol{r}) = n_c\left[1 + \langle\bar{\psi}\rangle - \bar{\psi}(\boldsymbol{r})\right]. \tag{C5}$$

The calculation of the linearized osmotic pressure $P_{\mathrm{DH}} = -\mathrm{d}F_{\mathrm{DH}}/\mathrm{d}V$ starting from the explicit form of the optimized linearized Helmholtz free energy $F_{\mathrm{DH}} = \mathscr{F}_{\mathrm{DH}}[\bar{n}_+(\boldsymbol{r})]$, Eq. (B9), turns out to be nontrivial, because both the linearized equilibrium counterion profile $\bar{n}_+(\boldsymbol{r})$, Eq. (B1), as well as the linearized equilibrium electrostatic potential $\bar{\psi}(\boldsymbol{r})$, Eq. (B4), depend implicitly on the WS-cell free volume V. However, because $\beta\mu_{\mathrm{el}}$ was introduced as a Lagrange multiplier to enforce the charge neutrality (A6), it is much easier to consider the total derivative with respect to the volume of the linearized version of the extended Helmholtz free-energy *functional* $\tilde{\mathscr{F}}_{\mathrm{DH}}[n_+(\boldsymbol{r})] = \mathscr{F}_{\mathrm{DH}}[n_+(\boldsymbol{r})] - \mu_{\mathrm{el}}\int \mathrm{d}^3\boldsymbol{r}\,\rho(\boldsymbol{r})$ — but now considering the Lagrange multiplier μ_{el} *independent* of the WS-cell free volume V — evaluated at the linearized optimized profile $n_+(\boldsymbol{r}) = \bar{n}_+(\boldsymbol{r})$,

$$\frac{\mathrm{d}\tilde{\mathscr{F}}_{\mathrm{DH}}[\bar{n}_+(\boldsymbol{r})]}{\mathrm{d}V} = \left.\frac{\delta\tilde{\mathscr{F}}_{\mathrm{DH}}[n_+(\boldsymbol{r})]}{\delta V}\right|_{\bar{n}_+(\boldsymbol{r})} = \left.\frac{\partial\tilde{\mathscr{F}}_{\mathrm{DH}}[n_+(\boldsymbol{r})]}{\partial V}\right|_{\bar{n}_+(\boldsymbol{r})} + \int \mathrm{d}^3\boldsymbol{r}'\left.\frac{\delta\tilde{\mathscr{F}}_{\mathrm{DH}}[n_+(\boldsymbol{r})]}{\delta n_+(\boldsymbol{r}')}\right|_{\bar{n}_+(\boldsymbol{r}')}\frac{\mathrm{d}\bar{n}_+(\boldsymbol{r}')}{\mathrm{d}V}, \tag{C6}$$

where the derivatives of $\tilde{\mathscr{F}}_{\mathrm{DH}}$ are taken with *fixed* μ_{el}. Because $\tilde{\mathscr{F}}_{\mathrm{DH}}[n_+(\boldsymbol{r})]$ is stationary with respect to the optimized profile $\bar{n}_+(\boldsymbol{r})$, $\left.\delta\tilde{\mathscr{F}}_{\mathrm{DH}}[n_+(\boldsymbol{r})]/\delta n_+(\boldsymbol{r}')\right|_{\bar{n}_+(\boldsymbol{r}')} = 0$, only the partial-derivative term contributes to the linearized osmotic pressure. Furthermore, because the only explicit dependence of $\tilde{\mathscr{F}}_{\mathrm{DH}}[n_+(\boldsymbol{r})]$ comes from the integration limit,[7] we are lead to

$$\frac{\partial\beta\tilde{\mathscr{F}}_{\mathrm{DH}}[n_+(\boldsymbol{r})]}{\partial V} = -n_c - \beta\mu_{\mathrm{el}}\frac{\partial}{\partial V}\int \mathrm{d}^3\boldsymbol{r}\,n_+(\boldsymbol{r}) + \frac{\partial}{\partial V}\int \mathrm{d}^3\boldsymbol{r}\,f[n_+(\boldsymbol{r})] + \frac{\mathrm{d}n_c}{\mathrm{d}V}\int \mathrm{d}^3\boldsymbol{r}\,\frac{\partial f[n_+(\boldsymbol{r})]}{\partial n_c}. \tag{C7}$$

Using the explicit form (C5) of $\bar{n}_+(\boldsymbol{r})$, we obtain

$$\left.\frac{\beta\bar{\mu}_{\mathrm{el}}}{n_c}\frac{\partial}{\partial V}\int \mathrm{d}^3\boldsymbol{r}\,n_+(\boldsymbol{r})\right|_{\bar{n}_+(\boldsymbol{r})} = \left[\ln\left(n_c\zeta_+^3\right) + \langle\bar{\psi}\rangle\right]\left[1 + \langle\bar{\psi}\rangle - \bar{\psi}(R)\right], \tag{C8}$$

$$\left.\frac{1}{n_c}\frac{\partial}{\partial V}\int \mathrm{d}^3\boldsymbol{r}\,f[n_+(\boldsymbol{r})]\right|_{\bar{n}_+(\boldsymbol{r})} = \bar{\psi}(R)\left[1 + \langle\bar{\psi}\rangle - \bar{\psi}(R)\right] + \ln\left(n_c\zeta_+^3\right)\left[\langle\bar{\psi}\rangle - \bar{\psi}(R)\right]$$

$$+ \frac{1}{2}\left[\langle\bar{\psi}\rangle - \bar{\psi}(R)\right]^2, \tag{C9}$$

$$\left.\frac{1}{n_c}\frac{\mathrm{d}n_c}{\mathrm{d}V}\int \mathrm{d}^3\boldsymbol{r}\,\frac{\partial f[n_+(\boldsymbol{r})]}{\partial n_c}\right|_{\bar{n}_+(\boldsymbol{r})} = \ln\left(n_c\zeta_+^3\right) + \frac{1}{2}\left\langle\left[\langle\bar{\psi}\rangle - \bar{\psi}\right]^2\right\rangle, \tag{C10}$$

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which yields the salt-free linearized osmotic pressure Eq. (C1).

D Canonical-ensemble equations

In this Appendix we derive and discuss some aspects of the canonical-ensemble equations.

For the nonlinear treatment, the PB Helmholtz free-energy functional,

$$\beta \mathscr{F}[n_\pm(\boldsymbol{r})] = \frac{1}{8\pi \ell_B} \int \mathrm{d}^3 \boldsymbol{r} \, [\nabla \psi(\boldsymbol{r})]^2 + \sum_{i=\pm} \int \mathrm{d}^3 \boldsymbol{r} \, n_i(\boldsymbol{r}) \left\{ \ln \left[n_i(\boldsymbol{r}) \zeta_i^3 \right] - 1 \right\}, \tag{D1}$$

is minimized with respect to $n_\pm(\boldsymbol{r})$ under the constraint of overall WS-cell charge neutrality, Eq. (16). We introduce a Lagrange multiplier μ_{el} and define the extended Helmholtz free-energy functional, $\tilde{\mathscr{F}} = \mathscr{F} - \mu_{\mathrm{el}} \int \mathrm{d}^3 \boldsymbol{r} \, \rho(\boldsymbol{r})$. Functional minimization of $\tilde{\mathscr{F}}$ with respect to $n_\pm(\boldsymbol{r})$ yields the Boltzmann factors, $n_\pm(\boldsymbol{r}) = \mathrm{e}^{\pm \beta \mu_{\mathrm{el}} \mp \psi(\boldsymbol{r})}/\zeta_\pm^3$. The Lagrange multiplier, $\beta \mu_{\mathrm{el}} = \pm \ln \left(c_\pm \zeta_\pm^3 \right) \mp \ln \left\langle \mathrm{e}^{\mp \psi(\boldsymbol{r})} \right\rangle$, is obtained by using the effective average definitions (11), which automatically satisfy the overall WS-cell charge neutrality, Eq. (16). Replacing into the Boltzmann factors, we obtain the nonlinear equilibrium density profiles, $n_\pm(\boldsymbol{r}) = c_\pm \, \mathrm{e}^{\mp \psi(\boldsymbol{r})} / \left\langle \mathrm{e}^{\mp \psi(\boldsymbol{r})} \right\rangle$. The simple ideal-gas relation (A17) between the nonlinear osmotic pressure and the WS-cell boundary density can be generalized in the presence of added salt. In this case, it can be shown that the nonlinear osmotic pressure is given by the total microionic density $n(\boldsymbol{r})$, Eq. (10), evaluated at the WS-cell boundary $r = R$,

$$\begin{aligned} \beta P &= - \left(\frac{\mathrm{d}\beta F}{\mathrm{d}V} \right)_s = n(R) = \frac{c_+ \, \mathrm{e}^{-\psi(R)}}{\left\langle \mathrm{e}^{-\psi(\boldsymbol{r})} \right\rangle} + \frac{c_- \, \mathrm{e}^{\psi(R)}}{\left\langle \mathrm{e}^{\psi(\boldsymbol{r})} \right\rangle} \\ &= (1 + 2s) n_c \left\{ 1 + \frac{1}{1 + 2s} \delta_1(R) + \frac{1}{2} \delta_2(R) - \frac{1}{2} \left\langle \delta_2(\boldsymbol{r}) \right\rangle + \mathscr{O} \left[\delta_3(R), \left\langle \delta_3(\boldsymbol{r}) \right\rangle \right] \right\}, \end{aligned} \tag{D2}$$

where the electrostatic potential differences $\delta_\nu(\boldsymbol{r})$ are given by (28). Let us now compare the linearized canonical osmotic pressure (20) with the quadratic truncation of the expansion of its nonlinear counterpart, Eq. (D2), about the uniform reference state. Because of the redefinition of the screening length κ^{-1} in terms of κ_c^{-1}, the spatial averages $\left\langle \Delta_1(\kappa R, \kappa r)/r \right\rangle$ and $\left\langle \Delta_1^2(\kappa R, \kappa r)/r^2 \right\rangle$ needed to evaluate $\left\langle \psi \right\rangle$ and $\left\langle \psi^2 \right\rangle$ will be multiplied by a factor $(1 + 2s)^{-1}$. Using the explicit DH-like solution to the electrostatic potential (B4), it is indeed possible to show that the linearized canonical osmotic pressure (20) corresponds to the truncation of the expansion (D2) up to the quadratic terms, i.e. $\beta P = \beta P_{\mathrm{DH}}^{\mathrm{can}} + \mathscr{O} \left[\delta_3(R), \left\langle \delta_3(\boldsymbol{r}) \right\rangle \right]$, with $\beta P_{\mathrm{DH}}^{\mathrm{can}} = n_{\mathrm{DH}}(R) + (1 + 2s) \left(n_c/2 \right) \left[\delta_2(R) - \left\langle \delta_2(\boldsymbol{r}) \right\rangle \right]$, where the first term corresponds to the sum of the *linearized* canonical densities at the WS-cell boundary. We see that the linearized canonical osmotic pressure *is not simply given* by the linearized boundary density $n_{\mathrm{DH}}(R)$, because of the presence of the quadratic terms.

For the linearized treatment, in order to minimize the linearized functional $\mathscr{F}_{\mathrm{DH}}[n_\pm(\boldsymbol{r})]$ under the overall WS-cell charge-neutrality constraint (16), we introduce a Lagrange multiplier μ_{el} and define the extended Helmholtz free-energy functional $\tilde{\mathscr{F}}_{\mathrm{DH}} = \mathscr{F}_{\mathrm{DH}} - \mu_{\mathrm{el}} \int \mathrm{d}^3 \boldsymbol{r} \, \rho(\boldsymbol{r})$. Functional minimization of $\tilde{\mathscr{F}}_{\mathrm{DH}}$ with respect to $n_\pm(\boldsymbol{r})$ leads to the equilibrium density profiles,

$$n_\pm(\boldsymbol{r}) = c_\pm \left[1 \pm \beta \mu_{\mathrm{el}} - \ln \left(c_\pm \zeta_\pm^3 \right) \mp \psi(\boldsymbol{r}) \right]. \tag{D3}$$

Using Eqs. (11) and (D3), we obtain that the Lagrange multiplier is related to the uniform-density chemical potentials and to the average electrostatic potential inside the WS cell,

$$\beta \mu_{\mathrm{el}} = \pm \ln \left(c_\pm \zeta_\pm^3 \right) + \left\langle \psi(\boldsymbol{r}) \right\rangle, \tag{D4}$$

analogously to the salt-free case, Eq. (B2). Inserting the equilibrium profiles (D3) into the Poisson equation (A2), leads to the linearized DH-like Eq. (18). Solving it for $\psi(\boldsymbol{r})$ leads again to the electrostatic potential (B4), with the average electrostatic potential inside the WS cell for an arbitrary cell-boundary potential $\psi(R)$ given by

$$\left\langle \psi(\boldsymbol{r}) \right\rangle = \psi(R) + \frac{2Z\kappa \ell_B}{\Delta_2(\kappa R, \kappa a)} - \frac{1}{1 + 2s}. \tag{D5}$$

At this point we should remark that — in the infinite-dilution limit $(R \to \infty, n_{\rm c} \to 0)$, but in the presence of excess salt $(s \to \infty$, finite $n_{\rm s})$ — the linearized electrostatic potential $\psi(r)$ reduces to the Yukawa screened electrostatic potential,

$$\lim_{\substack{R \to \infty \\ s \to \infty}} [\psi(r) - \psi(R)] = -\frac{Z\ell_B {\rm e}^{-\kappa(r-a)}}{(1+\kappa a)\, r}, \qquad \kappa = \sqrt{8\pi\ell_B n_{\rm s}}, \tag{D6}$$

which leads to the repulsive electrostatic component of the traditional DLVO interaction potential[27, 28] between two identical spherical particles of radius a whose centers are a distance r apart,

$$W(r) = Z^2 \ell_B \left(\frac{{\rm e}^{\kappa a}}{1+\kappa a}\right)^2 \frac{{\rm e}^{-\kappa r}}{r}. \tag{D7}$$

The phase diagram and dynamical properties of a suspension of spherical particles interacting through the effective DLVO pairwise potential (D7) were systematically investigated in Ref. [29] using molecular and lattice dynamics techniques. We should note that the polyion-polyion interaction potential within the traditional (symmetric) DH framework may be obtained from the *exact* (non-spherically symmetric) solution of the Helmholtz equation $\nabla^2 \psi(\boldsymbol{r}) = \kappa^2 \psi(\boldsymbol{r})$ for two spherical charged particles.[30] The large-separation $(r \to \infty)$ asymptotics of this pairwise potential leads directly to the DLVO interaction potential (D7). One should also keep in mind that the exact limiting laws (within the RPM) of the underlying DH theory[25] — associated with the Helmholtz equation — are only valid in the asymptotic limit of vanishing ionic strengths $(\kappa \to 0)$. Most likely this exactness does not apply for the asymmetric case of strongly charged colloids. Alternatively, the DLVO interaction potential (D7) may also be obtained by the large-separation asymptotics of the microion-averaged polyion-polyion potential of mean-force, obtained using the MSA integral equation for the polyion- and the microion-microion correlations in the PM.[31]

Inserting the linearized equilibrium density profiles (D3) into the linearized Helmholtz free-energy functional $\mathscr{F}_{\rm DH}$, Eq. (15), leads to the linearized Helmholtz free energy,

$$\begin{aligned} \beta F_{\rm DH} = \beta \mathscr{F}_{\rm DH}[n_\pm(\boldsymbol{r})]_{\rm equil} &= (1+s)Z \left\{ \ln\left[(1+s)n_{\rm c}\zeta_+^3\right] - 1 \right\} + sZ \left[\ln\left(sn_{\rm c}\zeta_-^3\right) - 1 \right] \\ &\quad + \frac{Z}{2} \left[\frac{Z\ell_B}{a} \frac{\Delta_1(\kappa R, \kappa a)}{\Delta_2(\kappa R, \kappa a)} - \frac{1}{1+2s} \right]. \end{aligned} \tag{D8}$$

The two first terms of (D8) correspond to the ideal-gas entropy of the uniform expansion densities $c_\pm$, while the last term represents the linearized excess Helmholtz free energy due to the polarization of the microionic cloud around the polyion. In the infinite-dilution limit and in the presence of excess salt $(R \to \infty, n_{\rm c} \to 0,$ but finite $n_{\rm s})$,

$$\lim_{\substack{R \to \infty \\ s \to \infty}} \frac{Z}{2} \left[\frac{Z\ell_B}{a} \frac{\Delta_1(\kappa R, \kappa a)}{\Delta_2(\kappa R, \kappa a)} - \frac{1}{1+2s} \right] = \frac{Z^2 \ell_B}{2a\,(1+\kappa a)}, \qquad \kappa = \sqrt{8\pi\ell_B n_{\rm s}}, \tag{D9}$$

it coincides with the polyion-counterion interaction free energy (including the polyion self-energy) obtained in an extended Debye-Hückel-Bjerrum approach for colloidal suspensions — cf. Eq. (2) of Ref. [32]. We note that the asymptotic *electrostatic excess free energy* (D9) — obtained by linearization of the PB WS-cell model functional — can be also obtained by computing the *electrostatic work* done in charging up the polyion surface in the framework of the traditional DH theory[33] — cf. Ref. [34], pp.339 — which is obtained by a Güntelberg charging process, where the polyion surface *is charged at fixed* screening length κ^{-1}. The Güntelberg[35] and the Debye[25] charging processes differ by the fact that in the latter the *whole system* (including the ionic atmosphere) is simultaneously charged.

The connection between the infinite-dilution $(R \to \infty)$ limit of the linearized excess Helmholtz free energy contained in Eq. (D8),

$$\lim_{\substack{R \to \infty \\ \text{finite } s}} \frac{Z}{2} \left[\frac{Z\ell_B}{a} \frac{\Delta_1(\kappa R, \kappa a)}{\Delta_2(\kappa R, \kappa a)} - \frac{1}{1+2s} \right] = \frac{Z}{2} \left[\frac{Z\ell_B}{a(1+\kappa a)} - \frac{1}{1+2s} \right], \tag{D10}$$

and the state-independent volume terms obtained by Roij *et al.*[36] was first reported by Warren, cf. Eqs. (7) and (11) of Ref. [37], followed by Denton, cf. Eq. (55) of Ref. [38]. Subtracting out from Eq. (D10) the polyion

self-energy, $Z^2\ell_B/(2a)$, and multiplying it by the polyion density of the suspension, $n_{\rm p} = \left(4\pi R^3/3\right)^{-1}$, yields the negative contributions of the state-independent volume terms obtained by Roij *et al.* — cf. Eq. (61) of Ref. [36],

$$\frac{Zn_{\rm p}}{2}\left[\frac{Z\ell_B}{a(1+\kappa a)} - \frac{1}{1+2s}\right] - \frac{Z^2\ell_B}{2a}n_{\rm p} = -\frac{Z^2\ell_B}{2}\,\frac{n_{\rm p}\kappa}{1+\kappa a} - \frac{2\pi\ell_B}{\kappa^2}\left(Zn_{\rm p}\right)^2. \tag{D11}$$

It has been claimed[36] that these volume-dependent (but state-independent) negative contributions to the Helmholtz free energy are responsible for driving a gas-liquid phase separation in dilute deionized aqueous colloidal suspensions.

In Subsection 3.2 it is shown that the linearized canonical osmotic pressure $P_{\rm DH}^{\rm can}$, Eq. (20), predicts the onset of a thermodynamical instability for some range of the parameters. Although it is not worthwhile to locate the binodal lines, since here the associated phase separation is a spurious result of the linearization, we would just like to mention how to determine them. For example, the salt-free binodal line that defines the boundary of the coexistence region is given by the coupled system of equations,

$$P_{\rm DH}^{\rm can}(\phi_{\rm G}, s=0) = P_{\rm DH}^{\rm can}(\phi_{\rm L}, s=0), \qquad \mu_{\rm p}(\phi_{\rm G}, s=0) = \mu_{\rm p}(\phi_{\rm L}, s=0), \tag{D12}$$

where $\mu_{\rm p}(\phi, s=0)$ is the salt-free chemical potential of the polyions,

$$\mu_{\rm p}(\phi, s=0) \equiv \frac{\rm d}{{\rm d}n_{\rm p}}\left(\frac{F_{\rm DH}}{\tilde{V}}\right)_{s=0} = F_{\rm DH}(\phi, s=0) + \frac{P_{\rm DH}^{\rm can}(\phi, s=0)}{n_{\rm p}(\phi)}, \tag{D13}$$

and $\tilde{V} \equiv 4\pi a^3/(3\phi) = 1/n_{\rm p}$ is the total WS-cell volume. In the presence of added salt ($s \neq 0$), the convexity of $P_{\rm DH}^{\rm can}$ is a necessary, but not sufficient condition for thermodynamical stability, as shown in Figure 1 by the comparison between the lines of vanishing canonical inverse compressibility, $\chi_{\rm can}^{-1} = 0$, and the canonical spinodal lines, $\Sigma(\phi, s) = 0$. Addition of salt *destabilizes* the suspension by increasing the unstable region to lower values of $\theta = 3Z\ell_B/a$, as also illustrated by the $s \neq 0$ spinodal lines in Figure 1. The corresponding binodal lines (not shown) are determined by generalizing Eqs. (D12) to the case of added salt ($s \neq 0$),

$$P_{\rm DH}^{\rm can}(\phi_{\rm G}, s) = P_{\rm DH}^{\rm can}(\phi_{\rm L}, s), \qquad \mu_{\rm p}(\phi_{\rm G}, s) = \mu_{\rm p}(\phi_{\rm L}, s), \tag{D14}$$

where the chemical potential of the polyions in the presence of added salt, $\mu_{\rm p}(\phi, s \neq 0) = F_{\rm DH}(\phi, s) - Zs\mu_{\rm s}(\phi, s) + P_{\rm DH}^{\rm can}(\phi, s)/n_{\rm p}(\phi)$, with the chemical potential of salt particles $\mu_{\rm s}(\phi, s)$ given by Eq. (G4). With added salt, there is (in the coexistence region) a redistribution of microion pairs between the dilute and the dense phases, which still obeys the WS-cell charge-neutrality constraint (16). Hence, inside the coexistence region ($\phi_{\rm G} < \phi < \phi_{\rm L}$) the two fluid phases will not have the same value of s (corresponding to the homogeneous system). Their values in the gas ($s_{\rm G}$) and the liquid ($s_{\rm L}$) phases are obtained by imposing the total conservation of salt particles,

$$s\phi\left(\phi_{\rm L} - \phi_{\rm G}\right) = s_{\rm L}\phi_{\rm L}\left(\phi - \phi_{\rm G}\right) + s_{\rm G}\phi_{\rm G}\left(\phi_{\rm L} - \phi\right), \tag{D15}$$

and the equality in both fluid phases of the chemical potential of salt particles $\mu_{\rm s}(\phi, s)$ — as given by Eq. (G4),

$$\mu_{\rm s}(\phi_{\rm G}, s_{\rm G}) = \mu_{\rm s}(\phi_{\rm L}, s_{\rm L}). \tag{D16}$$

An important and useful concept in charged colloidal systems is the charge renormalization[39,40] of the polyion bare charge Z for finite volume fractions ϕ. For highly charged polyions, i.e. in the $\sigma \equiv Z/(4\pi a^2) \to \infty$ limit, it has been shown by Alexander *et al.*[12] that the renormalized effective charge $Z_{\rm eff}$ in the salt-free system approaches a saturation value $Z_{\rm sat} \approx aw(\phi)/\ell_B$, with $w(\phi)$ assuming numerical values[12,41] around 9 to 15 in the volume-fraction range $0.01 \leq \phi \leq 0.1$. A self-consistent linearized osmotic pressure including charge renormalization effects would require the inclusion of additional terms due to the volume-fraction dependence of the effective charge $Z_{\rm eff} = Z_{\rm eff}(V)$, since the osmotic pressure is defined as the negative *total derivative* of the Helmholtz free energy with respect to the volume V. In other words, the linearized canonical osmotic pressure $P_{\rm DH}^{\rm can}$ taking into account charge-renormalization effects *is not simply* given by replacing $Z \to Z_{\rm eff}$ into Eq. (20). This point will be considered in a future work.[42] It is interesting to note, however, that the linearized critical threshold $\theta_{\rm crit}$ given by Eq. (24) is very close to the (largest) salt-free saturation ($Z \to \infty$) effective charge $\theta_{\rm sat} = 3Z_{\rm sat}\ell_B/a \approx 45$ determined by Alexander *et al.*[12] It has been speculated[3] that this

curious coincidence drives suspensions of highly charged colloids close to criticality. This might account for some of the experimental findings in dilute deionized aqueous suspensions of highly charged colloids,[43–45] which then would be explained by the presence of strong density fluctuations near the criticality.[3] Another consequence that effective charges are below the saturation value, and therefore also below the linearized critical threshold, is that charge renormalization would stabilize the suspension against phase separation, because the unstable region predicted by linearized theory is unreachable (or at least drastically reduced) when including renormalized effective charges. This fact was pointed out previously[46] using a generalized Debye-Hückel-Bjerrum approach for charged colloidal suspensions. In the present calculation, however, the critical behaviour is an artifact of the linearization, which is absent in the full nonlinear treatment. Therefore, the occurrence of a thermodynamical instability can only be explained beyond the WS-cell mean-field approximation, by including excluded-volume effects, *intercell* polyion-polyion, polyion-microion and microion-microion correlations that are neglected in the WS-cell mean-field PB picture.

E Semi-grand-canonical ensemble osmotic pressure

In this Appendix we discuss the relations between the nonlinear and the linearized versions of the semi-grand-canonical osmotic pressure.

For the nonlinear treatment, the PB semi-grand-canonical functional $\Omega \equiv \mathscr{F} - \sum_{i=\pm} \mu_i \int \mathrm{d}^3 r\, n_i(\boldsymbol{r})$, associated to fixed microion chemical potentials $\beta\mu_\pm = \ln\left(n_\mathrm{b}\zeta_\pm^3\right)$,

$$\beta\Omega[n_\pm(\boldsymbol{r})] = \frac{1}{8\pi\ell_B} \int \mathrm{d}^3 r\, [\nabla\psi(\boldsymbol{r})]^2 + \sum_{i=\pm} \int \mathrm{d}^3 r\, n_i(\boldsymbol{r}) \left\{ \ln\left[\frac{n_i(\boldsymbol{r})}{n_\mathrm{b}}\right] - 1 \right\}, \tag{E1}$$

is minimized with respect to $n_\pm(\boldsymbol{r})$ under the constraint of overall WS-cell charge neutrality, Eq. (16). We introduce a Lagrange multiplier μ_el and define the extended semi-grand-canonical functional, $\tilde{\Omega} = \Omega - \mu_\mathrm{el} \int \mathrm{d}^3 r\, \rho(\boldsymbol{r})$. Functional minimization of $\tilde{\Omega}$ with respect to $n_\pm(\boldsymbol{r})$ yields the Boltzmann factors, $n_\pm(\boldsymbol{r}) = n_\mathrm{b} e^{\pm\beta\mu_\mathrm{el}\mp\psi(\boldsymbol{r})}$. The Lagrange multiplier μ_el is obtained by imposing the overall WS-cell charge neutrality, Eq. (16) — see also Ref. [47] for a detailed derivation of the nonlinear Lagrange multiplier. After inserting it into the Boltzmann factors, we obtain the nonlinear equilibrium density profiles,

$$n_\pm(\boldsymbol{r}) = \frac{\sqrt{n_\mathrm{c}^2 + (2n_\mathrm{b})^2\alpha_+\alpha_-} \pm n_\mathrm{c}}{2\alpha_\pm} e^{\pm\langle\psi\rangle\mp\psi(\boldsymbol{r})} = \left[c_\pm^{(1)} + \frac{1}{4}(1-\eta^2)\frac{n_\mathrm{c}}{\eta}\langle\delta_2(\boldsymbol{r})\rangle \right] \times$$

$$\times \left[1 \pm \delta_1(\boldsymbol{r}) + \frac{1}{2}\delta_2(\boldsymbol{r}) - \frac{1}{2}\langle\delta_2(\boldsymbol{r})\rangle \right] + \mathscr{O}\left[\delta_3(\boldsymbol{r}), \langle\delta_3(\boldsymbol{r})\rangle\right], \tag{E2}$$

with $c_\pm^{(1)}$, $\delta_\nu(\boldsymbol{r})$ and η, given, respectively, by Eqs. (26), (28) and (32) in Subsection 3.3, and $\alpha_\pm \equiv \left\langle e^{\pm\langle\psi\rangle\mp\psi(\boldsymbol{r})} \right\rangle = 1 + \frac{1}{2}\langle\delta_2(\boldsymbol{r})\rangle + \mathscr{O}\left[\langle\delta_3(\boldsymbol{r})\rangle\right]$. At the nonlinear PB mean-field level the simple ideal-gas relation between the osmotic pressure and the total microionic density $n(\boldsymbol{r})$, Eq. (10), evaluated at the WS-cell boundary $r = R$ is still valid, leading to

$$\beta P = -\left(\frac{\mathrm{d}\beta\Omega}{\mathrm{d}V}\right)_{\mu_\pm} = n(R) = \frac{n_\mathrm{c}}{\eta}\left\{ 1 + \eta\delta_1(R) + \frac{1}{2}\delta_2(R) - \frac{\eta^2}{2}\langle\delta_2(\boldsymbol{r})\rangle + \mathscr{O}\left[\delta_3(R), \langle\delta_3(\boldsymbol{r})\rangle\right] \right\}. \tag{E3}$$

Let us again compare the linearized semi-grand-canonical osmotic pressure (35) with a quadratic expansion about the zero-th order Donnan densities $c_\pm^{(1)}$, Eqs. (26), of its nonlinear counterpart, Eq. (E3). Now, because of the redefinition of κ, the spatial averages $\langle\Delta_1(\kappa R, \kappa r)/r\rangle$ and $\langle\Delta_1^2(\kappa R, \kappa r)/r^2\rangle$ needed to evaluate $\langle\psi\rangle$ and $\langle\psi^2\rangle$ are multiplied by a factor η. Using again the explicit DH solution (B4), it is possible to show that the linearized semi-grand-canonical osmotic pressure (35) corresponds to the truncation of the expansion (E3) up to the quadratic terms, i.e. $\beta P = \beta P_\mathrm{DH}^\mathrm{sgc} + \mathscr{O}\left[\delta_3(R), \langle\delta_3(\boldsymbol{r})\rangle\right]$, with $\beta P_\mathrm{DH}^\mathrm{sgc} = n_\mathrm{DH}(R) + [n_\mathrm{c}/(2\eta)]\left[\delta_2(R) - \eta^2\langle\delta_2(\boldsymbol{r})\rangle\right]$, where the first term represents the sum of the *linearized* semi-grand-canonical densities at the WS-cell boundary. We see again that the linearized semi-grand-canonical osmotic pressure *does not correspond* to the linearized boundary density $n_\mathrm{DH}(R)$, because of the presence of the quadratic terms.

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F Linearized averaged densities for the semi-grand-canonical ensemble

In this Appendix it will be shown that the self-consistent linearized averaged densities for the semi-grand-canonical ensemble are given by the state-independent zero-th order Donnan densities, which are obtained by a self-consistent minimization of the linearized semi-grand-canonical functional under the WS-cell charge-neutrality constraint.

To obtain the self-consistent averaged densities *up to quadratic order* we need to expand the nonlinear semi-grand-canonical functional, Eq. (E1), *up to cubic order* about the (*a priori* unknown) effective average densities $\langle n_\pm(\boldsymbol{r}) \rangle \equiv (1/V) \int \mathrm{d}^3 \boldsymbol{r}\, n_\pm(\boldsymbol{r})$,

$$
\beta \Omega[n_\pm(\boldsymbol{r})] = \frac{1}{8\pi\ell_B} \int \mathrm{d}^3\boldsymbol{r}\, [\nabla\psi(\boldsymbol{r})]^2 + V \sum_{i=\pm} \langle n_i \rangle \left[\ln \frac{\langle n_i \rangle}{n_{\mathrm{b}}} - 1 \right] + \sum_{i=\pm} \left[\langle n_i \rangle \ln \frac{\langle n_i \rangle}{n_{\mathrm{b}}} \right] \int \mathrm{d}^3\boldsymbol{r}\, \delta_i(\boldsymbol{r})
$$
$$
+ \frac{1}{2} \sum_{i=\pm} \langle n_i \rangle \int \mathrm{d}^3\boldsymbol{r}\, \delta_i^2(\boldsymbol{r}) - \frac{1}{6} \sum_{i=\pm} \langle n_i \rangle \int \mathrm{d}^3\boldsymbol{r}\, \delta_i^3(\boldsymbol{r}) + \mathscr{O}\left[\int \mathrm{d}^3\boldsymbol{r}\, \delta_i^4(\boldsymbol{r}) \right], \tag{F1}
$$

where we introduced the relative deviations about the averaged densities,

$$
\delta_\pm(\boldsymbol{r}) \equiv \frac{n_\pm(\boldsymbol{r})}{\langle n_\pm \rangle} - 1. \tag{F2}
$$

Keeping only quadratic terms in Eq. (F1) is *similar in spirit* to the quadratic expansion presented in Eq. (13) of Ref. [24]. However, we want to stress that, in general, the unknown average expansion densities $\langle n_\pm \rangle$ depend itself on the ionic profiles. Functional minimization of Eq. (F1) with respect to the profiles $n_\pm(\boldsymbol{r})$ must take this fact into account, in addition to the WS-cell charge-neutrality constraint, Eq. (16). Eventually, for a linearized theory, the self-consistent expansion densities $c_\pm^{(1)}$ turn out to be indeed independent on the ionic profiles, cf. Eqs. (26), but this can only be derived *a posteriori*.

We introduce a Lagrange multiplier μ_{el} to ensure the overall WS-cell charge neutrality (16), and define the extended semi-grand-canonical functional, $\tilde{\Omega} = \Omega - \mu_{\mathrm{el}} \int \mathrm{d}^3\boldsymbol{r}\, \rho(\boldsymbol{r})$. Functional minimization of $\tilde{\Omega}$ with respect to $n_\pm(\boldsymbol{r})$ leads to the Euler-Lagrange or stationary conditions, $\delta\tilde{\Omega}/\delta n_\pm(\boldsymbol{r}) = 0$, which may be cast in the form

$$
n_\pm(\boldsymbol{r}) = \langle n_\pm \rangle \left\{ 1 \pm [\beta\mu_{\mathrm{el}} - \psi(\boldsymbol{r})] - \ln \frac{\langle n_\pm \rangle}{n_{\mathrm{b}}} + \frac{1}{2}\delta_\pm^2(\boldsymbol{r}) + \mathscr{O}\left[\delta_\pm^3(\boldsymbol{r}), \langle \delta_\pm^3(\boldsymbol{r}) \rangle \right] \right\}, \tag{F3}
$$

where we have neglected the cubic averaged contribution, $\mathscr{O}\left[\langle \delta_\pm^3(\boldsymbol{r}) \rangle \right]$, because the neglected quartic term of (F1) will also contributed to it. To obtain the averages $\langle n_\pm \rangle$ self-consistently, we integrate $n_\pm(\boldsymbol{r})$ over the volume to obtain the consistency relations,

$$
\langle n_\pm(\boldsymbol{r}) \rangle = n_{\mathrm{b}} \exp \left\{ \pm [\beta\mu_{\mathrm{el}} - \langle \psi(\boldsymbol{r}) \rangle] + \frac{1}{2} \langle \delta_\pm^2(\boldsymbol{r}) \rangle + \mathscr{O}\left[\langle \delta_\pm^3(\boldsymbol{r}) \rangle \right] \right\}, \tag{F4}
$$

where the Lagrange multiplier μ_{el} is found by imposing the overall WS-cell charge neutrality (16). We should stress that in addition to the chemical potentials of microions $\mu_\pm = \beta^{-1} \ln\left(n_{\mathrm{b}}\zeta_\pm^3\right)$ that define the semi-grand-canonical ensemble, we introduced a *Lagrange multiplier* μ_{el}, whose role is twofold: besides the overall WS-cell charge neutrality (16), it also ensures the gauge invariance of the electrostatic potential $\psi(\boldsymbol{r})$. We should not confuse the chemical potentials of microions $\mu_\pm$, which are fixed by the bulk salt concentration n_{b} of the reservoir, with the linearized Lagrange multiplier μ_{el}, which is associated with the Donnan effect and ensures the charge neutrality of the WS cell, Eq. (16).

Before we derive the averages consistent with a *linearization* of the PB equation, let us also obtain the self-consistent averages corresponding to a *quadratic approximation* of the nonlinear equation. Noting that $\delta_\pm(\boldsymbol{r}) = \pm\delta_1(\boldsymbol{r}) + \mathscr{O}[\delta_2(\boldsymbol{r}), \langle \delta_2(\boldsymbol{r}) \rangle]$ and neglecting cubic terms in Eqs. (F3) and (F4) leads to the quadratic self-consistent averages, Eqs. (29),

$$
c_\pm^{(2)} \equiv \langle n_\pm(\boldsymbol{r}) \rangle = \frac{\sqrt{n_{\mathrm{c}}^2 + (2n_{\mathrm{b}})^2 \mathrm{e}^{\langle \delta_2(\boldsymbol{r}) \rangle}} \pm n_{\mathrm{c}}}{2}, \tag{F5}
$$

and the quadratic equilibrium density profiles,

$$n_\pm(\boldsymbol{r}) = c_\pm^{(2)} \left[1 \pm \delta_1(\boldsymbol{r}) + \frac{1}{2}\delta_2(\boldsymbol{r}) - \frac{1}{2}\langle \delta_2(\boldsymbol{r}) \rangle \right], \tag{F6}$$

where the electrostatic potential ν-th order difference $\delta_\nu(\boldsymbol{r})$ is defined by (28), and the superscript in $c_\pm^{(2)}$ emphasizes the fact that the average densities $c_\pm$ were obtained under a quadratic approximation. These correspond indeed to the *quadratic* expansions of the nonlinear PB average densities and equilibrium density profiles, respectively, and are correct up to $\delta_2(\boldsymbol{r})$ (quadratic) terms. Here we may see another advantage of the gauge-invariant formulation: it provides us a systematic way to consider self-consistent higher-order approximations of the nonlinear equations, while the fixed-gauge analysis of Deserno and von Grünberg[24] does not allow them to extend their calculations to include higher-order terms.

However, in order to be consistent with a *linearization* of the PB equation one needs to neglect also the quadratic terms in the approximate Euler-Lagrange conditions (F3), although ensemble invariance associated with a *global* self-consistency of the Legendre transformation will require to include them — cf. Appendix G. It is clear that ignoring these terms will yield the *state-independent* zero-th order Donnan densities, Eqs. (26), as the self-consistent linearized averaged densities,

$$c_\pm^{(1)} \equiv \langle n_\pm(\boldsymbol{r}) \rangle = \frac{\sqrt{n_c^2 + (2n_b)^2} \pm n_c}{2}, \tag{F7}$$

and the linearized equilibrium density profiles,

$$n_\pm(\boldsymbol{r}) = c_\pm^{(1)} \left[1 \pm \delta_1(\boldsymbol{r}) \right], \tag{F8}$$

where the superscript in $c_\pm^{(1)}$ emphasizes the fact that the average densities $c_\pm$ were obtained under a linearized approximation. Deserno and von Grünberg[24] justify this choice for the expansion densities — written in terms of an optimal linearization point $\bar{\psi}_{\mathrm{opt}}$ defined by $c_\pm^{(1)} = n_b e^{\mp \bar{\psi}_{\mathrm{opt}}}$ — by arguing that any other choice for the linearization point would lead to conflicting inequalities involving nonlinear and linearized averages. In a gauge-invariant formulation, however, the justification is indeed based on the self-consistent *minimization* of the linearized semi-grand-canonical functional $\Omega_{\mathrm{DH}}[n_\pm(\boldsymbol{r})]$, which is obtained by truncating the expansion of the nonlinear functional $\Omega[n_\pm(\boldsymbol{r})]$, given by Eq. (F1), only up to the quadratic terms and neglecting (consistently under linearization) the quadratic contribution in the approximated averaged Euler-Lagrange equations, Eq. (F4). Although *internal* self-consistency (within the semi-grand-canonical ensemble) is achieved by using the linearized self-consistent averaged densities (26), we show in Appendix G that *global* self-consistency under linearization — associated with ensemble-invariant linearized equations — will also require the inclusion of the quadratic state-dependent terms of the self-consistent averaged densities (29).

We should remark that compared to the salt-free and canonical cases, cf. Eqs. (B2) and (D4), here the linearized equilibrium Lagrange multiplier $\beta\mu_{\mathrm{el}}$ has an additional contribution due to the microion chemical potentials of the infinite salt reservoir,

$$\beta\mu_{\mathrm{el}} = \pm \ln \left[c_\pm^{(1)} \zeta_\pm^3 \right] + \langle \psi(\boldsymbol{r}) \rangle \mp \beta\mu_\pm. \tag{F9}$$

Inserting the linearized equilibrium profiles (F8) into the Poisson equation (A2), leads to the DH-like Eq. (31). Solving it for $\psi(\boldsymbol{r})$ leads again to the electrostatic potential (B4), with the average electrostatic potential inside the WS cell for an arbitrary boundary potential $\psi(R)$ given by

$$\langle \psi(\boldsymbol{r}) \rangle = \psi(R) + \frac{2Z\kappa\ell_B}{\Delta_2(\kappa R, \kappa a)} - \eta. \tag{F10}$$

Inserting the linearized equilibrium density profiles (F8) into the linearized semi-grand-canonical functional Ω_{DH}, Eq. (25), leads to the linearized semi-grand-canonical potential,

$$\beta\Omega_{\mathrm{DH}} = \beta\Omega_{\mathrm{DH}}[n_\pm(\boldsymbol{r})]_{\mathrm{equil}} = \sum_{i=\pm} V c_i^{(1)} \left\{ \ln \left[\frac{c_i^{(1)}}{n_b} \right] - 1 \right\} + \frac{Z}{2} \left[\frac{Z\ell_B}{a} \frac{\Delta_1(\kappa R, \kappa a)}{\Delta_2(\kappa R, \kappa a)} - \eta \right]$$

$$= Z \left[\operatorname{arctanh} \eta - \frac{1}{\eta} - \frac{\eta}{2} + \frac{Z\ell_B}{2a} \frac{\Delta_1(\kappa R, \kappa a)}{\Delta_2(\kappa R, \kappa a)} \right]. \tag{F11}$$

G   Legendre transformation at the linearized level

In this Appendix we discuss the differences between the Legendre transformation connecting the canonical and the semi-grand-canonical ensembles at the level of the linearized functionals (before the functional minimization) and of the linearized thermodynamic potentials (after the functional minimization). It is shown that, in order to preserve the ensemble invariance of the linearized equations, quadratic contributions to the linearized expansion densities should be included in the former case, which are automatically included in the latter case.

At the nonlinear PB level the osmotic pressures obtained in the two distinct (canonical and semi-grand-canonical) ensembles are completely equivalent,[48] provided we map them using the nonlinear relation

$$(n_{\rm c} + n_{\rm s})n_{\rm s} = \langle n_+(\boldsymbol{r}) \rangle \langle n_-(\boldsymbol{r}) \rangle = n_{\rm b}^2 \left\langle {\rm e}^{\psi(\boldsymbol{r})} \right\rangle \left\langle {\rm e}^{-\psi(\boldsymbol{r})} \right\rangle , \tag{G1}$$

where $n_{\rm s} \equiv \langle n_-(\boldsymbol{r}) \rangle$ is the effective average salt concentration in the colloidal suspension. The exact (at the mean-field level) relation (G1) follows directly from the gauge-invariant forms of the nonlinear average densities (27). Therefore, up to quadratic order, the linearized osmotic pressures are related by the transformation of the effective total average density of microions in the two ensembles,

$$n \equiv n_{\rm c} + 2n_{\rm s} = (1 + 2s)\, n_{\rm c} \to \langle n_+(\boldsymbol{r}) \rangle + \langle n_-(\boldsymbol{r}) \rangle = \frac{n_{\rm c}}{\eta} \left\{ 1 + \frac{1}{2}\left(1 - \eta^2\right) \langle \delta_2(\boldsymbol{r}) \rangle + \mathscr{O}\left[\langle \delta_3(\boldsymbol{r}) \rangle \right] \right\}. \tag{G2}$$

Because of the quadratic contribution in Eq. (G2), the linearized osmotic pressures obtained in the two ensembles *do not have the same form* when they are mapped using the zero-th order renormalization $(1 + 2s) \to \eta^{-1}$. In other words, although for the nonlinear equations the Legendre transformation between the canonical and the semi-grand-canonical ensembles is exact, the same does not hold for the linearized equations: one needs to use the approximated mapping (G2) and expand consistently the linearized osmotic pressure up to quadratic-order terms. This introduces an additional source of deviations for the linearized semi-grand-canonical equations of state. In particular, the thermodynamically-conjugated density — in the semi-grand-canonical ensemble, where $\Omega_{\rm DH} = \Omega_{\rm DH}(\mu_{\rm s}, n_{\rm p})$ — to the (total) chemical potential of salt particles, $\mu_{\rm s} = \mu_+ + \mu_-$, that should correspond to the (effective) total average density of microions inside the colloidal suspension, $n \equiv -2\,(\partial/\partial\mu_{\rm s})\,(\Omega_{\rm DH}/V)$, is indeed given by the right-hand side of Eq. (G2) neglecting cubic and higher-order contributions. This conjugated density, however, is *inconsistent* — up to the quadratic order, but consistent under *linearization* — with the state-independent zero-th order Donnan densities (26), i.e. $n = \langle n_+(\boldsymbol{r}) \rangle + \langle n_-(\boldsymbol{r}) \rangle \neq c_+^{(1)} + c_-^{(1)} = n_{\rm c}/\eta$, because of the presence of the quadratic contribution in Eq. (G2).

An alternative procedure to the Legendre transformation of the linearized Helmholtz free-energy *functional* $\mathscr{F}_{\rm DH}[n_\pm(\boldsymbol{r})]$ — which is done, as presented in Appendix F, *before* the functional minimization with respect to the profiles — is to perform it *after* the functional minimization, at the Helmholtz *free-energy* level, $F_{\rm DH} = \mathscr{F}_{\rm DH}[n_\pm(\boldsymbol{r})]_{\rm equil}$. Because in the canonical ensemble the total number of positive and negative microions $Q_\pm$ inside a WS cell are known *a priori*, the Legendre transformation that maps the linearized Helmholtz free energy $F_{\rm DH}$ into the linearized semi-grand-canonical potential,[49] $\hat{\Omega}_{\rm DH} = F_{\rm DH} - \mu_+ Q_+ - \mu_- Q_-$, can then be obtained without any further approximations for the expansion densities. For this purpose it is convenient to recall the definition of the *total* volume of the WS cell $\tilde{V}$ and of the *nominal* densities of counterions, polyions and salt particles,

$$\tilde{V} \equiv \frac{V}{1 - \phi}, \qquad \tilde{n}_{\rm c} \equiv n_{\rm c}\,(1 - \phi), \qquad n_{\rm p} \equiv \frac{1}{\tilde{V}} = \phi \left(\frac{4\pi}{3} a^3 \right)^{-1}, \qquad \tilde{n}_{\rm s} \equiv n_{\rm s}\,(1 - \phi). \tag{G3}$$

It is important to stress that the *nominal* densities should be used, instead of the *effective* ones. Introducing the linearized Helmholtz free-energy density, $f_{\rm DH} \equiv F_{\rm DH}/\tilde{V} = f_{\rm DH}\,(\tilde{n}_{\rm s}, n_{\rm p})$, where $F_{\rm DH}$ in the presence of added salt is given by Eq. (D8), one may check that the Legendre transformation at the linearized *free-energy* level is indeed *exact*, since the *explicit* computation of the linearized chemical potentials of polyions $\mu_{\rm p} \equiv \partial f_{\rm DH}/\partial n_{\rm p}$, and of salt particles,

$$\beta\mu_{\rm s} \equiv \frac{\partial \beta f_{\rm DH}}{\partial \tilde{n}_{\rm s}} = \ln\left[(1 + s)n_{\rm c}\zeta_+^3 \right] + \ln\left(sn_{\rm c}\zeta_-^3 \right) - \langle \delta_2(\boldsymbol{r}) \rangle , \tag{G4}$$

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shows that they satisfy the Euler relation

$$P_{\text{DH}}^{\text{can}} = \tilde{n}_{\text{s}}\mu_{\text{s}} + n_{\text{p}}\mu_{\text{p}} - f_{\text{DH}}, \tag{G5}$$

where the linearized *canonical* osmotic pressure entering into Eq. (G5), $P_{\text{DH}}^{\text{can}}$, is given by Eq. (20) and the quadratic electrostatic-potential deviation in the canonical ensemble reads

$$
\begin{aligned}
\langle \delta_2(\boldsymbol{r}) \rangle = {} & -\frac{1}{(1+2s)^2} - \frac{1}{1+2s} \frac{Z\kappa\ell_B}{2\Delta_2^2(\kappa R, \kappa a)} \times \\
& \times \left[\frac{\Delta_1(\kappa R, \kappa a)}{\kappa a} [\Delta_1(\kappa R, \kappa a) - \Delta_2(\kappa R, \kappa a)] - 4\kappa a \left(1 - \kappa^2 R^2\right) - 4\kappa^3 R^3 \right].
\end{aligned}
\tag{G6}
$$

It should also be remarked that Eq. (G4) corresponds to the truncation of the expansion of the exact nonlinear mapping (G1) up to quadratic-order terms,

$$\beta\mu_{\text{s}} = \ln\left[\frac{(n_{\text{c}}+n_{\text{s}})n_{\text{s}}\zeta_+^3\zeta_-^3}{\langle e^{\psi(\boldsymbol{r})} \rangle \langle e^{-\psi(\boldsymbol{r})} \rangle}\right] = \ln\left[(1+s)n_{\text{c}}\zeta_+^3\right] + \ln\left(sn_{\text{c}}\zeta_-^3\right) - \langle\delta_2(\boldsymbol{r})\rangle + \mathcal{O}\left[\langle\delta_3(\boldsymbol{r})\rangle\right]. \tag{G7}$$

The thermodynamical relation (G5) can also be viewed as defining the Legendre transformation. Instead of obtaining the osmotic-pressure isotherms for a constant number of salt particles inside the WS cell (canonical case, fixed s), we may consider them at fixed chemical potential of salt particles μ_{s} (semi-grand-canonical case), which corresponds to a system in electrochemical equilibrium with an infinite salt reservoir of bulk density n_{b}, defined by

$$\beta\mu_{\text{s}} \equiv \beta\mu_+ + \beta\mu_- = \ln\left(n_{\text{b}}^2\zeta_+^3\zeta_-^3\right). \tag{G8}$$

Solution of the nonlinear equation defined by (G4) and (G8) yields the Legendre transformation in an implicit parametric form,

$$s(\phi, n_{\text{b}}) = \frac{\sqrt{1 + [2n_{\text{b}}/n_{\text{c}}(\phi)]^2\, e^{\langle\delta_2(\boldsymbol{r})\rangle}} - 1}{2}, \qquad n_{\text{c}}(\phi) = \frac{3Z}{4\pi a^3}\left(\frac{\phi}{1-\phi}\right), \tag{G9}$$

with $\langle\delta_2(\boldsymbol{r})\rangle$ given by Eq. (G6). The linearized *semi-grand-canonical* osmotic pressure, $\hat{P}_{\text{DH}}^{\text{sgc}} = \hat{P}_{\text{DH}}^{\text{sgc}}(\phi, n_{\text{b}})$, is then obtained by inserting the Legendre transformation $s = s(\phi, n_{\text{b}})$ into the linearized *canonical* osmotic pressure $P_{\text{DH}}^{\text{can}} = P_{\text{DH}}^{\text{can}}(\phi, s)$, Eq. (20). In other words, if the linearized osmotic pressures would be ensemble invariant, they would be related by $\hat{P}_{\text{DH}}^{\text{sgc}}(\phi, n_{\text{b}}) \equiv P_{\text{DH}}^{\text{can}}[\phi, s(\phi, n_{\text{b}})]$. We should remark that the linearized semi-grand-canonical osmotic pressure obtained by this procedure, $\hat{P}_{\text{DH}}^{\text{sgc}}(\phi, n_{\text{b}})$, which should in principle agree with $P_{\text{DH}}^{\text{sgc}}(\phi, n_{\text{b}})$, given by Eq. (35), in fact *do not coincide,* revealing that their thermodynamic self-consistency is only satisfied internally to the specific ensemble.

The disagreement between the two distinct linearized semi-grand-canonical osmotic pressures, $\hat{P}_{\text{DH}}^{\text{sgc}}(\phi, n_{\text{b}}) \neq P_{\text{DH}}^{\text{sgc}}(\phi, n_{\text{b}})$ — obtained by Legendre transformations performed pre- and pos-minimization of the linearized functional $\mathscr{F}_{\text{DH}}[n_\pm(\boldsymbol{r})]$ with respect to the profiles — may be traced back to the neglected quadratic contribution in the self-consistent linearized averaged densities (26). Although the neglect of this state-dependent contribution in the average densities (29) is justified to ensure mathematical consistency of the truncation under the linearized approximation, in order to obtain *global* thermodynamic self-consistency (i.e., in order to preserve the ensemble invariance) one needs to keep *all terms* of the quadratic truncation of the Euler-Lagrange equations, regardless of its apparent mathematical inconsistency. This leads to the average densities (29), which include the quadratic state-dependent contribution $\langle\delta_2(\boldsymbol{r})\rangle$ — in contrast to Eqs. (26), which neglect it. Compared to the linearized semi-grand-canonical potential Ω_{DH}, Eq. (F11), which uses the state-independent zero-th order Donnan densities (26) as expansion densities, an augmented version $\hat{\Omega}_{\text{DH}}$ using the quadratic average densities (29) will have an additional state-dependent quadratic contribution,

$$\beta\hat{\Omega}_{\text{DH}}\left(\mu_{\text{s}}, n_{\text{p}}\right) = Z\left[\operatorname{arctanh}\hat{\eta} - \frac{1}{\hat{\eta}} - \frac{\hat{\eta}}{2} + \frac{Z\ell_B}{2a}\frac{\Delta_1(\hat{\kappa}R, \hat{\kappa}a)}{\Delta_2(\hat{\kappa}R, \hat{\kappa}a)} + \frac{1}{2\hat{\eta}}\langle\delta_2(\boldsymbol{r})\rangle\right], \tag{G10}$$

where the parameter $\hat{\eta}$ and the (effective) Debye screening length $\hat{\kappa}^{-1}$ in the suspension,

$$\hat{\eta} \equiv \frac{n_{\text{c}}}{\sqrt{n_{\text{c}}^2 + (2n_{\text{b}})^2 e^{\langle\delta_2(\boldsymbol{r})\rangle}}}, \qquad \hat{\kappa}^2 = \frac{\kappa_{\text{c}}^2}{\hat{\eta}} = \frac{\kappa_{\text{b}}^2 e^{\langle\delta_2(\boldsymbol{r})\rangle/2}}{\sqrt{1-\hat{\eta}^2}}, \tag{G11}$$

are now given implicitly in terms of the quadratic electrostatic-potential deviation in the *semi-grand-canonical* ensemble, which is obtained by replacing $(1 + 2s) \to \hat{\eta}^{-1}$ and $\kappa \to \hat{\kappa}$ in the expression of its canonical counterpart, Eq. (G6). These yield the ensemble invariant, *globally* self-consistent linearized semi-grand-canonical equations of state,

$$\hat{n} \equiv -\frac{2\partial}{\partial\mu_{\mathrm{s}}}\left(\frac{\hat{\Omega}_{\mathrm{DH}}}{V}\right) = \frac{n_{\mathrm{c}}}{\hat{\eta}} = \sqrt{n_{\mathrm{c}}^2 + (2n_{\mathrm{b}})^2 \mathrm{e}^{\langle\delta_2(\boldsymbol{r})\rangle}} = c_+^{(2)} + c_-^{(2)}, \tag{G12}$$

$$\beta\hat{P}_{\mathrm{DH}}^{\mathrm{sgc}} \equiv -\left(\frac{\mathrm{d}\beta\hat{\Omega}_{\mathrm{DH}}}{\mathrm{d}V}\right)_{\mu_{\mathrm{s}}} = \frac{n_{\mathrm{c}}}{\hat{\eta}}\left\{1 + \frac{Z\hat{\kappa}\ell_B\hat{\eta}}{4\Delta_2^2(\hat{\kappa}R,\hat{\kappa}a)}\left[\frac{\Delta_1(\hat{\kappa}R,\hat{\kappa}a)}{\hat{\kappa}a} \times \right.\right.$$

$$\left.\left. \times \, [\Delta_1(\hat{\kappa}R,\hat{\kappa}a) - \Delta_2(\hat{\kappa}R,\hat{\kappa}a)] - 4\hat{\kappa}a\left(1 + \frac{2}{3}\hat{\kappa}^2a^2 - \hat{\kappa}^2R^2\right) - \frac{4}{3}\hat{\kappa}^3R^3\right]\right\}, \tag{G13}$$

where the derivatives must take the $\langle\delta_2(\boldsymbol{r})\rangle$ parametric implicit dependence of Eqs. (G11) into account,

$$\frac{\partial}{\partial\mu_{\mathrm{s}}} = -\hat{\eta}\left(1 - \hat{\eta}^2\right)\left(1 + \frac{1}{2}\frac{\partial\langle\delta_2\rangle}{\partial\mu_{\mathrm{s}}}\right)\frac{\partial}{\partial\hat{\eta}} + \frac{\hat{\kappa}}{2}\left(1 - \hat{\eta}^2\right)\left(1 + \frac{1}{2}\frac{\partial\langle\delta_2\rangle}{\partial\mu_{\mathrm{s}}}\right)\frac{\partial}{\partial\hat{\kappa}}, \tag{G14}$$

$$\frac{\mathrm{d}}{\mathrm{d}V} = \frac{\partial}{\partial V} - \frac{\hat{\eta}}{V}\left(1 - \hat{\eta}^2\right)\left(1 + \frac{V}{2}\frac{\mathrm{d}\langle\delta_2\rangle}{\mathrm{d}V}\right)\frac{\partial}{\partial\hat{\eta}} - \frac{\hat{\kappa}\hat{\eta}^2}{2V}\left[1 - \frac{V}{2}\left(\frac{1 - \hat{\eta}^2}{\hat{\eta}^2}\right)\frac{\mathrm{d}\langle\delta_2\rangle}{\mathrm{d}V}\right]\frac{\partial}{\partial\hat{\kappa}}. \tag{G15}$$

The (effective) total average density of microions $\hat{n}$, Eq. (G12), and the linearized semi-grand-canonical osmotic pressure $\hat{P}_{\mathrm{DH}}^{\mathrm{sgc}}$, Eq. (G13), are now fully consistent with their canonical counterparts, given respectively by $n = (1 + 2s)n_{\mathrm{c}}$ and Eq. (20). They are related by the linearized Legendre transformation $(1 + 2s) = \hat{\eta}^{-1}$, where $\hat{\eta}$ — given implicitly by Eq. (G11) — also includes quadratic contributions. A further Legendre transformation of the linearized semi-grand-canonical potential $\hat{\Omega}_{\mathrm{DH}}$ regains, as it should, the linearized ensemble-invariant semi-grand-canonical osmotic pressure, $\hat{P}_{\mathrm{DH}}^{\mathrm{sgc}} = n_{\mathrm{p}}\hat{\mu}_{\mathrm{p}} - \hat{\Omega}_{\mathrm{DH}}/\tilde{V}$, where the chemical potential of polyions $\hat{\mu}_{\mathrm{p}} \equiv (\partial/\partial n_{\mathrm{p}})\left(\hat{\Omega}_{\mathrm{DH}}/\tilde{V}\right)$.

The ensemble-invariant linearized osmotic pressure $\hat{P}_{\mathrm{DH}}^{\mathrm{sgc}}$, Eq. (G13), leads to results qualitatively similar to those of Eq. (35). In particular, the nonmonotonic behaviour of the spinodal lines for weak screening ($\kappa_{\mathrm{b}}a \ll 1$) and the intrinsic instability of the low-ϕ phase are still predicted by $\hat{P}_{\mathrm{DH}}^{\mathrm{sgc}}$, as shown in Figure 3, where we compare the spinodal lines associated with the two distinct semi-grand-canonical linearized osmotic-pressure definitions, given by Eqs. (35) and (G13). We should mention, however, that *explicit analytical* comparison in the exactly solvable planar case[15] does not show any improvement of the agreement between the nonlinear and linearized equations with the inclusion of the quadratic contribution to the average densities. Any *numerical* indications in this direction, which were indeed observed in the planar case,[15] are purely fortuitous. In fact, asymptotic expansions in the weak-coupling ($\ell_B \to 0$) and in the counterionic ideal-gas limit of both linearized osmotic pressures in the planar case, $P_{\mathrm{DH}}^{\mathrm{sgc}}$ and $\hat{P}_{\mathrm{DH}}^{\mathrm{sgc}}$, agree with the full nonlinear PB version up to the *same order of the expansion*. However, these results can only be obtained *a posteriori*. It is not possible to predict *a priori* that the inclusion of the quadratic contributions will not improve the agreement between the linearized and the nonlinear equations. On the contrary, due to its extended ensemble invariance, one could expect an improvement in the agreement.

H Spinodal lines in the presence of added salt

In this Appendix we discuss the stability criteria for the canonical and the semi-grand-canonical descriptions of the system. We show that both cases are defined by the same stability condition if they are mapped by the linearized Legendre transformation introduced at the end of Appendix G, that includes quadratic contributions and preserves the ensemble invariance of the linearized equations.

In the canonical ensemble at the linearized level, the spinodal-line condition for the two-component system[50] with nominal salt density $\tilde{n}_{\mathrm{s}}$ and polyion density n_{p} — which represents the limit of stability of the stationary point $(\tilde{n}_{\mathrm{s}}, n_{\mathrm{p}})$ of the Helmholtz free-energy density $f_{\mathrm{DH}}(\tilde{n}_{\mathrm{s}}, n_{\mathrm{p}})$ — is defined by the vanishing of the smallest eigenvalue of associated Hessian matrix, which implies the vanishing of its determinant,

$$\left(\frac{\partial^2 f_{\mathrm{DH}}}{\partial\tilde{n}_{\mathrm{s}}^2}\right)\left(\frac{\partial^2 f_{\mathrm{DH}}}{\partial n_{\mathrm{p}}^2}\right) = \left(\frac{\partial^2 f_{\mathrm{DH}}}{\partial\tilde{n}_{\mathrm{s}}\partial n_{\mathrm{p}}}\right)^2, \qquad \text{or} \qquad \frac{\partial\mu_{\mathrm{s}}}{\partial\tilde{n}_{\mathrm{s}}}\frac{\partial\mu_{\mathrm{p}}}{\partial n_{\mathrm{p}}} = \left(\frac{\partial\mu_{\mathrm{p}}}{\partial\tilde{n}_{\mathrm{s}}}\right)^2 = \left(\frac{\partial\mu_{\mathrm{s}}}{\partial n_{\mathrm{p}}}\right)^2. \tag{H1}$$

Using the explicit expressions of the linearized chemical potentials of salt particles μ_s, Eq. (G4), and of polyions, $\mu_p \equiv \partial f_{DH}/\partial n_p$, the *canonical* spinodal-line condition (H1) may be cast in terms of the vanishing of the function

$$\Sigma(\phi, s) \equiv \left(\frac{1+2s}{1+s} - s \frac{\partial \langle \delta_2 \rangle}{\partial s} \right) 4\pi a^2 \ell_B \beta \chi_{\text{can}}^{-1} - \theta s \phi \left(\frac{2}{1-\phi} - \phi \frac{\partial \langle \delta_2 \rangle}{\partial \phi} \right)^2 = 0, \tag{H2}$$

where $\langle \delta_2 \rangle$, given by Eq. (G6), is expressed in terms of (ϕ, s) and recalling that the linearized *canonical* inverse isothermal compressibility reads

$$\chi_{\text{can}}^{-1} \equiv \phi \left(\frac{\mathrm{d}P_{\text{DH}}^{\text{can}}}{\mathrm{d}\phi} \right)_s = \phi^2 \left(\frac{\mathrm{d}^2 f_{\text{DH}}}{\mathrm{d}\phi^2} \right)_s. \tag{H3}$$

We should remark that in the canonical ensemble the spinodal-line condition $\Sigma(\phi, s) = 0$, Eq. (H2), reduces to the vanishing of the inverse isothermal compressibility, $\chi_{\text{can}}^{-1} = 0$, *only in the salt-free limit* $(s \to 0)$, when the macroion suspension (and its neutralizing counterions) is effectively described as a one-component system. In the presence of added salt $(s \neq 0)$, however, in general one needs to solve the nonlinear equation (H2).

On the other hand, the ensemble-invariant linearized semi-grand-canonical spinodal line is simply related to the vanishing of the ensemble-invariant linearized *semi-grand-canonical* inverse isothermal compressibility,

$$\hat{\chi}_{\text{sgc}}^{-1} \equiv \phi \left(\frac{\mathrm{d}\hat{P}_{\text{DH}}^{\text{sgc}}}{\mathrm{d}\phi} \right)_{n_b} = \phi^2 \frac{\mathrm{d}^2}{\mathrm{d}\phi^2} \left(\frac{\hat{\Omega}_{\text{DH}}}{\tilde{V}} \right)_{n_b} = 0, \tag{H4}$$

with an analogous definition for the internally self-consistent — but *not ensemble-invariant* — inverse compressibility χ_{sgc}^{-1}, which is related to $P_{\text{DH}}^{\text{sgc}}$ and Ω_{DH}. Although the two spinodal-line conditions, Eqs. (H2) and (H4), seem to be very different, in fact they describe the same locii on the (ϕ, θ) plane, if they are connected by the linearized Legendre transformation including quadratic contributions introduced at the end of Appendix G, $(1 + 2s) \to \hat{\eta}^{-1}$ and $\kappa \to \hat{\kappa}$. In other words, coincidence of the stability analyses in the canonical and the semi-grand-canonical ensembles — i.e., ensemble invariance — is only achieved if one uses the linearized Legendre transformation that also includes quadratic contributions.

I   Comparison with Deserno and von Grünberg results

In this Appendix we show that the linearized semi-grand-canonical osmotic pressure is intrinsically unstable in the infinite-dilution limit. We show that this instability is not related to an improper definition of the linearized osmotic pressure, but rather reflects the breakdown of the linearization scheme when applied outside its range of validity.

As already pointed out previously in the literature,[24, 51] the linearized semi-grand-canonical osmotic pressure $P_{\text{DH}}^{\text{sgc}}$ defined by Eq. (35) yields artifacts in the low-temperature, high-surface charge or infinite-dilution (of polyions) limits. In contradiction to the exact nonlinear result (E3), which yields an osmotic-pressure difference that is always positive,[52] $\beta \Delta P = \beta P - 2n_b > 0$, the linearized version $\beta \Delta P_{\text{DH}}$ becomes negative in the above mentioned limits. In an attempt to define the osmotic pressure in a linearized framework, Deserno and von Grünberg[24] introduced an alternative definition, P_1, that has the advantage of being exempt from any instabilities (in the particular case of symmetric electrolytes) and it is obtained via the *partial derivative* of the linearized semi-grand-canonical potential Ω_{DH} with respect to the WS-cell free volume V, keeping the optimal linearization point $\bar{\psi}_{\text{opt}}$ (to be defined below) fixed. Their second osmotic-pressure definition coincides with the linearized version (35) obtained in Subsection 3.3, $P_2 \equiv P_{\text{DH}}^{\text{sgc}}$, and it is obtained via the *total derivative* of Ω_{DH} with respect to V. These two distinct osmotic-pressure definitions are given, respectively, by Eqs. (43) and (44) of Ref. [24] for $d = 3$,

$$\frac{\beta P_1}{2n_b} = 1 + \frac{\left(\cosh \bar{\psi}_{\text{opt}} - 1 \right)^2}{2 \cosh \bar{\psi}_{\text{opt}}} + \frac{\sinh^2 \bar{\psi}_{\text{opt}}}{2 \cosh \bar{\psi}_{\text{opt}}} \left(\frac{1-\phi}{3\mathcal{D}\sqrt{\phi}} \right)^2 \geq 1, \tag{I1}$$

$$\frac{\beta P_2}{2n_b} = \frac{\beta P_1}{2n_b} - \frac{\sinh^4 \bar{\psi}_{\text{opt}}}{2 \cosh^3 \bar{\psi}_{\text{opt}}} \left\{ \frac{1-\phi}{6\phi} \left[\frac{1}{\mathcal{D}^2} - \kappa a \frac{\mathcal{E}}{\mathcal{D}} + \kappa^2 a^2 \left(1 - \frac{\mathcal{E}^2}{\mathcal{D}^2} \right) \right] - 1 \right\}, \tag{I2}$$

$$\mathcal{D} = I_{3/2}(\kappa R) \, K_{3/2}(\kappa a) - K_{3/2}(\kappa R) \, I_{3/2}(\kappa a), \tag{I3}$$

$$\mathcal{E} = I_{3/2}(\kappa R) \, K_{1/2}(\kappa a) + K_{3/2}(\kappa R) \, I_{1/2}(\kappa a), \tag{I4}$$

where $\{I_\nu, K_\nu\}$ are the modified Bessel functions[53] of the first and the second kind, respectively, and the optimal linearization point $\bar{\psi}_{\mathrm{opt}}$ satisfies the relations

$$\tanh \bar{\psi}_{\mathrm{opt}} = -\eta, \qquad \cosh \bar{\psi}_{\mathrm{opt}} = \left(\frac{\kappa}{\kappa_{\mathrm{b}}}\right)^2 = \frac{1}{\sqrt{1-\eta^2}}, \qquad \sinh \bar{\psi}_{\mathrm{opt}} = -\frac{n_{\mathrm{c}}}{2n_{\mathrm{b}}} = -\frac{\eta}{\sqrt{1-\eta^2}}. \tag{I5}$$

In accordance with Eqs. (23) and (26) of Ref. [24], they can be recast in a simpler formal form in terms of the gauge-invariant electrostatic potential differences $\delta_\nu(\boldsymbol{r})$, defined by Eq. (28),

$$\beta P_1 = \frac{n_{\mathrm{c}}}{\eta}\left[1 - \frac{\eta^2}{2} + \frac{2Z^2\kappa^2\ell_B^2}{\Delta_2^2(\kappa R, \kappa a)}\right] = \frac{n_{\mathrm{c}}}{\eta}\left[1 + \eta\delta_1(R) + \frac{1}{2}\delta_2(R)\right], \tag{I6}$$

$$\beta P_2 = \frac{n_{\mathrm{c}}}{\eta}\left[1 + \eta\delta_1(R) + \frac{1}{2}\delta_2(R) - \frac{\eta^2}{2}\langle\delta_2(\boldsymbol{r})\rangle\right], \tag{I7}$$

from which one can see that they differ by a term that is quadratic in the electrostatic-potential difference. Looking at Eq. (C10) of Appendix C, one may trace back that the omitted contribution in P_1 originates from the volume dependence of the optimal linearization point $\bar{\psi}_{\mathrm{opt}}$, in accordance to the interpretation given by Deserno and von Grünberg[24] for the two distinct pressure definitions. We should recall that the linearized semi-grand-canonical osmotic-pressure (35) coincides with the second pressure definition, $P_{\mathrm{DH}}^{\mathrm{sgc}} \equiv P_2$, as shown in Appendix E by a quadratic expansion of the nonlinear osmotic pressure. It corresponds indeed to the negative *total derivative* of the linearized semi-grand-canonical potential Ω_{DH} with respect to the WS-cell free volume V, which we thus believe to be the thermodynamically consistent and correct definition of the osmotic pressure.

It is convenient to introduce the dimensionless linearized osmotic-pressure differences,

$$\Pi_i \equiv \frac{\beta\Delta P_i}{2n_{\mathrm{b}}} = \frac{\beta P_i}{2n_{\mathrm{b}}} - 1, \qquad i = 1, 2. \tag{I8}$$

In the vanishing volume fraction of polyions (infinite-dilution) limit, $\phi = (a/R)^3 \to 0$, we may write the asymptotic linearized osmotic-pressure differences in terms of $\theta \equiv 3Z\ell_B/a$ and $\hat{a} \equiv \kappa_{\mathrm{b}}a$,

$$\Pi_1 = \frac{\theta^4\phi^4}{8\hat{a}^8} + \mathscr{O}\left[\phi^5, \theta^2\phi^{2/3}\exp\left(-2\hat{a}\phi^{-1/3}\right)\right], \tag{I9}$$

$$\Pi_2 = -\frac{\theta^4\phi^3}{12\hat{a}^5(1+\hat{a})^2} - \frac{5\theta^4\phi^4}{8\hat{a}^8}\left[\frac{2\hat{a}^3}{5(1+\hat{a})^2} - 1\right] + \mathscr{O}\left[\phi^5, \theta^2\phi^{2/3}\exp\left(-2\hat{a}\phi^{-1/3}\right)\right], \tag{I10}$$

which lead to the asymptotic linearized inverse isothermal compressibilities in the semi-grand-canonical ensemble,

$$\beta\chi_1^{-1} \equiv 2n_{\mathrm{b}}n_{\mathrm{p}}\left(\frac{\mathrm{d}\Pi_1}{\mathrm{d}n_{\mathrm{p}}}\right)_{n_{\mathrm{b}}} = \frac{Zn_{\mathrm{p}}\theta^3\phi^3}{2\hat{a}^6} + \mathscr{O}\left[\phi^4, \theta\phi^{-2/3}\exp\left(-2\hat{a}\phi^{-1/3}\right)\right], \tag{I11}$$

$$\beta\chi_2^{-1} \equiv 2n_{\mathrm{b}}n_{\mathrm{p}}\left(\frac{\mathrm{d}\Pi_2}{\mathrm{d}n_{\mathrm{p}}}\right)_{n_{\mathrm{b}}} = -Zn_{\mathrm{p}}\theta^3\left\{\frac{\phi^2}{4\hat{a}^3(1+\hat{a})^2} + \frac{5\phi^3}{2\hat{a}^6}\left[\frac{2\hat{a}^3}{5(1+\hat{a})^2} - 1\right]\right\}$$
$$+ \mathscr{O}\left[\phi^4, \theta\phi^{-2/3}\exp\left(-2\hat{a}\phi^{-1/3}\right)\right]. \tag{I12}$$

While neglecting the contribution of the last quadratic term in the linearized osmotic pressure P_1 always leads to positive isothermal compressibilities, $\lim_{\phi\to 0}\chi_1 > 0$, its inclusion in P_2 *always* yields negative isothermal compressibilities in the infinite-dilution limit for nonvanishing ℓ_B, $\lim_{\phi\to 0}\chi_2 < 0$. This means that the pressure definition P_2 predicts that the infinite-dilution phase is unstable, in contrast to the canonical case, as shown in Figure 3. Therefore the *thermodynamically consistent* linearized osmotic pressure P_2 *intrinsically fails at infinite dilution,* leading to negative isothermal compressibilities in this limit. This fact was first noticed for the spherical case in Ref. [51] and generalized to WS cells in d-dimensions in Ref. [24]. For finite densities, in contrast to the canonical case (Figure 1), the low-ϕ dilute (gas) phase may only be stable

for sufficiently small bulk salt concentrations, as shown in Figure 3. For sufficiently large $\kappa_{\mathrm{b}}a$ the finite-temperature critical point — located in the vicinity of the salt-free critical point (the black circle in Figure 3) — disappears. Note the nonmonotonic behaviour of the spinodal lines associated to P_2 for $\kappa_{\mathrm{b}}a = 10^{-1}$ and $\kappa_{\mathrm{b}}a = 10^{2}$ (inset), which leads to oscillating osmotic pressures — i.e., Π_2 changes sign more than one time. We should note, however, that the WS-cell model ceases to be meaningful for such high volume fractions in the latter case of strong screening. Finally we should remark that *beyond* the linearized PB WS-cell model approximation the thermodynamical instability at the infinite-dilution limit will be removed by taking into account the translational entropy of the polyions, which yields an osmotic-pressure contribution that is linear in ϕ and, therefore, overcomes the negative cubic leading term in the asymptotic linearized osmotic-pressure difference (I10). However, because our analysis restricts to the linearization of the PB WS-cell model, the effect of this stabilizing entropic contribution — which may drastically alter the spinodal lines, specially in the low-volume fraction region — is not considered here. Note that the PB WS-cell model, in its full nonlinear version, is fully stable[54] even without invoking this stabilizing contribution.

Let us stress again that thermodynamic consistency and stability are independent concepts. This can be illustrated by inspecting the two linearized osmotic-pressure definitions proposed in Ref. [24]. The linearized osmotic pressure Π_2, although not fully stable, is self-consistent with quadratic expansions of the nonlinear osmotic pressure. The unstable region of Π_2 just reflects the breakdown of the linearization scheme to the nonlinear PB equation. On the other hand, Π_1, that displays positive isothermal compressibilities in the infinite-dilution limit and does not present any instabilities for symmetric electrolytes, is not *thermodynamically consistent,* its stability being purely fortuitous. This can be further fortified by comparing the *exact* analytical expressions of the nonlinear osmotic pressure for the planar geometry[15] with the two corresponding linearized versions. In this related paper[15] we show that both linearized expressions, Π_1 and Π_2, approach asymptotically the exact nonlinear result in the appropriate (weak-coupling, $\ell_B \to 0$) limit. Their convergence, however, are very different and it is the self-consistent definition Π_2 that gives a better approximation to the full nonlinear equation. Although analytical proofs can only be obtained for the planar case, we believe the same argument applies for any geometry.

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