Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary material for "Strong-coupling theory of counterions between symmetrically charged walls: from crystal to fluid phases"

Ladislav Šamaj, Martin Trulsson, and Emmanuel Trizac

We present below some results from previous work for self-containedness (sections A and B), and calculations explaining the results presented in the main text (sections C and D). Section C reports the bulk of our analysis. We start by ground state features, before working out the harmonic expansion treatment leading to the free energy in the crystal phase, from which thermodynamic properties and ionic profiles follow.

A. SERIES REPRESENTATIONS OF THE GROUND-STATE ENERGY

Taking the particle at point $(0,0)$ of plate 1 as a reference, the Coulomb interaction energy per particle of structures I-III can be written as

$$e_0(\eta,\Delta) = \frac{e^2}{2\epsilon a} \sum_{(i_x,i_y)\neq(0,0)} \frac{1}{\sqrt{i_x^2+\Delta^2 i_y^2}} + \frac{e^2}{2\epsilon a} \sum_{i_x,i_y} \frac{1}{\sqrt{\left(i_x-\frac{1}{2}\right)^2+\Delta^2\left(i_y-\frac{1}{2}\right)^2+\left(\frac{d}{a}\right)^2}} + \text{background}, \tag{S1}$$

where the first sum corresponds to the interactions with particles on the same plate 1 and the second sum with particles on plate 2. The background term cancels an infinite constant due to the slow decay of the Coulomb potential at large distances.

The energy can be reexpressed in terms of a rapidly converging series by using the method presented in Ref. [1]. We rewrite the ground-state energy per particle as in Eq. (2.5). First, using the gamma identity

$$\frac{1}{z^{\nu/2}} = \frac{1}{\Gamma(\nu/2)} \int_0^\infty \mathrm{d}t\, t^{\frac{\nu}{2}-1} \mathrm{e}^{-zt} \tag{S2}$$

(Γ denotes the Gamma function) with $\nu=1$, the Σ-function is expressed in terms of Jacobi theta functions with zero argument [2] $\theta_3(q)=\sum_j q^{j^2}$ and $\theta_2(q)=\sum_j q^{\left(j-\frac{1}{2}\right)^2}$ as follows

$$\begin{aligned}\Sigma(\eta,\Delta) = \int_0^\infty \frac{\mathrm{d}t}{\sqrt{t}} \Big\{ & \left[\theta_3\left(\mathrm{e}^{-t\Delta}\right)\theta_3\left(\mathrm{e}^{-t/\Delta}\right) - 1 - \frac{\pi}{t}\right] \\ & + \mathrm{e}^{-\eta^2 t}\left[\theta_2\left(\mathrm{e}^{-t\Delta}\right)\theta_2\left(\mathrm{e}^{-t/\Delta}\right) - \frac{\pi}{t}\right]\Big\}.\end{aligned} \tag{S3}$$

Here, the effect of the background charge density on the plates is to subtract the singularity π/t of the product of theta functions as $t\to 0$. Using the Poisson summation formula

$$\sum_{j=-\infty}^{\infty} \mathrm{e}^{-(j+\phi)^2 t} = \sqrt{\frac{\pi}{t}} \sum_{j=-\infty}^{\infty} \mathrm{e}^{2\pi \mathrm{i} j\phi} \mathrm{e}^{-(\pi j)^2/t}, \tag{S4}$$

one can reduce the integration support to $t\in[0,\pi]$. Applying then once more the Poisson summation formula, the Σ-function can be expressed as a series in the generalized Misra functions (2.6):

$$\begin{aligned}\Sigma(\eta,\Delta) = & 4\sum_{j=1}^{\infty}\left[z_{3/2}\left(0,j^2/\Delta\right)+z_{3/2}\left(0,j^2\Delta\right)\right] + 8\sum_{j,k=1}^{\infty} z_{3/2}\left(0,j^2/\Delta+k^2\Delta\right) \\ & +2\sum_{j=1}^{\infty}(-1)^j\left[z_{3/2}\left((\pi\eta)^2,j^2/\Delta\right)+z_{3/2}\left((\pi\eta)^2,j^2\Delta\right)\right] + 4\sum_{j,k=1}^{\infty}(-1)^j(-1)^k z_{3/2}\left((\pi\eta)^2,j^2/\Delta+k^2\Delta\right) \\ & +4\sum_{j,k=1}^{\infty} z_{3/2}\left(0,\eta^2+(j-1/2)^2/\Delta+(k-1/2)^2\Delta\right) - 4\sqrt{\pi} - \pi z_{1/2}(0,\eta^2).\end{aligned} \tag{S5}$$

B. GENERALIZED MISRA FUNCTIONS

The first few generalized Misra functions $z_\nu(x,y)$ (2.6) with half-integer arguments are expressible in terms of the complementary error function [2]

$$\mathrm{erfc}(u) = \frac{2}{\sqrt{\pi}} \int_u^\infty \exp\left(-t^2\right)\, \mathrm{d}t, \tag{S6}$$

as follows [3]:

$$\begin{aligned}
z_{1/2}(x,y) &= \sqrt{\frac{\pi}{x}} \mathrm{e}^{-2\sqrt{xy}} \left[1 - \frac{1}{2}\, \mathrm{erfc}\left(\sqrt{\frac{x}{\pi}} - \sqrt{\pi y} \right) - \frac{1}{2} \mathrm{e}^{4\sqrt{xy}}\, \mathrm{erfc}\left(\sqrt{\frac{x}{\pi}} + \sqrt{\pi y} \right) \right], \\
z_{3/2}(x,y) &= \sqrt{\frac{\pi}{y}} \mathrm{e}^{-2\sqrt{xy}} \left[1 - \frac{1}{2}\, \mathrm{erfc}\left(\sqrt{\frac{x}{\pi}} - \sqrt{\pi y} \right) + \frac{1}{2} \mathrm{e}^{4\sqrt{xy}}\, \mathrm{erfc}\left(\sqrt{\frac{x}{\pi}} + \sqrt{\pi y} \right) \right], \\
z_{5/2}(x,y) &= \frac{\sqrt{\pi x}}{y} \mathrm{e}^{-2\sqrt{xy}} \left(1 + \frac{1}{2\sqrt{xy}} \right) - \frac{\sqrt{\pi}}{4 y^{3/2}} \Bigg[- 4 \mathrm{e}^{-x/\pi - \pi y} \sqrt{y} \\
&\quad + \mathrm{e}^{-2\sqrt{xy}} \left(1 + 2\sqrt{xy}\right)\, \mathrm{erfc}\left(\sqrt{\frac{x}{\pi}} - \sqrt{\pi y} \right) + \mathrm{e}^{2\sqrt{xy}} \left(-1 + 2\sqrt{xy}\right)\, \mathrm{erfc}\left(\sqrt{\frac{x}{\pi}} + \sqrt{\pi y} \right) \Bigg].
\end{aligned} \tag{S7}$$

The case of the ordinary Misra functions $z_\nu(0,y)$ [4] should be understood in the sense of the limit $x \to 0$,

$$\begin{aligned}
z_{1/2}(0,y) &= \frac{2}{\sqrt{\pi}} \left[\mathrm{e}^{-\pi y} - \pi \sqrt{y}\, \mathrm{erfc}(\sqrt{\pi y}) \right], \\
z_{3/2}(0,y) &= \sqrt{\frac{\pi}{y}}\, \mathrm{erfc}(\sqrt{\pi y}), \\
z_{5/2}(0,y) &= \frac{\sqrt{\pi}}{2 y^{3/2}} \left[2 \mathrm{e}^{-\pi y} \sqrt{y}\ + \mathrm{erfc}(\sqrt{\pi y}) \right].
\end{aligned} \tag{S8}$$

C. LARGE-COUPLING DESCRIPTION OF THE CRYSTAL PHASE

1. Harmonic expansion of the energy

Starting from a crystalline configuration, let us shift each particle i at plate Σ_1 from its reference Wigner-lattice position (2.3) to

$$\mathbf{r}_i = (a i_x + x_i, \Delta a i_y + y_i, z_i), \tag{S9}$$

where the coordinate shifts x_i, y_i and z_i are assumed to be small. Similarly, we shift the Wigner position (2.4) of each particle at plate Σ_2 to the one

$$\mathbf{r}_i = \left(a\left(i_x - \frac{1}{2} \right) + x_i, \Delta a \left(i_y - \frac{1}{2} \right) + y_i, d - (d - z_i) \right), \tag{S10}$$

where now x_i, y_i and $d - z_i$ are assumed to be small.

If the particles $i \to (i_x, i_y)$ and $j \to (j_x, j_y)$ are localized on the same plate, either Σ_1 or Σ_2, the change of the Coulomb energy due to the particle shifts reads as

$$\delta E_{ij} = \frac{e^2}{\epsilon} \left[\frac{1}{\sqrt{[a(i_x - j_x) + (x_i - x_j)]^2 + [a\Delta(i_y - j_y) + (y_i - y_j)]^2 + (z_i - z_j)^2}} - \frac{1}{\sqrt{a^2 (i_x - j_x)^2 + a^2 \Delta^2 (i_y - j_y)^2}} \right]. \tag{S11}$$

If both particles are at plate Σ_1, the expansion of δE_{ij} in small deviations (x_i, x_j), (y_i, y_j) and (z_i, z_j) is straightforward. Since $z_i - z_j \equiv (d - z_j) - (d - z_i)$, the same holds for two particles being at plate Σ_2 where the deviations $d - z_i$ and $d - z_j$ are small. If particles i and j belong to different plates, say $i \in \Sigma_1$ and $j \in \Sigma_2$, the energy change is given by

$$\begin{aligned}
\delta E_{ij} = \frac{e^2}{\epsilon} \Bigg[& \frac{1}{\sqrt{[a(i_x - j_x - 1/2) + (x_i - x_j)]^2 + [a\Delta(i_y - j_y - 1/2) + (y_i - y_j)]^2 + (z_i - z_j)^2}} \\
& - \frac{1}{\sqrt{a^2 (i_x - j_x - 1/2)^2 + a^2 \Delta^2 (i_y - j_y - 1/2)^2 + d^2}} \Bigg].
\end{aligned} \tag{S12}$$

In this case, we write $z_i - z_j \equiv -d + z_i + (d - z_j)$ and perform the expansion of the energy change in the small quantities z_i and $(d - z_j)$. The total energy is expressible as

$$E(\{\mathbf{r}_i\}) = Ne_0(\eta,\Delta) + \delta E, \qquad \delta E = \sum_{i<j} \delta E_{ij}. \tag{S13}$$

Within the harmonic approximation, we expand every δE_{ij} up to quadratic terms in small deviations, supposing that the ratios x_i/a, y_i/a, z_i/a are small variables for particles $i \in \Sigma_1$ and that x_i/a, y_i/a, $(d - z_i)/a$ are small variables for particles $i \in \Sigma_2$. Many terms disappear because of the symmetry of the energy with respect to the reflection transformations $x \to -x$ and $y \to -y$. The final result for the energy change is Eq. (4.5) in the main text:

$$-\beta\delta E = -\kappa(\eta,\Delta)\left[\sum_{i\in\Sigma_1} \widetilde{z}_i + \sum_{i\in\Sigma_2} (\widetilde{d} - \widetilde{z}_i)\right] + \frac{1}{\sqrt{\Xi}} S_z - \sqrt{\frac{\Xi}{2\pi}}\frac{\sigma}{2}\sum_{i<j}\left[B^x_{ij}(x_i - x_j)^2 + B^y_{ij}(y_i - y_j)^2\right] + \cdots, \tag{S14}$$

with

$$\begin{aligned}\kappa(\eta,\Delta) &= \frac{\eta}{2\pi}\sum_{i_x,i_y} \frac{\Delta^{3/2}}{[(i_x - 1/2)^2 + \Delta^2(i_y - 1/2)^2 + \Delta\eta^2]^{3/2}} \\ &= \frac{\eta}{\pi^{3/2}}\int_0^\infty \mathrm{d}t\,\sqrt{t}\,\mathrm{e}^{-\eta^2 t}\theta_2\left(\mathrm{e}^{-t\Delta}\right)\theta_2\left(\mathrm{e}^{-t/\Delta}\right) = -\frac{1}{2\pi^{3/2}}\frac{\partial}{\partial\eta}\Sigma(\eta,\Delta) + 1.\end{aligned} \tag{S15}$$

The quantity S_z involves all terms quadratic in variables $\widetilde{z}_i$ if $i \in \Sigma_1$ and $(\widetilde{d} - \widetilde{z}_i)$ if $i \in \Sigma_2$,

$$\begin{aligned}S_z(\eta,\Delta) = \frac{\Delta^{3/2}}{2(2\pi)^{3/2}}\Bigg\{ &\sum_{\substack{i,j\in\Sigma_1\\(i<j)}} \frac{1}{[(i_x - j_x)^2 + \Delta^2(i_y - j_y)^2]^{3/2}}\left(\widetilde{z}_i^2 + \widetilde{z}_j^2 - 2\widetilde{z}_i\widetilde{z}_j\right) \\ &+ \sum_{\substack{i,j\in\Sigma_2\\(i<j)}} \frac{1}{[(i_x - j_x)^2 + \Delta^2(i_y - j_y)^2]^{3/2}}\left[(\widetilde{d} - \widetilde{z}_i)^2 + (\widetilde{d} - \widetilde{z}_j)^2 - 2(\widetilde{d} - \widetilde{z}_i)(\widetilde{d} - \widetilde{z}_j)\right] \\ &+ \sum_{i\in\Sigma_1}\sum_{j\in\Sigma_2}\Bigg[\frac{1}{[(i_x - j_x - 1/2)^2 + \Delta^2(i_y - j_y - 1/2)^2 + \Delta\eta^2]^{3/2}} \\ &- \frac{3\Delta\eta^2}{[(i_x - j_x - 1/2)^2 + \Delta^2(i_y - j_y - 1/2)^2 + \Delta\eta^2]^{5/2}}\Bigg]\left[\widetilde{z}_i^2 + (\widetilde{d} - \widetilde{z}_j)^2 + 2\widetilde{z}_i(\widetilde{d} - \widetilde{z}_j)\right]\Bigg\}\end{aligned} \tag{S16}$$

and the expansion coefficients in the (x, y)-plane are given by

$$\begin{aligned}B^x_{ij}(\Delta) &= \Delta^{3/2}\frac{2(i_x - j_x)^2 - \Delta^2(i_y - j_y)^2}{[(i_x - j_x)^2 + \Delta^2(i_y - j_y)^2]^{5/2}}, \\ B^y_{ij}(\Delta) &= \Delta^{3/2}\frac{2\Delta^2(i_y - j_y)^2 - (i_x - j_x)^2}{[(i_x - j_x)^2 + \Delta^2(i_y - j_y)^2]^{5/2}}\end{aligned} \tag{S17}$$

if particles i and j belong to the same plate and by

$$\begin{aligned}B^x_{ij}(\eta,\Delta) &= \Delta^{3/2}\frac{2(i_x - j_x - 1/2)^2 - \Delta^2(i_y - j_y - 1/2)^2 - \Delta\eta^2}{[(i_x - j_x - 1/2)^2 + \Delta^2(i_y - j_y - 1/2)^2 + \Delta\eta^2]^{5/2}}, \\ B^y_{ij}(\eta,\Delta) &= \Delta^{3/2}\frac{2\Delta^2(i_y - j_y - 1/2)^2 - (i_x - j_x - 1/2)^2 - \Delta\eta^2}{[(i_x - j_x - 1/2)^2 + \Delta^2(i_y - j_y - 1/2)^2 + \Delta\eta^2]^{5/2}}\end{aligned} \tag{S18}$$

if particles i and j belong to different plates.

2. Thermodynamics

To express $\ln Q_z$ as a perturbative series in S_z, we introduce the counterpart of (4.11) for non-interacting ($S_z = 0$) particles in the external potential only:

$$Q^{(0)}_z(\eta,\Delta) = \int_0^{\widetilde{d}}\prod_{i\in\Sigma_1}\mathrm{d}\widetilde{z}_i\,\mathrm{e}^{-\kappa\widetilde{z}_i}\int_0^{\widetilde{d}}\prod_{i\in\Sigma_2}\mathrm{d}\widetilde{z}_i\,\mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z}_i)} = \left(\frac{1 - \exp(-\kappa\widetilde{d})}{\kappa}\right)^N. \tag{S19}$$

We have

$$\ln\left(\frac{Q_z}{Q_z^{(0)}}\right) = \ln\langle\exp(S_z)\rangle_0, \tag{S20}$$

where $\langle\cdots\rangle_0$ denotes the statistical averaging over the system of non-interacting particles defined by the partition sum $Q_z^{(0)}$. The quantity $\ln\langle\exp(S_z)\rangle_0$ can be written as the cumulant expansion:

$$\ln\langle\exp(S_z)\rangle_0 = \langle S_z\rangle_0 + \frac{1}{2!}\left(\langle S_z^2\rangle_0 - \langle S_z\rangle_0^2\right) + \cdots , \tag{S21}$$

where each term of the expansion is extensive, i.e. proportional to the particle number N. Restricting ourselves to the lowest cumulant order, we obtain

$$\frac{1}{N}\ln Q_z = \ln\left(\frac{1-\exp(-\kappa\widetilde{d})}{\kappa}\right) + \frac{1}{N}\langle S_z\rangle_0 \tag{S22}$$

with $\widetilde{d} \equiv d/\mu = \eta/(\mu\sqrt{\sigma}) = \eta\sqrt{2\pi\Xi}$. The evaluation of $\langle S_z\rangle_0/N$ yields:

$$\begin{aligned}\frac{1}{N}\langle S_z\rangle_0 = \frac{1}{2(2\pi)^{3/2}}\Bigg\{\frac{F(\Delta)}{2}\Big[\left(\langle\widetilde{z}^2\rangle_0 - \langle\widetilde{z}\rangle_0^2\right) + \left(\langle(\widetilde{d}-\widetilde{z})^2\rangle_0 - \langle(\widetilde{d}-\widetilde{z})\rangle_0^2\right)\Big] \\ +\pi\frac{\partial\kappa(\eta,\Delta)}{\partial\eta}\Big[\langle\widetilde{z}^2\rangle_0 + \langle(\widetilde{d}-\widetilde{z})^2\rangle_0 + 2\langle\widetilde{z}\rangle_0\langle(\widetilde{d}-\widetilde{z})\rangle_0\Big]\Bigg\},\end{aligned} \tag{S23}$$

where $F(\Delta)$ corresponds to the lattice sum

$$F(\Delta) = \sum_{(i_x,i_y)\neq(0,0)} \frac{\Delta^{3/2}}{(i_x^2+\Delta^2 i_y^2)^{3/2}} \tag{S24}$$

and the one-body averages

$$\langle\widetilde{z}^p\rangle_0 = \frac{\int_0^{\widetilde{d}} \mathrm{d}\widetilde{z}\,\widetilde{z}^p \mathrm{e}^{-\kappa\widetilde{z}}}{\int_0^{\widetilde{d}} \mathrm{d}\widetilde{z}\,\mathrm{e}^{-\kappa\widetilde{z}}}, \qquad \langle(\widetilde{d}-\widetilde{z})^p\rangle_0 = \frac{\int_0^{\widetilde{d}} \mathrm{d}\widetilde{z}\,(\widetilde{d}-\widetilde{z})^p \mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}}{\int_0^{\widetilde{d}} \mathrm{d}\widetilde{z}\,\mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}}. \tag{S25}$$

In particular, we shall need

$$\langle\widetilde{z}\rangle_0 = \langle(\widetilde{d}-\widetilde{z})\rangle_0 = \frac{1}{\kappa} - \frac{\widetilde{d}}{\mathrm{e}^{\kappa\widetilde{d}}-1}, \tag{S26}$$

$$\langle\widetilde{z}^2\rangle_0 = \langle(\widetilde{d}-\widetilde{z})^2\rangle_0 = \frac{2}{\kappa^2} - \frac{\widetilde{d}(2+\kappa\widetilde{d})}{\kappa\left(\mathrm{e}^{\kappa\widetilde{d}}-1\right)}. \tag{S27}$$

To calculate the integral Q_x in (4.12), we respect the x-coordinate constraint (4.9) and rescale the particle x-coordinates by the factor $(2\pi/\Xi)^{1/4}/\sqrt{\sigma}$ to obtain

$$Q_x(\eta,\Delta) = \left(\frac{2\pi}{\Xi}\right)^{N/4}\frac{1}{(\lambda\sqrt{\sigma})^N}\int_{-L}^{L}\prod_{i\in\Sigma_1\cup\Sigma_2}\mathrm{d}x_i\,\exp\left[-\frac{1}{2}\sum_{i<j}B_{ij}^x(x_i-x_j)^2\right], \tag{S28}$$

where $L \propto \Xi^{1/4}$ goes to infinity in the large-Ξ limit. Here, going back to dimensioned lengths, a new relevant length scale arises, $a/\Xi^{1/4}$. It is readily checked that it measures the amplitude of in plane x-fluctuations around a lattice position. Incidentally, we note first that a similar scaling arises for the minimum of the pressure curves, in the regime of like-charge attraction, that is largely met here [5, 6]. Second, this provides a new light on the melting criterion alluded to above, where the critical coupling in the 2D-confined problem is around 15000. This yields $a/\Xi^{1/4} \simeq 0.09a$, a value close to Lindeman type of criteria [7]. To avoid the divergence of the consequent integral manifesting itself by the invariance of $\sum_{i<j} B_{ij}^x(x_i-x_j)^2$ with respect to a uniform coordinate shift $x_i \to x_i + c$, we shall make provision

for finiteness of the L-bound for a large but finite Ξ and ignore the zero Fourier mode, see below. Omitting in (S28) irrelevant prefactors we end up with the integral of Gaussian type

$$Q_x(\eta,\Delta) = \int_{-\infty}^{\infty} \prod_{i=1}^{N} \mathrm{d}x_i \, \exp\left[-\frac{1}{2} \sum_{i,j=1}^{N} A_{ij}^x x_i x_j \right] = \frac{(2\pi)^{N/2}}{\sqrt{\mathrm{Det}\,\mathbf{A}^x}}, \tag{S29}$$

where the $\mathbf{A}^x$-matrix is defined by

$$A_{ii}^x = \sum_{k\neq i} B_{ik}^x, \qquad A_{ij}^x = -B_{ij}^x \quad \text{for } (i \neq j). \tag{S30}$$

According to Fig. 1, within the (x,y) plane we can represent the Wigner bilayer as the regular 2D lattice of alternating white (belonging to plate Σ_1) and black (belonging to Σ_2) points, with the primitive translation vectors

$$\boldsymbol{\alpha} = a(1,0), \qquad \boldsymbol{\beta} = \frac{a}{2}(1,\Delta) \tag{S31}$$

and the surface of the elementary cell $S = \Delta a^2/2$. The matrix elements A_{ij}^x depend only on the distance of lattice points i,j and therefore $\mathbf{A}^x$ is an $N \times N$ circulant matrix with known eigenvalue spectrum. Let us define the 2D Fourier transform of any lattice function $h_{ij} = f(|\mathbf{r}_i - \mathbf{r}_j|)$ as follows

$$h(\mathbf{q}) = \sum_k h_{jk} \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{r}_j - \mathbf{r}_k)}, \tag{S32}$$

where the N vectors $\mathbf{q} = (q_x, q_y)$ belong to the first Brillouin zone (BZ) of the reciprocal lattice with the primitive vectors $\boldsymbol{\alpha}^*$, $\boldsymbol{\beta}^*$ defined by the relations

$$\boldsymbol{\alpha}^* \cdot \boldsymbol{\alpha} = \boldsymbol{\beta}^* \cdot \boldsymbol{\beta} = 2\pi, \qquad \boldsymbol{\alpha}^* \cdot \boldsymbol{\beta} = \boldsymbol{\alpha} \cdot \boldsymbol{\beta}^* = 0. \tag{S33}$$

In particular,

$$\boldsymbol{\alpha}^* = \frac{2\pi}{a}\left(1, -\frac{1}{\Delta}\right), \qquad \boldsymbol{\beta}^* = \frac{4\pi}{a}\left(0, \frac{1}{\Delta}\right) \tag{S34}$$

and the surface of the BZ is given by $S^* = 8\pi^2/(\Delta a^2)$. Since the $A^x(\mathbf{q})$ with $\mathbf{q} \in \mathrm{BZ}$ are the N eigenvalues of the matrix $\mathbf{A}^x$, we have

$$\mathrm{Det}\,\mathbf{A}^x = \prod_{\substack{\mathbf{q}\in\mathrm{BZ}\\ \mathbf{q}\neq 0}} A^x(\mathbf{q}), \qquad -\frac{1}{N} \ln Q_x(\eta,\Delta) = \frac{1}{2N} \sum_{\substack{\mathbf{q}\in\mathrm{BZ}\\ \mathbf{q}\neq 0}} \ln A^x(\mathbf{q}), \tag{S35}$$

the zero-mode being excluded. In the thermodynamic limit $N \to \infty$, the $\mathbf{q}$-vectors cover uniformly the BZ defined by the primitive vectors (S34) and we can write

$$\begin{aligned}
\frac{1}{N} \sum_{\substack{\mathbf{q}\in\mathrm{BZ}\\ \mathbf{q}\neq 0}} \ln A^x(\mathbf{q}) &= \frac{1}{S^*} \int_{\mathrm{BZ}} \mathrm{d}\mathbf{q} \, \ln A^x(\mathbf{q}) = \frac{\Delta a^2}{8\pi^2} \int_0^{2\pi/a} \mathrm{d}q_x \int_{-q_x/\Delta}^{4\pi/(a\Delta) - q_x/\Delta} \mathrm{d}q_y \, \ln A^x(q_x, q_y) \\
&= \frac{1}{2} \int_0^1 \mathrm{d}q_x \int_0^2 \mathrm{d}q_y \, \ln A^x \left[\frac{2\pi}{a} q_x, \frac{2\pi}{a\Delta}(q_y - q_x) \right].
\end{aligned} \tag{S36}$$

Consequently,

$$-\lim_{N\to\infty} \frac{1}{N} \ln Q_x(\eta,\Delta) = \frac{1}{4} \int_0^1 \mathrm{d}q_x \int_0^2 \mathrm{d}q_y \, \ln A^x \left[\frac{2\pi}{a} q_x, \frac{2\pi}{a\Delta}(q_y - q_x) \right]. \tag{S37}$$

Now we want to express appropriately the Fourier component $A^x(2\pi q_x/a, 2\pi q_y/(a\Delta))$, the elements of the $\mathbf{A}^x$-matrix being defined in terms of those of the $\mathbf{B}^x$-matrix [see formulas (S17) and (S18)] in Eq. (S30). We introduce the auxiliary Fourier lattice functions

$$F(\Delta;\mathbf{q}) = \sum_{(i_x,i_y)\neq(0,0)} \frac{\Delta^{3/2}}{(i_x^2 + \Delta^2 i_y^2)^{3/2}} \mathrm{e}^{\mathrm{i}2\pi(q_x i_x + q_y i_y)}, \tag{S38}$$

$$G(\eta,\Delta;\mathbf{q}) = \sum_{(i_x,i_y)} \frac{\Delta^{3/2}}{((i_x - 1/2)^2 + \Delta^2(i_y - 1/2)^2 + \Delta\eta^2)^{3/2}} \mathrm{e}^{\mathrm{i}2\pi[q_x(i_x - 1/2) + q_y(i_y - 1/2)]}. \tag{S39}$$

Note that the previous lattice sum (S24) is expressible as $F(\Delta) = F(\Delta, \mathbf{0})$. The Misra series representations of $F(\Delta; \mathbf{q})$ and $G(\eta, \Delta; \mathbf{q})$ are given in Eqs. (S61) and (S62) in section D, respectively. Introducing the function

$$C^x(\mathbf{q}) = \frac{1}{2}F(\Delta;\mathbf{q}) + \Delta\frac{\partial}{\partial\Delta}F(\Delta;\mathbf{q}) + \frac{1}{2}G(\eta,\Delta;\mathbf{q}) + \Delta\frac{\partial}{\partial\Delta}G(\eta,\Delta;\mathbf{q}) + \frac{\eta}{2}\frac{\partial}{\partial\eta}G(\eta,\Delta;\mathbf{q}) \tag{S40}$$

it holds that

$$A^x\left(\frac{2\pi}{a}q_x, \frac{2\pi}{a\Delta}q_y\right) = C^x(0,0) - C^x(q_x,q_y). \tag{S41}$$

To evaluate the integral Q_y (4.13), we proceed analogously. The $\mathbf{A}^y$-matrix is defined by

$$A^y_{ii} = \sum_{k\neq i} B^y_{ik}, \qquad A^y_{ij} = -B^y_{ij} \quad \text{for } (i \neq j), \tag{S42}$$

see Eqs. (S17) and (S18) for the $\mathbf{B}^y$-matrix elements. In the thermodynamic limit we find that

$$-\lim_{N\to\infty}\frac{1}{N}\ln Q_y(\eta,\Delta) = \frac{1}{4}\int_0^1 \mathrm{d}q_x \int_0^2 \mathrm{d}q_y \,\ln A^y\left[\frac{2\pi}{a}q_x, \frac{2\pi}{a\Delta}(q_y - q_x)\right]. \tag{S43}$$

Here,

$$A^y\left(\frac{2\pi}{a}q_x, \frac{2\pi}{a\Delta}q_y\right) = C^y(0,0) - C^y(q_x,q_y), \tag{S44}$$

where the auxiliary function

$$C^y(\mathbf{q}) = \frac{1}{2}F(\Delta;\mathbf{q}) - \Delta\frac{\partial}{\partial\Delta}F(\Delta;\mathbf{q}) + \frac{1}{2}G(\eta,\Delta;\mathbf{q}) - \Delta\frac{\partial}{\partial\Delta}G(\eta,\Delta;\mathbf{q}) + \frac{\eta}{2}\frac{\partial}{\partial\eta}G(\eta,\Delta;\mathbf{q}). \tag{S45}$$

3. Particle density profile and pressure

We start from

$$Z_N[w] = \frac{1}{N!}\int_\Lambda \prod_{i=1}^N \frac{\mathrm{d}\mathbf{r}_i}{\lambda^3}\, w(\mathbf{r}_i) \mathrm{e}^{-\beta E(\{\mathbf{r}_i\})}, \tag{S46}$$

a functional of the generating Boltzmann weight $w(\mathbf{r}) = \exp[-\beta u(\mathbf{r})]$, such that

$$\rho(\mathbf{r}) = \frac{\delta}{\delta w(\mathbf{r})} \ln Z_N[w]\Big|_{w(\mathbf{r})=1}. \tag{S47}$$

For our z-dependent density $\rho(z)$ one can ignore harmonic modes along the (x, y) plane as well as w-independent terms. After simple algebra, we find that

$$\ln Z_N[w] = \frac{N}{2}\ln\left[\int_\Lambda \mathrm{d}\mathbf{r}\, w(\mathbf{r})\mathrm{e}^{-\kappa\widetilde{z}}\right] + \frac{N}{2}\ln\left[\int_\Lambda \mathrm{d}\mathbf{r}\, w(\mathbf{r})\mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}\right] + \frac{1}{\sqrt{\Xi}}\langle S_z[w]\rangle_0, \tag{S48}$$

where the functional $\langle S_z[w]\rangle_0$ is given by Eq. (S23) with the moments redefined as follows

$$\langle \widetilde{z}^p\rangle_0 \to \langle \widetilde{z}^p[w]\rangle_0 = \frac{\int_\Lambda \mathrm{d}\mathbf{r}\, w(\mathbf{r})\widetilde{z}^p \mathrm{e}^{-\kappa\widetilde{z}}}{\int_\Lambda \mathrm{d}\mathbf{r}\, w(\mathbf{r})\mathrm{e}^{-\kappa\widetilde{z}}},$$
$$\langle (\widetilde{d}-\widetilde{z})^p\rangle_0 \to \langle (\widetilde{d}-\widetilde{z})^p[w]\rangle_0 = \frac{\int_\Lambda \mathrm{d}\mathbf{r}\, w(\mathbf{r})(\widetilde{d}-\widetilde{z})^p \mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}}{\int_\Lambda \mathrm{d}\mathbf{r}\, w(\mathbf{r})\mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}}. \tag{S49}$$

Then the (rescaled) particle density can be represented as the WSC expansion

$$\widetilde{\rho}(\widetilde{z}) = \widetilde{\rho}^{(0)}(\widetilde{z}) + \frac{1}{\sqrt{\Xi}}\widetilde{\rho}^{(1)}(\widetilde{z}) + \cdots . \tag{S50}$$

Since

$$\frac{\delta}{\delta w(\mathbf{r})}\frac{N}{2}\ln\left[\int_\Lambda \mathrm{d}\mathbf{r}\, w(\mathbf{r})\mathrm{e}^{-\kappa\widetilde{z}}\right]\Bigg|_{w(\mathbf{r})=1} = \frac{N\mathrm{e}^{-\kappa\widetilde{z}}}{2\int_\Lambda \mathrm{d}\mathbf{r}\,\mathrm{e}^{-\kappa\widetilde{z}}} = \frac{N\kappa}{2S\mu\left(1-\mathrm{e}^{-\kappa\widetilde{d}}\right)}\mathrm{e}^{-\kappa\widetilde{z}} \tag{S51}$$

and $N/(2S\mu) = 2\pi\ell_\mathrm{B}\sigma^2$, we have in the leading WSC order

$$\widetilde{\rho}^{(0)}(\widetilde{z}) = \frac{\kappa}{1-\mathrm{e}^{-\kappa\widetilde{d}}}\left[\mathrm{e}^{-\kappa\widetilde{z}} + \mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}\right]. \tag{S52}$$

The first correction to the particle density $\widetilde{\rho}^{(1)}(\widetilde{z})$ is generated from $\langle S_z[w]\rangle_0$ by using the functional derivatives of the moments

$$\frac{\delta}{\delta w(\mathbf{r})}\langle \widetilde{z}^p[w]\rangle_0\Big|_{w(\mathbf{r})=1} = \frac{\kappa}{S\mu\left(1-\mathrm{e}^{-\kappa\widetilde{d}}\right)}\mathrm{e}^{-\kappa\widetilde{z}}\left(\widetilde{z}^p - \langle\widetilde{z}^p\rangle_0\right), \tag{S53}$$

$$\frac{\delta}{\delta w(\mathbf{r})}\langle (\widetilde{d}-\widetilde{z})^p[w]\rangle_0\Big|_{w(\mathbf{r})=1} = \frac{\kappa}{S\mu\left(1-\mathrm{e}^{-\kappa\widetilde{d}}\right)}\mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}\left[(\widetilde{d}-\widetilde{z})^p - \langle(\widetilde{d}-\widetilde{z})^p\rangle_0\right]. \tag{S54}$$

In particular,

$$\begin{aligned}\widetilde{\rho}^{(1)}(\widetilde{z}) = {}& \frac{\kappa}{(2\pi)^{3/2}\left(1-\mathrm{e}^{-\kappa\widetilde{d}}\right)}\Bigg\{F(\Delta)\mathrm{e}^{-\kappa\widetilde{z}}\left[\frac{\widetilde{z}^2-\langle\widetilde{z}^2\rangle_0}{2} - \langle\widetilde{z}\rangle_0\left(\widetilde{z}-\langle\widetilde{z}\rangle_0\right)\right] \\ &+F(\Delta)\mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}\left[\frac{(\widetilde{d}-\widetilde{z})^2-\langle(\widetilde{d}-\widetilde{z})^2\rangle_0}{2} - \langle(\widetilde{d}-\widetilde{z})\rangle_0\left((\widetilde{d}-\widetilde{z})-\langle(\widetilde{d}-\widetilde{z})\rangle_0\right)\right] \\ &+2\pi\frac{\partial\kappa(\eta,\Delta)}{\partial\eta}\Bigg[\mathrm{e}^{-\kappa\widetilde{z}}\frac{\widetilde{z}^2-\langle\widetilde{z}^2\rangle_0}{2} + \mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}\frac{(\widetilde{d}-\widetilde{z})^2-\langle(\widetilde{d}-\widetilde{z})^2\rangle_0}{2} \\ &+\mathrm{e}^{-\kappa\widetilde{z}}\langle(\widetilde{d}-\widetilde{z})\rangle_0\left(\widetilde{z}-\langle\widetilde{z}\rangle_0\right) + \mathrm{e}^{-\kappa(\widetilde{d}-\widetilde{z})}\langle\widetilde{z}\rangle_0\left((\widetilde{d}-\widetilde{z})-\langle(\widetilde{d}-\widetilde{z})\rangle_0\right)\Bigg]\Bigg\}.\end{aligned} \tag{S55}$$

Because of the equalities

$$\int_\Lambda \mathrm{d}\mathbf{r}\frac{\delta}{\delta w(\mathbf{r})}\langle\widetilde{z}^p[w]\rangle_0\Big|_{w(\mathbf{r})=1} = \int_\Lambda \mathrm{d}\mathbf{r}\frac{\delta}{\delta w(\mathbf{r})}\langle(\widetilde{d}-\widetilde{z})^p[w]\rangle_0\Big|_{w(\mathbf{r})=1} = 0, \tag{S56}$$

we have

$$\int_0^{\widetilde{d}} \mathrm{d}\widetilde{z}\,\widetilde{\rho}^{(1)}(\widetilde{z}) = 0, \tag{S57}$$

so that the electroneutrality condition is met.

Finally, the contact theorem for planar walls [8] relates the total contact density of particles on the wall and the pressure. Within our notation, it is expressible as

$$\widetilde{P}_\mathrm{c} = \widetilde{\rho}(0) - 1 = \left[\widetilde{\rho}^{(0)}(0)-1\right] + \frac{1}{\sqrt{\Xi}}\widetilde{\rho}^{(1)}(0) + \cdots . \tag{S58}$$

Writing the WSC expansion for the "contact" pressure as $\widetilde{P}_\mathrm{c} = \widetilde{P}_\mathrm{c}^{(0)} + \widetilde{P}_\mathrm{c}^{(1)}/\sqrt{\Xi} + \cdots$, we get

$$\widetilde{P}_c^{(0)} = \kappa\left(\frac{1+\mathrm{e}^{-\kappa\widetilde{d}}}{1-\mathrm{e}^{-\kappa\widetilde{d}}}\right) - 1, \tag{S59}$$

and the first correction reads as

$$\widetilde{P}_c^{(1)} = \frac{\kappa}{(2\pi)^{3/2}\left(1-\mathrm{e}^{-\kappa\widetilde{d}}\right)}\Bigg\{F(\Delta)\left(\langle\widetilde{z}\rangle_0^2 - \frac{\langle\widetilde{z}^2\rangle_0}{2}\right) + F(\Delta)\mathrm{e}^{-\kappa\widetilde{d}}\left[\frac{\widetilde{d}^2 - \langle(\widetilde{d}-\widetilde{z})^2\rangle_0}{2} - \langle(\widetilde{d}-\widetilde{z})\rangle_0\left(\widetilde{d} - \langle(\widetilde{d}-\widetilde{z})\rangle_0\right)\right]$$
$$+2\pi\frac{\partial\kappa(\eta,\Delta)}{\partial\eta}\left[-\frac{\langle\widetilde{z}^2\rangle_0}{2} + \mathrm{e}^{-\kappa\widetilde{d}}\frac{\widetilde{d}^2 - \langle(\widetilde{d}-\widetilde{z})^2\rangle_0}{2} - \langle(\widetilde{d}-\widetilde{z})\rangle_0\langle\widetilde{z}\rangle_0 + \mathrm{e}^{-\kappa\widetilde{d}}\langle\widetilde{z}\rangle_0\left(\widetilde{d} - \langle(\widetilde{d}-\widetilde{z})\rangle_0\right)\right]\Bigg\}. \tag{S60}$$

D. SERIES REPRESENTATIONS OF CERTAIN LATTICE FUNCTIONS

The function $F(\Delta)$ defined by Eq. (S24) corresponds to a special case of $F(\Delta;\mathbf{q})$ introduced by expression (S38), since $F(\Delta) = F(\Delta,\mathbf{0})$. This Fourier lattice sum can be written as the series

$$F(\Delta;\mathbf{q}) = -\frac{4}{3}\pi + \frac{4}{\sqrt{\pi}}\sum_{j=1}^{\infty}\left[\cos(2\pi q_x j) z_{5/2}(0, j^2/\Delta) + \cos(2\pi q_y j) z_{5/2}(0, j^2\Delta)\right]$$
$$+\frac{8}{\sqrt{\pi}}\sum_{j,k=1}^{\infty}\cos(2\pi q_x j)\cos(2\pi q_y k) z_{5/2}(0, j^2/\Delta + k^2\Delta)$$
$$+2\pi^{3/2}\sum_{j,k=-\infty}^{\infty} z_{1/2}[0, (j-q_x)^2\Delta + (k-q_y)^2/\Delta]. \tag{S61}$$

The function $G(\eta,\Delta;\mathbf{q})$ defined by Eq. (S39) is expressible as the series

$$G(\eta,\Delta;\mathbf{q}) = \frac{8}{\sqrt{\pi}}\sum_{j,k=1}^{\infty}\cos\left[2\pi q_x(j-1/2)\right]\cos\left[2\pi q_y(k-1/2)\right] z_{5/2}[0, (j-1/2)^2/\Delta + (k-1/2)^2\Delta + \eta^2]$$
$$+2\pi^{3/2}\sum_{j,k=-\infty}^{\infty}(-1)^j(-1)^k z_{1/2}[(\pi\eta)^2, (j-q_x)^2\Delta + (k-q_y)^2/\Delta]. \tag{S62}$$

---

[1] L. Šamaj and E. Trizac, Europhys. Lett. **98**, 36004 (2012); Phys. Rev. B **85**, 205131 (2012).
[2] I. S. Gradshteyn and I. M. Ryzhik, Table of Integrals, Series, and Products, 6th ed. (Academic, London, 2000).
[3] I. Travěnec and L. Šamaj, Phys. Rev. E **92**, 022306 (2015).
[4] R. D. Misra, Math. Proc. Cambridge Philos. Soc. **36**, 173 (1940); M. Born and R. D. Misra, Math. Proc. Cambridge Philos. Soc. **36**, 466 (1940).
[5] Y. G. Chen and J. D. Weeks, Proc. Natl. Acad. Sci. U. S. A. **103**, 7560 (2006); J. M. Rodgers, C. Kaur, and Y. G. Chen, Phys. Rev. Lett. **97**, 097801 (2006).
[6] L. Šamaj and E. Trizac, Phys. Rev. Lett. **106**, 078301 (2011); Phys. Rev. E **84**, 041401 (2011).
[7] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Academic Press, Amsterdam (2007).
[8] D. Henderson and L. Blum, J. Chem. Phys. **69**, 5441 (1978); D. Henderson, L. Blum, and J.L. Lebowitz, J. Electroanal. Chem. **102**, 315 (1979); S.L. Carnie, D.Y.C. Chan, J. Chem. Phys. **74**, 1293 (1981); H. Wennerström, B. Jönsson, and P. Linse, J. Chem. Phys. **76**, 4665 (1982).