Reviews in Computational Chemistry
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Appendix F

Mathematical aspects of Ewald summation

F.1 Three-dimensional Coulombic systems

F.1.1 Energy contributions in Ewald formulation

F.1.1.1 Real-space contribution

To derive Eq. (6.8) for the real-space part of the Ewald potential, we start from Eq. (6.7) for the set of screened charges and apply Poisson's formula [see Eq. (6.3)]. This gives

$$\Phi^{(1)}(\boldsymbol{r}_i) = \sum_{\{\boldsymbol{n}\}}{}' \sum_{j=1}^{N} \left(\frac{q_j}{|\boldsymbol{r}_{ij} + \boldsymbol{n}|} + \Phi_{j,\boldsymbol{n}}(\boldsymbol{r}_i) \right) \tag{F.1}$$

where the first term in parentheses is the usual Coulomb potential and

$$\Phi_{j,\boldsymbol{n}}(\boldsymbol{r}_i) \equiv \int \mathrm{d}\boldsymbol{r}' \frac{\rho_{j,\boldsymbol{n}}(\boldsymbol{r}')}{|\boldsymbol{r}_i - \boldsymbol{r}'|} = -q_j \left(\frac{\alpha}{\sqrt{\pi}} \right)^3 \int \mathrm{d}\boldsymbol{r}' \frac{\exp\left[-\alpha^2 (\boldsymbol{r}' - \boldsymbol{r}_j + \boldsymbol{n})^2\right]}{|\boldsymbol{r}_i - \boldsymbol{r}'|} \tag{F.2}$$

is the potential due to a Gaussian charge cloud (total charge $-q_j$) located at $\boldsymbol{r}_j - \boldsymbol{n}$ [see Eq. (6.5)]. To evaluate the integral on the far right side of Eq. (F.2), we transform variables according to $\boldsymbol{r}' \rightarrow \boldsymbol{R} = \boldsymbol{r}' - \boldsymbol{r}_j + \boldsymbol{n}$, which gives

$$\Phi_{j,\boldsymbol{n}}(\boldsymbol{r}_i) = -q_j \left(\frac{\alpha}{\sqrt{\pi}} \right)^3 \int \mathrm{d}\boldsymbol{R} \frac{\exp\left[-\alpha^2 R^2\right]}{|\boldsymbol{r}_{ij} + \boldsymbol{n} - \boldsymbol{R}|} \tag{F.3}$$

In Eq. (F.3) the integration is carried out over the entire three-dimensional space.

The most convenient way of doing this is to transform to spherical coordinates $R = |\boldsymbol{R}|$, θ, and φ, where θ and φ are the polar and azimuthal angles, respectively, associated with the orientation of $\boldsymbol{R}$ in a space-fixed coordinate system. We may split the integral over R into two contributions from regions characterized by the inequalities

$$R < |\boldsymbol{r}_{ij} + \boldsymbol{n}| \equiv x \tag{F.4a}$$

$$R > x \tag{F.4b}$$

This separation of the integral can be effected by using an expansion in terms of spherical harmonics $\{Y_l^m\}$[258] valid for arbitrary vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$[1]; that is,

$$|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-1} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2) \tag{F.5}$$

where θ_i and φ_i are polar and azimuthal angles associated with vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, respectively. Notice that the complex conjugate $Y_{lm}^* = Y_{l,-m}$. In Eq. (F.5), $r_<$ ($r_>$) is the magnitude of the smaller (larger) vector of the pair $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. Setting $\boldsymbol{r}_1 = \boldsymbol{R}$ and $\boldsymbol{r}_2 = \boldsymbol{r}_{ij} + \boldsymbol{n}$, and inserting Eq. (F.5) into Eq. (F.3), one realizes that only terms characterized by $l = m = 0$ (with $Y_{00} = 1/\sqrt{4\pi}$) survive because [258]

$$\int_0^{2\pi} \mathrm{d}\varphi \int_{-1}^{1} \mathrm{d}\cos\theta Y_{lm}(\theta, \varphi) = \sqrt{4\pi}\delta_{l,0}\delta_{m,0} \tag{F.6}$$

Equation (F.3) can therefore be rewritten as

$$\Phi_{j,\boldsymbol{n}}(\boldsymbol{r}_i) = -4\pi q_j \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \left[\frac{1}{x}\int_0^x \mathrm{d}R R^2 \exp\left(-\alpha^2 R^2\right) + \int_x^{\infty} \mathrm{d}R R \exp\left(-\alpha^2 R^2\right)\right] \tag{F.7}$$

where the first integral appearing in brackets can be recast by using

$$\begin{aligned}
\int_0^x \mathrm{d}R R^2 \exp\left(-\alpha^2 R^2\right) &= -\frac{1}{2\alpha}\frac{\partial}{\partial\alpha}\int_0^x \mathrm{d}R \exp\left(-\alpha^2 R^2\right) \\
&= -\frac{1}{2\alpha}\frac{\partial}{\partial\alpha}\left[\frac{1}{\alpha}\int_0^{\alpha x} \mathrm{d}u \exp\left(-u^2\right)\right] \\
&= -\frac{1}{2\alpha}\frac{\partial}{\partial\alpha}\left[\frac{\sqrt{\pi}}{2\alpha}\mathrm{erf}(\alpha x)\right]
\end{aligned} \tag{F.8}$$

[1] See Eq. (3.70) in Ref. 242.

where we have employed the definition of the error function [11, 37, 330],

$$\operatorname{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y \mathrm{d}u \exp\left(-u^2\right) \tag{F.9}$$

to arrive at the third line of Eq. (F.8). The remaining partial derivative can be carried out by using

$$\frac{\partial}{\partial y} \operatorname{erf}(y) = \frac{2}{\sqrt{\pi}} \exp\left(-y^2\right) \tag{F.10}$$

which follows immediately from the Eq. (F.9) and Leibniz's rule for the differentiation of a parameter integral [11, 330]. One finally obtains

$$\int_0^x \mathrm{d}R R^2 \exp\left(-\alpha^2 R^2\right) = \frac{\sqrt{\pi}}{4\alpha^3} \operatorname{erf}(\alpha x) - \frac{1}{2\alpha^2} x \exp\left(-\alpha^2 x^2\right) \tag{F.11}$$

The second integral in Eq. (F.7) gives

$$\int_x^\infty \mathrm{d}R R \exp\left(-\alpha^2 R^2\right) = -\frac{1}{2\alpha^2} \int_x^\infty \mathrm{d}R \frac{\partial}{\partial R} \exp\left(-\alpha^2 R^2\right) = \frac{1}{2\alpha^2} \exp\left(-\alpha^2 x^2\right) \tag{F.12}$$

Inserting Eqs. (F.11) and (F.12) into Eq. (F.7) and replacing x by $|\boldsymbol{r}_{ij} + \boldsymbol{n}|$ the electrostatic potential at $\boldsymbol{r}_i$ due to one Gaussian located at $\boldsymbol{r}_j - \boldsymbol{n} \neq \boldsymbol{r}_i$ reduces to

$$\Phi_{j,\boldsymbol{n}}(\boldsymbol{r}_i) = -q_j \frac{\operatorname{erf}\left(\alpha |\boldsymbol{r}_{ij} + \boldsymbol{n}|\right)}{|\boldsymbol{r}_{ij} + \boldsymbol{n}|} \tag{F.13}$$

Finally, inserting Eq. (F.13) into our initial Eq. (F.1) and using the identity

$$1 - \operatorname{erf}(y) = \operatorname{erfc}(y) \tag{F.14}$$

we eventually arrive at Eq. (6.8).

F.1.1.2 Fourier-space contribution for nonzero wavevectors

To evaluate the electrostatic potential $\Phi^{(2)}(\boldsymbol{r})$ [see Eq. (6.11)] from the periodic Gaussian charge distribution $\rho^{(2)}(\boldsymbol{r})$ [see Eq. (6.10a)], it is most convenient to start from Laplace's equation [242], which says that

$$\Delta \Phi^{(2)}(\boldsymbol{r}) = -4\pi \rho^{(2)}(\boldsymbol{r}) \tag{F.15}$$

where $\Delta = \nabla \cdot \nabla$ is the Laplace operator. The Laplace equation is equivalent to Poisson's equation [see Eq. (6.3)] and follows directly from the first Maxwell equation of electrostatics,

$$\nabla \cdot \boldsymbol{E}(\boldsymbol{r}) = 4\pi\rho(\boldsymbol{r}) \tag{F.16}$$

using the definition

$$\boldsymbol{E}(\boldsymbol{r}) = -\nabla\Phi(\boldsymbol{r}) \tag{F.17}$$

for the electric field $\boldsymbol{E}$. From Eq. (F.15) it is evident that the Laplace equation is a second-order differential equation that can be solved conveniently in Fourier space. To this end, we expand the charge distribution and the corresponding potential according to the (discrete) Fourier series

$$\rho^{(2)}(\boldsymbol{r}) = \sum_{\{\boldsymbol{k}\}} \widetilde{\rho}^{(2)}(\boldsymbol{k}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \tag{F.18a}$$

$$\Phi^{(2)}(\boldsymbol{r}) = \sum_{\{\boldsymbol{k}\}} \widetilde{\Phi}^{(2)}(\boldsymbol{k}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \tag{F.18b}$$

where $\boldsymbol{k}$ is a vector of the reciprocal lattice related to the set of real-space lattice vectors $\{\boldsymbol{n}\}$ [see text above Eq. (6.11)], and the quantities $\widetilde{\rho}^{(2)}(\boldsymbol{k})$ and $\widetilde{\Phi}^{(2)}(\boldsymbol{k})$ are Fourier coefficients of the charge distribution and the potential, respectively. These Fourier coefficients can be obtained from the corresponding real-space quantities via

$$\widetilde{\rho}^{(2)}(\boldsymbol{k}) = \frac{1}{V_{\text{sys}}} \int d\boldsymbol{r}\rho^{(2)}(\boldsymbol{r}) \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}) \tag{F.19a}$$

$$\widetilde{\Phi}^{(2)}(\boldsymbol{k}) = \frac{1}{V_{\text{sys}}} \int d\boldsymbol{r}\Phi^{(2)}(\boldsymbol{r}) \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}) \tag{F.19b}$$

where V_{sys} is the volume of the *entire* system consisting of the basic cell plus its periodic replicas. Thus, $V_{\text{sys}} = Vn_{\text{cell}}$, where n_{cell} is the total number of cells.

Inserting the expansions (F.18) into Eq. (F.15), we have

$$\begin{aligned} \Delta\Phi^{(2)}(\boldsymbol{r}) &= \sum_{\{\boldsymbol{k}\}} \widetilde{\Phi}^{(2)}(\boldsymbol{k}) \Delta \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \\ &= -\sum_{\{\boldsymbol{k}\}} k^2 \widetilde{\Phi}^{(2)}(\boldsymbol{k}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \\ &= -4\pi \sum_{\{\boldsymbol{k}\}} \widetilde{\rho}^{(2)}(\boldsymbol{k}) \exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \end{aligned} \tag{F.20}$$

We now recall that Fourier expansions (F.18) are orthogonal expansions (see, e.g., Ref. 242). It follows that each summand on the second line of Eq. (F.20) has to be equal to its counterpart on the third line so that

$$\tilde{\Phi}^{(2)}(\boldsymbol{k}) = \frac{4\pi}{k^2}\tilde{\rho}^{(2)}(\boldsymbol{k}) \tag{F.21}$$

which is Laplace's equation in Fourier space. Thus, given the Fourier coefficients of the charge distribution (see below), we can easily calculate from Eq. (F.21) all Fourier coefficients of the corresponding potential, except its contribution at $\boldsymbol{k} = \boldsymbol{0}$, which will be discussed in the subsequent Appendix F.1.1.3. Replacing in Eq. (F.18b), $\tilde{\Phi}^{(2)}(\boldsymbol{k})$ by the expression given in Eq. (F.21) permits us to calculate the desired potential $\Phi^{(2)}(\boldsymbol{r})$.

Having in mind this strategy we start by evaluating the Fourier coefficients of $\tilde{\rho}^{(2)}(\boldsymbol{k})$. Inserting the explicit expression for $\rho^{(2)}(\boldsymbol{r})$ given in Eq. (6.10a) into Eq. (F.19a), we have

$$\tilde{\rho}^{(2)}(\boldsymbol{k}) = \frac{1}{V_{\text{sys}}}\left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \sum_{\{\boldsymbol{n}\}}\sum_{j=1}^{N} q_j \int \mathrm{d}\boldsymbol{r} \exp\left[-i\boldsymbol{k}\cdot\boldsymbol{r} - \alpha^2(\boldsymbol{r} - \boldsymbol{r}_j + \boldsymbol{n})^2\right] \tag{F.22}$$

The spatial integral on the right side is a standard (three-dimensional) Gaussian integral and can be carried out analytically [330]. Using, in addition, the relation $\exp(-i\boldsymbol{k}\cdot\boldsymbol{n}) = 1$ (which *defines* $\boldsymbol{k}$ as a reciprocal lattice vector), one finds

$$\begin{aligned}\tilde{\rho}^{(2)}(\boldsymbol{k}) &= \frac{1}{V_{\text{sys}}}\sum_{\{\boldsymbol{n}\}}\exp\left(-\frac{k^2}{4\alpha^2}\right)\sum_{j=1}^{N} q_j \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_j) \\ &= \frac{1}{V}\exp\left(-\frac{k^2}{4\alpha^2}\right)\sum_{j=1}^{N} q_j \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_j)\end{aligned} \tag{F.23}$$

where the second line has been obtained by employing the relation

$$\frac{1}{V_{\text{sys}}}\sum_{\{\boldsymbol{n}\}} 1 = \frac{1}{V_{\text{sys}}} n_{\text{cell}} = \frac{1}{V} \tag{F.24}$$

Inserting Eq. (F.23) into Eq. (F.21) then yields

$$\tilde{\Phi}^{(2)}(\boldsymbol{k}) = \frac{1}{V}\frac{4\pi}{k^2}\exp\left[-\frac{k^2}{4\alpha^2}\right]\sum_{j=1}^{N} q_j \exp[-i\boldsymbol{k}\cdot\boldsymbol{r}_j]\,. \quad \boldsymbol{k} \neq \boldsymbol{0} \tag{F.25}$$

Finally, inserting the coefficients (F.25) into Eq. (F.18b) together with $\boldsymbol{r} = \boldsymbol{r}_i$ gives the first term on the right side of Eq. (6.11), which is the contribution to the electrostatic potential $\Phi^{(2)}(\boldsymbol{r}_i)$. The missing "long-range" term related to the special case $\boldsymbol{k} = \boldsymbol{0}$ is discussed in the subsequent Appendix F.1.1.3.

F.1.1.3 Long-range contribution

Evaluation of the long-range part of the electrostatic potential, $\Phi^{(2)}_{\mathrm{LR}}(\boldsymbol{r}_i)$, which results from the long-wavelength limit ($\boldsymbol{k} = \boldsymbol{0}$) of the corresponding Fourier expansion, is the "trickiest" part in the derivation of the Ewald expression for the electrostatic potential of a Coulombic system. The problem is immediately apparent from Laplace's equation in Fourier space [see Eq. (F.21)] which, when solved for $\widetilde{\Phi}^{(2)}(\boldsymbol{k})$ *directly* at $\boldsymbol{k} = \boldsymbol{0}$, yields a *divergent* result because of the factor $1/k^2$. Fortunately, we are not really interested in the value of $\widetilde{\Phi}^{(2)}(\boldsymbol{k})$ for $\boldsymbol{k} = \boldsymbol{0}$. To realize the irrelevance of the value of $\widetilde{\Phi}^{(2)}(\boldsymbol{k})$ at $\boldsymbol{k} = \boldsymbol{0}$, consider the corresponding energy contribution

$$U^{(2)}(\boldsymbol{0}) \equiv \frac{1}{2}\sum_{j=1}^{N} q_j \widetilde{\Phi}^{(2)}(\boldsymbol{0}) \tag{F.26}$$

where [see Eq. (F.19b)]

$$\widetilde{\Phi}^{(2)}(\boldsymbol{0}) = \frac{1}{V_{\mathrm{sys}}}\int \mathrm{d}\boldsymbol{r}\Phi^{(2)}(\boldsymbol{r}) \tag{F.27}$$

is the spatial integral over the potential which must be independent of (particle) index j. Now recall that we are dealing with a *globally neutral* system, meaning that $\sum_{j=1}^{N} q_j = 0$. Consequently, $U^{(2)}(\boldsymbol{0})$ vanishes regardless of the actual value of $\widetilde{\Phi}^{(2)}(\boldsymbol{0})$.

Thus, in the following discussion we focus on the *limit* $\boldsymbol{k} \to \boldsymbol{0}$ of the full product $\widetilde{\Phi}^{(2)}(\boldsymbol{k})\exp(i\boldsymbol{k}\cdot\boldsymbol{r})$ appearing in Eq. (F.18b). More explicitly, given that we are dealing with an isotropic system where the direction of the wavevector $\boldsymbol{k}$ should not matter, we consider the angle–averaged quantity

$$\begin{aligned}\Phi^{(2)}_{\mathrm{LR}}(\boldsymbol{r}) &= \frac{1}{4\pi}\lim_{\boldsymbol{k}\to\boldsymbol{0}}\int_{-1}^{1}\mathrm{d}\cos\theta_{\boldsymbol{k}}\int_{0}^{2\pi}\mathrm{d}\varphi_{\boldsymbol{k}}\widetilde{\Phi}^{(2)}(\boldsymbol{k})\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) \\ &= \frac{1}{4\pi}\lim_{\boldsymbol{k}\to\boldsymbol{0}}\int \mathrm{d}\omega_{\boldsymbol{k}}\widetilde{\Phi}^{(2)}(\boldsymbol{k})\exp(i\boldsymbol{k}\cdot\boldsymbol{r})\end{aligned} \tag{F.28}$$

where $\theta_{\boldsymbol{k}}$ and $\varphi_{\boldsymbol{k}}$ are the angles specifying the orientation of $\boldsymbol{k}$ and $\omega_{\boldsymbol{k}} = (\theta_{\boldsymbol{k}}, \varphi_{\boldsymbol{k}})$.

To evaluate the right side of Eq. (F.28) we consider first the charge-density coefficients $\tilde{\rho}^{(2)}(\boldsymbol{k})$ that give rise to the potential $\Phi^{(2)}$ for small, but nonvanishing $\boldsymbol{k}$. Expanding these coefficients in a Taylor series around $\boldsymbol{k} = \boldsymbol{0}$ and using Laplace's equation [see Eq. (F.21)], we obtain

$$\widetilde{\Phi}^{(2)}(\boldsymbol{k}) = \frac{4\pi}{k^2}\left[\widetilde{\rho}^{(2)}\big|_{\boldsymbol{0}} + \boldsymbol{k}\cdot\nabla_{\boldsymbol{k}}\widetilde{\rho}^{(2)}(\boldsymbol{k})\big|_{\boldsymbol{0}} + \frac{1}{2}\boldsymbol{k}\boldsymbol{k}\cdot\nabla_{\boldsymbol{k}}\nabla_{\boldsymbol{k}}\widetilde{\rho}^{(2)}(\boldsymbol{k})\big|_{\boldsymbol{0}} + \mathcal{O}(k^3)\right] \tag{F.29}$$

We now consider the lowest-order expansion coefficients of $\widetilde{\rho}^{(2)}(\boldsymbol{k})$ appearing on the right side of Eq. (F.29). Using the general definition (F.19a) for the Fourier coefficients and performing the required derivatives, we obtain

$$\widetilde{\rho}^{(2)}\big|_{\mathbf{0}} = \frac{1}{V_{\text{sys}}}\int \mathrm{d}\boldsymbol{r}\,\rho^{(2)}(\boldsymbol{r}) = \frac{1}{V_{\text{sys}}}Q^{(2)} \tag{F.30a}$$

$$\nabla_{\boldsymbol{k}}\widetilde{\rho}^{(2)}(\boldsymbol{k})\big|_{\mathbf{0}} = -\frac{i}{V_{\text{sys}}}\int \mathrm{d}\boldsymbol{r}\,\boldsymbol{r}\rho^{(2)}(\boldsymbol{r}) = -\frac{i}{V_{\text{sys}}}\boldsymbol{P}^{(2)} \tag{F.30b}$$

$$\nabla_{\boldsymbol{k}}\nabla_{\boldsymbol{k}}\widetilde{\rho}^{(2)}(\boldsymbol{k})\big|_{\mathbf{0}} = -\frac{1}{V_{\text{sys}}}\int \mathrm{d}\boldsymbol{r}\,\boldsymbol{r}\boldsymbol{r}\rho^{(2)}(\boldsymbol{r}) = -\frac{1}{V_{\text{sys}}}\mathbf{A}^{(2)} \tag{F.30c}$$

The quantities on the right side of Eqs. (F.30) have a simple and lucid physical interpretation in terms of the multipole moments of the charge distribution $\rho^{(2)}(\boldsymbol{r})$ [242]. Indeed, $Q^{(2)}$ is nothing but the monopole moment, $\boldsymbol{P}^{(2)}$ is the dipole moment, and the second-rank tensor $\mathbf{A}^{(2)}$ is related closely to the quadrupole moment. Explicit expressions for these quantities can be easily obtained by inserting Eq. (6.10a) into Eqs. (F.30) and carrying out the (Gaussian) spatial integrals. For the monopole, this procedure gives

$$\begin{aligned}\frac{Q^{(2)}}{V_{\text{sys}}} &= \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \frac{1}{V_{\text{sys}}}\sum_{\{\boldsymbol{n}\}}\sum_{j=1}^{N} q_j \int \mathrm{d}\boldsymbol{r}\exp\left[-\alpha^2(\boldsymbol{r}-\boldsymbol{r}_j+\boldsymbol{n})^2\right] \\ &= \frac{1}{V_{\text{sys}}}\sum_{\{\boldsymbol{n}\}}\sum_{j=1}^{N} q_j = \frac{1}{V}\sum_{j=1}^{N} q_j = 0\end{aligned} \tag{F.31}$$

where we used Eq. (F.24). Thus, the monopole moment vanishes due to the global charge neutrality of the system. The dipole moment of the charge distribution $\rho^{(2)}(\boldsymbol{r})$ coincides with that of the original delta-like distribution in Eq. (6.4); that is,

$$\begin{aligned}\frac{\boldsymbol{P}^{(2)}}{V_{\text{sys}}} &= \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \frac{1}{V_{\text{sys}}}\sum_{\{\boldsymbol{n}\}}\sum_{j=1}^{N} q_j \int \mathrm{d}\boldsymbol{r}\,\boldsymbol{r}\exp\left[-\alpha^2(\boldsymbol{r}-\boldsymbol{r}_j+\boldsymbol{n})^2\right] \\ &= \frac{1}{V_{\text{sys}}}\sum_{\{\boldsymbol{n}\}}\sum_{j=1}^{N} q_j(\boldsymbol{r}_j-\boldsymbol{n}) = \frac{\boldsymbol{M}}{V}\end{aligned} \tag{F.32}$$

In writing the last member of Eq. (F.32) we have used the definition $\boldsymbol{M} = \sum_{j=1}^{N} q_j\boldsymbol{r}_j$ for the total dipole moment of the central cell and the fact that each replicated cell has exactly the same total dipole moment. Using similar arguments we obtain for the cartesian components $\left(\mathbf{A}^{(2)}\right)_{kl}$ (k, l = x, y, or z)

of the second-rank tensor $\mathbf{A}^{(2)}$,

$$\begin{aligned}\frac{\left(\mathbf{A}^{(2)}\right)_{kl}}{V_{\text{sys}}} &= \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \frac{1}{V_{\text{sys}}} \sum_{\{\boldsymbol{n}\}} \sum_{j=1}^{N} q_j \int \mathrm{d}\boldsymbol{r}\, (\boldsymbol{r})_k (\boldsymbol{r})_l \exp\left[-\alpha^2 (\boldsymbol{r}-\boldsymbol{r}_j+\boldsymbol{n})^2\right] \\ &= \frac{1}{V}\left[\frac{1}{2\alpha^2}\delta_{kl} + \sum_{j=1}^{N} q_j (\boldsymbol{r}_j)_k (\boldsymbol{r}_j)_l (1-\delta_{kl})\right] \\ &\equiv \frac{1}{V}\left(\mathbf{D}^{(2)}\right)_{kl} \end{aligned} \tag{F.33}$$

We proceed by inserting the nonvanishing multipole moments defined in Eqs. (F.30)–(F.33) into the expansion in Eq. (F.29), which gives

$$\widetilde{\Phi}^{(2)}(\boldsymbol{k}) = -i\frac{4\pi}{k^2 V}\boldsymbol{k}\cdot\boldsymbol{M} - \frac{2\pi}{k^2 V}\boldsymbol{k}\mathbf{D}^{(2)}\boldsymbol{k} + \mathcal{O}(k) \tag{F.34}$$

As we emphasized before we are interested in the long-wavelength limit of $\widetilde{\Phi}^{(2)}(\boldsymbol{k})$ times the phase factor $\exp(i\boldsymbol{k}\cdot\boldsymbol{r})$. Expanding the latter in a Taylor series around $\boldsymbol{k}=\mathbf{0}$, that is

$$\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) = 1 + i\boldsymbol{k}\cdot\boldsymbol{r} - \frac{1}{2}(\boldsymbol{k}\cdot\boldsymbol{r})^2 + \mathcal{O}(k^3) \tag{F.35}$$

and combining this expansion with Eq. (F.34), we obtain

$$\begin{aligned}\widetilde{\Phi}^{(2)}(\boldsymbol{k})\exp(i\boldsymbol{k}\cdot\boldsymbol{r}) &= -i\frac{4\pi}{k^2 V}\boldsymbol{k}\cdot\boldsymbol{M} - \frac{2\pi}{k^2 V}\boldsymbol{k}\mathbf{D}^{(2)}\boldsymbol{k} \\ &\quad + \frac{4\pi}{k^2 V}(\boldsymbol{k}\cdot\boldsymbol{r})(\boldsymbol{k}\cdot\boldsymbol{M}) - i(\boldsymbol{k}\cdot\boldsymbol{r})\frac{2\pi}{k^2 V}\boldsymbol{k}\mathbf{D}^{(2)}\boldsymbol{k} \\ &\quad + \frac{1}{2}(\boldsymbol{k}\cdot\boldsymbol{r})^2\left(i\frac{4\pi}{k^2 V}\boldsymbol{k}\cdot\boldsymbol{M} + \frac{2\pi}{k^2 V}\boldsymbol{k}\mathbf{D}^{(2)}\boldsymbol{k}\right) + \mathcal{O}(k^2)\end{aligned} \tag{F.36}$$

We now consider separately the terms on the right side of Eq. (F.36), focusing on the question whether they contribute to the desired (angle-averaged) potential $\Phi_{\text{LR}}^{(2)}(\boldsymbol{r})$ [defined in Eq. (F.28)]. The first term depends on $1/k$ and may therefore seem to diverge as we take the limit $\boldsymbol{k}\to\mathbf{0}$. However, as this first term also contains $\boldsymbol{k}\cdot\boldsymbol{M}$, it vanishes already for nonvanishing $\boldsymbol{k}$ because of the angle average in Eq. (F.28). To see this result, we note that the scalar product of two arbitrary unit vectors $\hat{\boldsymbol{a}}$ and $\hat{\boldsymbol{b}}$ can be expressed in terms of spherical harmonics as [258]

$$\hat{\boldsymbol{a}}\cdot\hat{\boldsymbol{b}} = \frac{4\pi}{3}\sum_{m=-1}^{1} Y_{1m}^{*}(\omega_{\boldsymbol{a}})\, Y_{1m}(\omega_{\boldsymbol{b}}) \tag{F.37}$$

Therefore,

$$\int \mathrm{d}\omega_{\boldsymbol{k}} \boldsymbol{k} \cdot \boldsymbol{M} = k\,|\boldsymbol{M}|\,\frac{4\pi}{3} \sum_{m=-1}^{1} \int \mathrm{d}\omega_{\boldsymbol{k}} Y_{1m}^{*}(\omega_{\boldsymbol{k}})\, Y_{1m}(\omega_{\boldsymbol{M}}) = 0, \qquad \text{(F.38)}$$

where we have also used Eq. (F.6).

The next term on the right side of Eq. (F.36) is constant in k and involves the product $\boldsymbol{k}\mathbf{D}^{(2)}\boldsymbol{k}$, which does not immediately vanish if averaged over orientations. Nevertheless, we can safely neglect this term. The reason is that it is independent of the position of particle i, with the immediate consequence that the corresponding energy contribution vanishes due to the global charge neutrality of the system [see text below Eq. (F.26)].

The third term on the right side of Eq. (F.36) contains the product $(\boldsymbol{k} \cdot \boldsymbol{r})(\boldsymbol{k} \cdot \boldsymbol{M})$. It has an explicit positional dependence even after performing the orientational average. Indeed, expanding both scalar products according to Eq. (F.37) and using the orthogonality of spherical harmonics given by [258]

$$\int \mathrm{d}\omega Y_{lm}^{*}(\omega) Y_{l'm'}(\omega) = \delta_{ll'}\delta_{mm'} \qquad \text{(F.39)}$$

we find

$$\begin{aligned}
\frac{1}{k^2} \int \mathrm{d}\omega_{\boldsymbol{k}} (\boldsymbol{k} \cdot \boldsymbol{r})(\boldsymbol{k} \cdot \boldsymbol{M}) &= |\boldsymbol{r}|\,|\boldsymbol{M}| \left(\frac{4\pi}{3}\right)^2 \sum_{m=-1}^{1} \sum_{m'=-1}^{1} \\
&\quad \times \int \mathrm{d}\omega_{\boldsymbol{k}} Y_{1m}^{*}(\omega_{\boldsymbol{k}})\, Y_{1m}(\omega_{\boldsymbol{r}})\, Y_{1m'}^{*}(\omega_{\boldsymbol{k}})\, Y_{1m'}(\omega_{\boldsymbol{M}}) \\
&= |\boldsymbol{r}|\,|\boldsymbol{M}| \left(\frac{4\pi}{3}\right)^2 \sum_{m=-1}^{1} Y_{1m}^{*}(\omega_{\boldsymbol{M}})\, Y_{1m}(\omega_{\boldsymbol{r}}) \\
&= \frac{4\pi}{3} \boldsymbol{r} \cdot \boldsymbol{M} \qquad \text{(F.40)}
\end{aligned}$$

where the last line has been obtained by using Eq. (F.37) in reverse direction.

The subsequent terms on the right side of Eq. (F.36) can be ignored because they are at least proportional to k and therefore vanish in the limit $\boldsymbol{k} \to \boldsymbol{0}$. Thus, the potential $\Phi_{\mathrm{LR}}^{(2)}(\boldsymbol{r})$ reduces to [see Eq. (F.28)]

$$\Phi_{\mathrm{LR}}^{(2)}(\boldsymbol{r}) = \frac{1}{k^2 V} \int \mathrm{d}\omega_{\boldsymbol{k}} (\boldsymbol{k} \cdot \boldsymbol{r})(\boldsymbol{k} \cdot \boldsymbol{M}) = \frac{4\pi}{3V} \boldsymbol{r} \cdot \boldsymbol{M} \qquad \text{(F.41)}$$

The above expression for the long-range part of the electrostatic potential is consistent with a well-known result from macroscopic electrostatics regarding

the average electric field inside a large sphere containing an (arbitrary) charge distribution. This field is given by [242]

$$\overline{\boldsymbol{E}} = -\frac{4\pi}{3}\boldsymbol{P} \tag{F.42}$$

where $\boldsymbol{P}$ is the polarization of the sphere. Clearly, $\overline{\boldsymbol{E}}$ is independent of the radius of the sphere. Moreover, it is constant within the sphere, implying that the corresponding electrostatic potential is given by

$$\overline{\Phi}(\boldsymbol{r}) = -\boldsymbol{r}\cdot\overline{\boldsymbol{E}} = \frac{4\pi}{3}\boldsymbol{r}\cdot\boldsymbol{P} \tag{F.43}$$

We now recall that our system is represented by one unit cell that is replicated in all three spatial directions. Thus, we can indeed take our system to be a (macroscopically) large sphere. As a consequence, the quantity $\boldsymbol{P}$ can be identified with the quantity $\boldsymbol{P}^{(2)}/V_{\text{sys}} = \boldsymbol{M}/V$ appearing in Eqs. (F.30b) and (F.32). We therefore conclude that the potential $\overline{\Phi}(\boldsymbol{r})$ is identical with long-range potential $\Phi_{\text{LR}}^{(2)}(\boldsymbol{r})$ given in Eq. (F.41).

The above considerations are useful because they permit one to understand from a macroscopic perspective why a long-range contribution to the electrostatic potential should arise. Moreover, they are particularly helpful because they indicate a strategy to introduce different boundary conditions into the Ewald summation technique. Indeed, the physical picture to which Eqs. (F.41)–(F.43) correspond is that the (macroscopically) large sphere is surrounded by a vacuum. In this case, any polarization in the sphere will generate surface charges at the interface between the sphere and the vacuum, and these charges in turn generate the average (or depolarization) field given in Eq. (F.42). If, on the other hand, the sphere is surrounded by a dielectricum with dielectric constant ϵ', the average field inside the sphere has to be corrected by the so-called reaction field [331],

$$\boldsymbol{E}_{\text{RF}} = \frac{2(\epsilon'-1)}{2\epsilon'+1}\frac{4\pi}{3}\boldsymbol{P} \tag{F.44}$$

which, as expected, vanishes for the special case $\epsilon' = 1$ (i.e., in the vacuum). Combining Eqs. (F.42) and (F.44), the total average field inside the sphere then becomes

$$\overline{\boldsymbol{E}} \to \overline{\boldsymbol{E}} + \boldsymbol{E}_{\text{RF}} = -\frac{4\pi}{2\epsilon'+1}\boldsymbol{P} = -\frac{4\pi}{2\epsilon'+1}\frac{\boldsymbol{M}}{V} \tag{F.45}$$

Inserting Eq. (F.45) into Eq. (F.43) and taking $\boldsymbol{r} = \boldsymbol{r}_i$, one obtains the final expression for the long-range contribution of the electrostatic potential given in Eq. (6.12).

F.1.1.4 Self-contribution

The self-part of the Ewald electrostatic potential given in Eq. (6.14) can be derived in a fashion similar to our derivation of the real-space contribution in Appendix F.1.1.1. Starting from Poisson's formula [see Eq. (6.3)] and inserting Eq. (6.10b) for the charge density $\rho^{(3)}(\boldsymbol{r}')$, we have

$$\Phi^{(3)}(\boldsymbol{r}_i) = \int \mathrm{d}\boldsymbol{r}' \frac{\rho^{(3)}(\boldsymbol{r}')}{|\boldsymbol{r}_i - \boldsymbol{r}'|} = -q_i \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \int \mathrm{d}\boldsymbol{r}' \frac{\exp\left[-\alpha^2 (\boldsymbol{r}' - \boldsymbol{r}_i)^2\right]}{|\boldsymbol{r}_i - \boldsymbol{r}'|} \quad \text{(F.46)}$$

The three-dimensional integral on the far right side of Eq. (F.46) can be evaluated by transforming variables according to $\boldsymbol{r}' \rightarrow \boldsymbol{R} = \boldsymbol{r}' - \boldsymbol{r}_i$ followed by a transformation to polar coordinates. This gives [330]

$$\Phi^{(3)}(\boldsymbol{r}_i) = -4\pi q_i \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \int_0^\infty \mathrm{d}R\, R \exp\left(-\alpha^2 R^2\right) \quad \text{(F.47)}$$

which can be easily be evaluated in closed form to give Eq. (6.14).

Finally, it seems worth noting that the self-part can also be derived directly from Eq. (F.13) representing the potential $\Phi_{j,\boldsymbol{n}}(\boldsymbol{r}_i)$ caused by a Gaussian located at $\boldsymbol{r}_j - \boldsymbol{n} \neq \boldsymbol{r}_i$. Indeed, considering $\Phi_{j,\boldsymbol{n}}$ at $\boldsymbol{n} = \boldsymbol{0}$, one obtains

$$\begin{aligned} -\lim_{r_{ij}\rightarrow 0} q_i \frac{\operatorname{erf}(\alpha r_{ij})}{r_{ij}} &= -\lim_{r_{ij}\rightarrow 0} q_i \left[\frac{2\alpha}{\sqrt{\pi}} - \frac{2}{3\sqrt{\pi}}\alpha^3 r_{ij}^2 + \mathcal{O}\left(r_{ij}^4\right)\right] \\ &= -q_i \frac{2\alpha}{\sqrt{\pi}} \overset{(6.14)}{=} \Phi^{(3)}(\boldsymbol{r}_i) \end{aligned} \quad \text{(F.48)}$$

in the limit $r_{ij} \rightarrow 0$ where we have used the first few terms in a Taylor expansion of the error function $\operatorname{erf}(x)$ around $x = 0$ given by

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} x - \frac{2}{3\sqrt{\pi}} x^3 + \mathcal{O}(x^5) \quad \text{(F.49)}$$

F.1.2 Force and stress tensor components

F.1.2.1 Force components

Based on Eqs. (6.15)–(6.17b) we can also derive the corresponding expressions for the force acting on particle i,

$$\boldsymbol{F}_{\mathrm{C},i}^{\mathrm{3d}} = -q_i \nabla_i \Phi(\boldsymbol{r}_i) \quad \text{(F.50)}$$

Because of Eqs. (6.16a) and (6.17a) we can split the total force into a sum of three individual contributions, namely

$$\boldsymbol{F}_{\mathrm{C},i}^{\mathrm{3d}} = \boldsymbol{F}_{\mathrm{CR},i}^{\mathrm{3d}} + \boldsymbol{F}_{\mathrm{CF},i}^{\mathrm{3d}} + \boldsymbol{F}_{\mathrm{CLR},i}^{\mathrm{3d}} \quad \text{(F.51)}$$

The reader should realize that the self-part makes no contribution because the summand in Eq. (6.17b) is independent of the coordinates of particle i. Considering the individual contributions to the total force separately, we obtain after straightforward differentiation

$$\begin{aligned}
\boldsymbol{F}^{\mathrm{3d}}_{\mathrm{CR},i} &= -q_i \sum_{j=1}^{N} \sum_{\boldsymbol{n}}{}' q_j \nabla_{ij} \frac{\operatorname{erfc}(\alpha |\boldsymbol{r}_{ij}+\boldsymbol{n}|)}{|\boldsymbol{r}_{ij}+\boldsymbol{n}|} \\
&= q_i \sum_{j=1}^{N} \sum_{\boldsymbol{n}}{}' q_j \left\{ \frac{2\alpha}{\sqrt{\pi}} \exp\left[-\alpha^2 (\boldsymbol{r}_{ij}+\boldsymbol{n})^2\right] \right. \\
&\quad \left. + \frac{\operatorname{erfc}(\alpha |\boldsymbol{r}_{ij}+\boldsymbol{n}|)}{|\boldsymbol{r}_{ij}+\boldsymbol{n}|} \right\} \frac{\boldsymbol{r}_{ij}+\boldsymbol{n}}{|\boldsymbol{r}_{ij}+\boldsymbol{n}|^2} \qquad \text{(F.52a)} \\
\boldsymbol{F}^{\mathrm{3d}}_{\mathrm{CF},i} &= -4\pi q_i \sum_{j=1}^{N} q_j \nabla_{ij} \left[\sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{1}{k^2 V} \exp\left(-\frac{k^2}{4\alpha^2}\right) \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_{ij}) \right] \\
&= 4\pi i q_i \sum_{j=1}^{N} q_j \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{\boldsymbol{k}}{k^2 V} \exp\left(-\frac{k^2}{4\alpha^2}\right) \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_{ij}) \\
&= 4\pi q_i \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{\boldsymbol{k}}{k^2 V} \exp\left(-\frac{k^2}{4\alpha^2}\right) \sum_{j=1}^{N} q_j \sin(\boldsymbol{k}\cdot\boldsymbol{r}_{ij}) \qquad \text{(F.52b)} \\
\boldsymbol{F}^{\mathrm{3d}}_{\mathrm{CLR},i} &= -q_i \nabla_i \left[\boldsymbol{r}_i \cdot \sum_{j=1}^{N} \frac{4\pi q_j \boldsymbol{r}_j}{V(2\epsilon'+1)} \right] = -q_i \frac{4\pi \boldsymbol{M}}{V(2\epsilon'+1)} \qquad \text{(F.52c)}
\end{aligned}$$

In writing Eqs. (F.52a) and (F.52b) we have taken into account that the operator ∇_i appearing in the original force expression [see Eq. (F.50)] can be replaced by its counterpart ∇_{ij} with respect to the distance vector $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ where, of course,

$$\nabla_{ij} \equiv \frac{\partial}{\partial \boldsymbol{r}_{ij}} = \frac{\boldsymbol{r}_{ij}}{r_{ij}} \frac{\mathrm{d}}{\mathrm{d}r_{ij}} \qquad \text{(F.53)}$$

and $r_{ij} = |\boldsymbol{r}_{ij}|$ also hold. In deriving Eq. (F.52a) we also used Eqs. (F.10) and (F.14). Moreover, the last line of Eq. (F.52b) has been obtained using

$$i\boldsymbol{k} \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_{ij}) = i\boldsymbol{k}\cos(\boldsymbol{k}\cdot\boldsymbol{r}_{ij}) + \boldsymbol{k}\sin(\boldsymbol{k}\cdot\boldsymbol{r}_{ij}) \qquad \text{(F.54)}$$

where the cosine term (contrary to sine term) changes sign upon inversion, that is, $\boldsymbol{k} \to -\boldsymbol{k}$, and therefore vanishes in the sum over *all* wavevectors.

F.1.2.2 Stress tensor components

By analogy with Appendix E.3 we derive molecular expressions for various (diagonal) components of the stress tensor $\tau_{\gamma\gamma}$ (γ = x, y, or z) by realizing that we may write

$$\tau^{3d}_{\gamma\gamma,C} = \tau^{id}_{\gamma\gamma} + \frac{\langle W^{3d}_{\gamma\gamma,C}\rangle}{A_{\gamma 0}} \tag{F.55}$$

in the grand canonical ensemble where $\tau^{id}_{\gamma\gamma}$ is given in Eq. (E.33). From the definition of the Clausius virial [see Eq. (E.35)] and Eq. (6.15) for the total configurational potential energy of the three-dimensional Coulomb system in Ewald formulation, we have

$$W^{3d}_{\gamma\gamma,C} = \frac{\partial U^{3d}_{C}}{\partial s_\gamma} = \frac{\partial U^{3d}_{CR}}{\partial s_\gamma} + \frac{\partial U^{3d}_{CF}}{\partial s_\gamma} + \frac{\partial U^{3d}_{CLR}}{\partial s_\gamma}, \qquad \gamma = \text{x, y, or z} \tag{F.56}$$

because U^{3d}_{Cs} is a constant that does not depend on the actual configuration [see Eq. (6.17b)]. To evaluate the partial derivatives on the right side of Eq. (F.56), it turns out to be convenient to transform to unit-cube coordinates via

$$\boldsymbol{r}_i \to \widetilde{\boldsymbol{r}}_i \equiv \begin{pmatrix} x_i/s_x \\ y_i/s_y \\ z_i/s_z \end{pmatrix}, \qquad i = 1, \ldots, N \tag{F.57}$$

Consider the first term on the right side of Eq. (F.56). From Eq. (6.16a) we obtain

$$\begin{aligned} \frac{\partial U^{3d}_{CR}}{\partial s_\gamma} &= \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{\sum_{\{\boldsymbol{n}\}}}' q_i q_j \frac{\partial}{\partial s_\gamma}\frac{\operatorname{erfc}(\alpha|\boldsymbol{r}_{ij}+\boldsymbol{n}|)}{|\boldsymbol{r}_{ij}+\boldsymbol{n}|} \\ &= -\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{\sum_{\{\boldsymbol{n}\}}}' q_i q_j \left\{ \frac{\operatorname{erfc}(\alpha|\boldsymbol{r}_{ij}+\boldsymbol{n}|)}{|\boldsymbol{r}_{ij}+\boldsymbol{n}|^2} \right. \\ &\quad \left. + \frac{2\alpha}{\sqrt{\pi}}\frac{1}{|\boldsymbol{r}_{ij}+\boldsymbol{n}|}\exp\left[-(\alpha|\boldsymbol{r}_{ij}+\boldsymbol{n}|)^2\right] \right\} \frac{\partial}{\partial s_\gamma}|\boldsymbol{r}_{ij}+\boldsymbol{n}| \end{aligned} \tag{F.58}$$

which follows with the aid of Eqs. (F.10) and (F.14). We now notice that because of Eq. (F.57)

$$|\boldsymbol{r}_{ij}+\boldsymbol{n}| = \sqrt{s_x^2(\widetilde{x}_{ij}+n_x)^2 + s_y^2(\widetilde{y}_{ij}+n_y)^2 + s_z^2(\widetilde{z}_{ij}+n_z)^2} \tag{F.59}$$

In the previous expression we used the fact that the lattice vectors $\boldsymbol{n} = (n_x s_x, n_y s_y, n_z s_z)$. Therefore,

$$\frac{\partial}{\partial s_\gamma}|\boldsymbol{r}_{ij}+\boldsymbol{n}| = \frac{s_\gamma(\gamma_{ij}+n_\gamma)^2}{|\boldsymbol{r}_{ij}+\boldsymbol{n}|} = \frac{1}{s_\gamma}\frac{[(\boldsymbol{r}_{ij}+\boldsymbol{n})\cdot\widehat{\boldsymbol{e}}_\gamma]^2}{|\boldsymbol{r}_{ij}+\boldsymbol{n}|} \tag{F.60}$$

where $\widehat{\boldsymbol{e}}_\gamma$ is a unit vector in the γ-direction and $\gamma_{ij} = \widetilde{\boldsymbol{r}}_{ij} \cdot \widehat{\boldsymbol{e}}_\gamma$ so that

$$\frac{\partial U_{\mathrm{CR}}^{\mathrm{3d}}}{\partial s_\gamma} = -\frac{1}{2s_\gamma} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\{\boldsymbol{n}\}}{}' q_i q_j \left\{ \frac{\operatorname{erfc}(\alpha |\boldsymbol{r}_{ij} + \boldsymbol{n}|)}{|\boldsymbol{r}_{ij} + \boldsymbol{n}|} + \frac{2\alpha}{\sqrt{\pi}} \exp\left[-(\alpha |\boldsymbol{r}_{ij} + \boldsymbol{n}|)^2\right] \right\} \frac{\left[(\boldsymbol{r}_{ij} + \boldsymbol{n}) \cdot \widehat{\boldsymbol{e}}_\gamma\right]^2}{|\boldsymbol{r}_{ij} + \boldsymbol{n}|^2} \tag{F.61}$$

follows without further ado.

Turning to the second term on the right side of Eqs. (F.56), we realize that $\widetilde{a}(\boldsymbol{k})$ is independent of $\{s_\gamma\}$ because each term in the sum [see Eq. (6.19)] can be written as

$$\exp(-i\boldsymbol{k} \cdot \boldsymbol{r}_i) = \exp\left[-2\pi i (m_x \widetilde{x}_i + m_y \widetilde{y}_i + m_z \widetilde{z}_i)\right] \tag{F.62}$$

where we used the definition of the wavevectors $\boldsymbol{k}$ [see text before Eq. (6.11)]. This leaves us with

$$\begin{aligned} \frac{\partial U_{\mathrm{CF}}^{\mathrm{3d}}}{\partial s_\gamma} &= -\frac{2\pi}{V} \sum_{\boldsymbol{k} \neq \boldsymbol{0}} \frac{1}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right) \left[\frac{1}{V}\frac{\partial V}{\partial s_\gamma} + \left(\frac{2}{k} + \frac{k}{2\alpha^2}\right)\frac{\partial k}{\partial s_\gamma}\right] |\widetilde{a}(\boldsymbol{k})|^2 \\ &= -\frac{2\pi}{V s_\gamma} \sum_{\boldsymbol{k} \neq \boldsymbol{0}} \frac{1}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right) \left[1 - \left(\frac{2}{k^2} + \frac{1}{2\alpha^2}\right) \right. \\ &\quad \left. \times (\boldsymbol{k} \cdot \widehat{\boldsymbol{e}}_\gamma)^2 |\widetilde{a}(\boldsymbol{k})|^2 \right] \end{aligned} \tag{F.63}$$

from Eq. (6.18) where we have used the fact that

$$V = A_{\gamma 0} s_\gamma \tag{F.64}$$

and

$$k = 2\pi \sqrt{\left(\frac{m_x}{s_x}\right)^2 + \left(\frac{m_y}{s_y}\right)^2 + \left(\frac{m_z}{s_z}\right)^2} \tag{F.65}$$

from which

$$\frac{\partial k}{\partial s_\gamma} = -\frac{2\pi}{\sqrt{(m_x/s_x)^2 + (m_y/s_y)^2 + (m_z/s_z)^2}} \frac{m_\gamma^2}{s_\gamma^3} = -\frac{(\boldsymbol{k} \cdot \widehat{\boldsymbol{e}}_\gamma)^2}{k} \frac{1}{s_\gamma} \tag{F.66}$$

follows directly where

$$\boldsymbol{k} \cdot \widehat{\boldsymbol{e}}_\gamma = \frac{2\pi m_\gamma}{s_\gamma} \tag{F.67}$$

is the projection of the wavevector $\boldsymbol{k}$ onto the γ-axis (i.e., the γ-component of $\boldsymbol{k}$).

To evaluate the third contribution to $W_{\gamma\gamma}$ in Eq. (F.56), we realize from Eq. (6.17a) that

$$\frac{\partial U_{\mathrm{CLR}}^{\mathrm{3d}}}{\partial s_\gamma} = \frac{2\pi}{2\epsilon'+1}\frac{\partial}{\partial s_\gamma}\frac{M^2}{V} = \frac{2\pi}{2\epsilon'+1}\left[\frac{2M_\gamma^2}{Vs_\gamma} - \left(\frac{M}{V}\right)^2\frac{\partial V}{\partial s_\gamma}\right] \tag{F.68}$$

In writing the first term on the right side of Eq. (F.68) we introduced the projection of the total dipole moment $\boldsymbol{M}$ [see Eq. (6.13)] onto the γ-axis, namely

$$M_\gamma = \boldsymbol{M}\cdot\widehat{\boldsymbol{e}}_\gamma = \sum_{i=1}^{N} q_i\boldsymbol{r}_i\cdot\widehat{\boldsymbol{e}}_\gamma = \sum_{i=1}^{N} q_i s_\gamma\widetilde{\boldsymbol{r}}_i\cdot\widehat{\boldsymbol{e}}_\gamma \tag{F.69}$$

Equation (F.68) may be rewritten to give

$$\frac{\partial U_{\mathrm{CLR}}^{\mathrm{3d}}}{\partial s_\gamma} = -\frac{1}{Vs_\gamma}\frac{2\pi}{2\epsilon'+1}\left[M^2 - 2\left(\boldsymbol{M}\cdot\widehat{\boldsymbol{e}}_\gamma\right)^2\right] \tag{F.70}$$

for the long-range contribution to $W_{\gamma\gamma,\mathrm{C}}^{\mathrm{3d}}$. Finally, putting all this together we have from Eqs. (F.55), (F.56), (F.61), (F.63), and (F.70) the somewhat lengthy expression

$$\begin{aligned}\tau_{\gamma\gamma,\mathrm{C}}^{\mathrm{3d}} = \tau_{\gamma\gamma}^{\mathrm{id}} &- \frac{1}{2V}\left\langle\sum_{i=1}^{N}\sum_{j=1}^{N}{\sum_{\{\boldsymbol{n}\}}}' q_iq_j\left\{\frac{\operatorname{erfc}\left(\alpha\left|\boldsymbol{r}_{ij}+\boldsymbol{n}\right|\right)}{\left|\boldsymbol{r}_{ij}+\boldsymbol{n}\right|}\right.\right.\\ &\left.\left.+\frac{2\alpha}{\sqrt{\pi}}\exp\left[-\left(\alpha\left|\boldsymbol{r}_{ij}+\boldsymbol{n}\right|\right)^2\right]\right\}\frac{\left[\left(\boldsymbol{r}_{ij}+\boldsymbol{n}\right)\cdot\widehat{\boldsymbol{e}}_\gamma\right]^2}{\left|\boldsymbol{r}_{ij}+\boldsymbol{n}\right|^2}\right\rangle\\ &-\frac{2\pi}{V^2}\left\langle\sum_{\boldsymbol{k}\neq\boldsymbol{0}}\frac{1}{k^2}\exp\left(-\frac{k^2}{4\alpha^2}\right)\left[1-\left(\frac{2}{k^2}+\frac{1}{2\alpha^2}\right)\left(\boldsymbol{k}\cdot\widehat{\boldsymbol{e}}_\gamma\right)^2\right]\left|\widetilde{a}\left(\boldsymbol{k}\right)\right|^2\right\rangle\\ &-\frac{1}{V^2}\frac{2\pi}{2\epsilon'+1}\left\langle\left[M^2-2\left(\boldsymbol{M}\cdot\widehat{\boldsymbol{e}}_\gamma\right)^2\right]\right\rangle, \qquad \gamma = \mathrm{x},\ \mathrm{y},\ \text{or}\ \mathrm{z}\end{aligned} \tag{F.71}$$

for the diagonal components of the stress tensor in a Coulombic bulk system.

F.2 Three-dimensional dipolar system

F.2.1 Self-energy

We now derive an expression for the self-contribution to the dipolar energy in Ewald formulation given in Eq. (6.32) by recalling that the corresponding

Coulombic contribution [see Eq. (6.17b)] results from the interaction of the charges q_i at $\boldsymbol{r}_i$ with the corresponding Gaussian charge clouds centered at $\boldsymbol{r}_i$ and representing a total charge of $-q_i$. Moreover, we have seen at the end of Appendix F.1.1.4 that for a given particle i the self-part of the electrostatic potential can be calculated from the potential generated by a Gaussian at $\boldsymbol{r}_j$ by taking the limit $r_{ij} \to 0$. Keeping this observation in mind and replacing the charges q_i by operators $\boldsymbol{\mu}_i \cdot \nabla_i$ as suggested by Eq. (6.22), we find the following prescription to calculate the dipolar self-contribution

$$U_{\mathrm{DSF}}^{\mathrm{3d}} = -\frac{1}{2} \lim_{r_{ij} \to 0} \lim_{\boldsymbol{\mu}_j \to \boldsymbol{\mu}_i} \sum_{i=1}^{N} (\boldsymbol{\mu}_i \cdot \nabla_i) (\boldsymbol{\mu}_j \cdot \nabla_j) \left(\frac{\operatorname{erf}(\alpha r_{ij})}{r_{ij}} \right) \tag{F.72}$$

Approximating $\operatorname{erf}(\alpha r_{ij}) / r_{ij}$ by its Taylor expansion for small distances r_{ij} given in Eq. (F.48), we obtain

$$(\boldsymbol{\mu}_i \cdot \nabla_i) (\boldsymbol{\mu}_j \cdot \nabla_j) \left(\frac{2\alpha}{\sqrt{\pi}} - \frac{2\alpha^3}{3\sqrt{\pi}} r_{ij}^2 \right) = \frac{4\alpha^3}{3\sqrt{\pi}} (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) \tag{F.73}$$

from which

$$U_{\mathrm{DSF}}^{\mathrm{3d}} = -\frac{2\alpha^3}{3\sqrt{\pi}} \sum_{i=1}^{N} \mu_i^2 \tag{F.74}$$

follows immediately by inserting Eq. (F.73) into Eq. (F.72) and taking the double limit. Equation (F.74) is identical to Eq. (6.32).

In Eq. (F.73) we used the fact that

$$\nabla_i = \nabla_{ij} = -\nabla_j \tag{F.75}$$

and Eq. (F.53). Therefore,

$$(\boldsymbol{\mu}_i \cdot \nabla_i) (\boldsymbol{\mu}_j \cdot \nabla_j) = -(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_{ij}) (\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_{ij}) \frac{\mathrm{d}^2}{\mathrm{d}r_{ij}^2} = -(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) \frac{\mathrm{d}^2}{\mathrm{d}r_{ij}^2} \tag{F.76}$$

F.2.2 Force and torque

According to Eqs. (6.26)–(6.32) the total force on particle i can be expressed as a sum of two contributions, namely

$$\boldsymbol{F}_{\mathrm{D},i}^{\mathrm{3d}} = \boldsymbol{F}_{\mathrm{DR},i}^{\mathrm{3d}} + \boldsymbol{F}_{\mathrm{DF},i}^{\mathrm{3d}} \tag{F.77}$$

because both long-range contributions and self-contributions in Eqs. (6.27c) and (6.32) turn out to be independent of the position of particle i and therefore do not contribute to the force. From Eq. (6.27a) it follows that

$$\begin{aligned} \boldsymbol{F}^{\mathrm{3d}}_{\mathrm{DR},i} &= -\nabla_{ij} \sum_{j=1}^{N} {\sum_{\{\boldsymbol{n}\}}}' \{(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j)\, B(|\boldsymbol{r}_{ij}+\boldsymbol{n}|, \alpha) \\ &\quad - [\boldsymbol{\mu}_i \cdot (\boldsymbol{r}_{ij}+\boldsymbol{n})]\, [\boldsymbol{\mu}_j \cdot (\boldsymbol{r}_{ij}+\boldsymbol{n})]\, C(|\boldsymbol{r}_{ij}+\boldsymbol{n}|, \alpha)\} \end{aligned} \tag{F.78}$$

where the functions B and C are defined in Eqs. (6.28a). Transforming variables according to $\boldsymbol{r}_{ij} \rightarrow \boldsymbol{r} = \boldsymbol{r}_{ij} + \boldsymbol{n}$, noting that $\nabla_{\boldsymbol{r}} = \nabla_{ij}$, and that

$$\nabla_{\boldsymbol{r}} = \frac{\boldsymbol{r}}{r} \frac{\mathrm{d}}{\mathrm{d}r} \tag{F.79}$$

direct differentiation on the right side of Eq. (F.78) gives

$$\begin{aligned} \boldsymbol{F}^{\mathrm{3d}}_{\mathrm{DR},i} &= \sum_{j=1}^{N} {\sum_{\{\boldsymbol{n}\}}}' \{[(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j)\, \boldsymbol{r} + \boldsymbol{\mu}_i\, (\boldsymbol{\mu}_j \cdot \boldsymbol{r}) + \boldsymbol{\mu}_j\, (\boldsymbol{\mu}_i \cdot \boldsymbol{r})]\, C(r, \alpha) \\ &\quad - (\boldsymbol{\mu}_i \cdot \boldsymbol{r})\, (\boldsymbol{\mu}_j \cdot \boldsymbol{r})\, \boldsymbol{r}\, D(r, \alpha)\} \end{aligned} \tag{F.80}$$

where the function $D(r, \alpha)$ is defined as [see Eqs. (6.28a)]

$$\begin{aligned} D(r, \alpha) &\equiv -\frac{1}{r}\frac{\mathrm{d}C}{\mathrm{d}r} = \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r}\frac{\mathrm{d}B}{\mathrm{d}r}\right) \\ &= \frac{1}{r^7}\left[\frac{2\alpha r}{\sqrt{\pi}}\left(15 + 10\alpha^2 r^2 + 4\alpha^4 r^4\right) \exp\left(-\alpha^2 r^2\right) + 15\,\mathrm{erfc}\,(\alpha r)\right] \end{aligned} \tag{F.81}$$

The Fourier-space contribution follows from Eq. (6.27b) as

$$\boldsymbol{F}^{\mathrm{3d}}_{\mathrm{DF},i} = -\frac{4\pi}{V} \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{1}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right) \sum_{j=1}^{N} \nabla_{ij}\, (\boldsymbol{\mu}_i \cdot \boldsymbol{k})\, (\boldsymbol{\mu}_j \cdot \boldsymbol{k}) \exp\left(-i\boldsymbol{k} \cdot \boldsymbol{r}_{ij}\right) \tag{F.82}$$

where we employed Eq. (6.29). Differentiating in Eq. (F.82) with respect to $\boldsymbol{r}_{ij}$ gives (see Appendix F.1.2 for the parallel derivation in the Coulombic case)

$$\begin{aligned} \boldsymbol{F}^{\mathrm{3d}}_{\mathrm{DF},i} &= \frac{4\pi}{V} \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{1}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right) \sum_{j=1}^{N} i\boldsymbol{k}\, (\boldsymbol{\mu}_i \cdot \boldsymbol{k})\, (\boldsymbol{\mu}_j \cdot \boldsymbol{k}) \exp\left(-i\boldsymbol{k} \cdot \boldsymbol{r}_{ij}\right) \\ &= \frac{4\pi}{V} \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{1}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right) \sum_{j=1}^{N} \boldsymbol{k}\, (\boldsymbol{\mu}_i \cdot \boldsymbol{k})\, (\boldsymbol{\mu}_j \cdot \boldsymbol{k}) \sin\left(\boldsymbol{k} \cdot \boldsymbol{r}_{ij}\right) \end{aligned} \tag{F.83}$$

where the last line is obtained via Eq. (F.54). Finally, using $\sin(x-y) = \sin x \cos y - \cos x \sin y$ and the definitions of real and imaginary parts of $\widetilde{M}(\boldsymbol{k})$ given in Eq. (6.29) we obtain

$$\begin{aligned} \boldsymbol{F}^{3d}_{DF,i} &= \frac{4\pi}{V}\sum_{\boldsymbol{k}\neq\boldsymbol{0}}\frac{1}{k^2}\exp\left(-\frac{k^2}{4\alpha^2}\right)\Big[\sin(\boldsymbol{k}\cdot\boldsymbol{r}_i)\,\mathrm{Re}\widetilde{M}(\boldsymbol{k}) \\ &\quad -\cos(\boldsymbol{k}\cdot\boldsymbol{r}_i)\,\mathrm{Im}\widetilde{M}(\boldsymbol{k})\Big](\boldsymbol{\mu}_i\cdot\boldsymbol{k})\,\boldsymbol{k} \end{aligned} \tag{F.84}$$

The torque acting on particle i is defined by [140]

$$\boldsymbol{T}^{3d}_{D,i} \equiv -\boldsymbol{\mu}_i \times \left(\nabla_{\boldsymbol{\mu}_i}\Phi^{3d}_{D,i}\right) \tag{F.85}$$

where $\Phi^{3d}_{D,i}$ is the energy of particle i. From Eqs. (6.27) we realize that $\Phi^{3d}_{D,i}$ can be written as a sum of three terms, namely

$$\Phi^{3d}_{D,i} = \Phi^{3d}_{DR,i} + \Phi^{3d}_{DF,i} + \Phi^{3d}_{DLR,i} \tag{F.86}$$

and the differentiation is performed with respect to $\boldsymbol{\mu}_i$. Referring back to Eqs. (6.26)–(6.32) we realize that

$$\boldsymbol{T}^{3d}_{D,i} = \boldsymbol{T}^{3d}_{DR,i} + \boldsymbol{T}^{3d}_{DF,i} + \boldsymbol{T}^{3d}_{DLR,i} \tag{F.87}$$

where

$$\boldsymbol{T}^{3d}_{DR,i} = -\boldsymbol{\mu}_i \times \sum_{j=1}^{N}{\sum_{\boldsymbol{n}}}' \left[\boldsymbol{\mu}_j B(r,\alpha) - \boldsymbol{r}\,(\boldsymbol{\mu}_i\cdot\boldsymbol{r})\,C(r,\alpha)\right] \tag{F.88a}$$

$$\begin{aligned} \boldsymbol{T}^{3d}_{DF,i} &= -\boldsymbol{\mu}_i \times \sum_{\boldsymbol{k}\neq\boldsymbol{0}}\frac{4\pi}{k^2 V}\exp\left(-\frac{k^2}{4\alpha^2}\right)\left[\boldsymbol{k} - \boldsymbol{\mu}_i\,(\boldsymbol{\mu}_i\cdot\boldsymbol{k})\right] \\ &\quad \times\left[\cos(\boldsymbol{k}\cdot\boldsymbol{r}_i)\,\mathrm{Re}\widetilde{M}(\boldsymbol{k}) + \sin(\boldsymbol{k}\cdot\boldsymbol{r}_i)\,\mathrm{Im}\widetilde{M}(\boldsymbol{k})\right] \end{aligned} \tag{F.88b}$$

$$\boldsymbol{T}^{3d}_{DLR,i} = -\boldsymbol{\mu}_i \times \left[\frac{4\pi}{2\epsilon'+1}\frac{\boldsymbol{M}}{V}\right] \tag{F.88c}$$

In Eq. (F.88a) we use again the shorthand notation $\boldsymbol{r} \equiv \boldsymbol{r}_{ij} + \boldsymbol{n}$ and $r = |\boldsymbol{r}|$ as before [see below Eq. (F.78)].

F.2.3 Stress tensor

As before in Section F.1.2.2 diagonal components of the stress tensor of a dipolar fluid can be obtained from the relation

$$\tau^{3d}_{\gamma\gamma,D} = \tau^{id}_{\gamma\gamma} + \frac{\langle W^{3d}_{\gamma\gamma,D}\rangle}{A_{\gamma 0}} \tag{F.89}$$

where the ideal-gas contribution $\tau_{\gamma\gamma}^{\mathrm{id}}$ is given in Eq. (E.33), invoking again the grand canonical ensemble for convenience. By analogy with Eq. (F.56) we have

$$W_{\gamma\gamma,\mathrm{D}}^{3\mathrm{d}} = \frac{\partial U_{\mathrm{D}}^{3\mathrm{d}}}{\partial s_\gamma} = \frac{\partial U_{\mathrm{DR}}^{3\mathrm{d}}}{\partial s_\gamma} + \frac{\partial U_{\mathrm{DF}}^{3\mathrm{d}}}{\partial s_\gamma} + \frac{\partial U_{\mathrm{DLR}}^{3\mathrm{d}}}{\partial s_\gamma}, \qquad \gamma = \mathrm{x,\ y,\ or\ z} \tag{F.90}$$

Based on the same transformation to unit-cube coordinates employed before [see Eq. (F.57)], we realize that the dependence on s_γ is buried in the argument of the functions B and C [see Eqs. (6.28a)] and in the factors $\boldsymbol{\mu}_{i,j} \cdot (\boldsymbol{r}_{ij} + \boldsymbol{n})$ as far as $U_{\mathrm{DR}}^{3\mathrm{d}}$ is concerned. Differentiating these terms with respect to s_γ, it is easy to verify that terms of the form

$$\frac{1}{s_\gamma} \left(\boldsymbol{\mu}_{i(j)} \cdot \widehat{\boldsymbol{e}}_\gamma\right) \left[(\boldsymbol{r}_{ij} + \boldsymbol{n}) \cdot \widehat{\boldsymbol{e}}_\gamma\right]$$

arise where $\boldsymbol{\mu}_{i(j)}$ stands for either $\boldsymbol{\mu}_i$ or $\boldsymbol{\mu}_j$. Employing also the relation among the functions B, C, and D [see Eqs. (6.28a), (F.81)] as well as Eq. (F.60), it is a simple matter to show that

$$\begin{aligned} \tau_{\gamma\gamma,\mathrm{DR}}^{3\mathrm{d}} = & -\frac{1}{2V} \Bigg\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\{\boldsymbol{n}\}}{}' \left\{ (\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) (\boldsymbol{r} \cdot \widehat{\boldsymbol{e}}_\gamma)^2 \right. \\ & + \left[(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_\gamma) (\boldsymbol{\mu}_j \cdot \boldsymbol{r}) + (\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_\gamma) (\boldsymbol{\mu}_i \cdot \boldsymbol{r}) \right] (\boldsymbol{r}_{ij} \cdot \widehat{\boldsymbol{e}}_\gamma) \Big\} C(r, \alpha) \\ & \left. + (\boldsymbol{\mu}_i \cdot \boldsymbol{r}) (\boldsymbol{\mu}_j \cdot \boldsymbol{r}) (\boldsymbol{r} \cdot \widehat{\boldsymbol{e}}_\gamma)^2 D(r, \alpha) \right\rangle \end{aligned} \tag{F.91}$$

where we again transformed variables according to $\boldsymbol{r}_{ij} \rightarrow \boldsymbol{r} = \boldsymbol{r}_{ij} + \boldsymbol{n}$ and $r = |\boldsymbol{r}|$.

Turning to the Fourier-space contribution next, we immediately see that $U_{\mathrm{DF}}^{3\mathrm{d}}$ contains a factor

$$\frac{1}{V} \frac{1}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right)$$

that has already been considered in the derivation of $\tau_{\gamma\gamma,\mathrm{CF}}^{3\mathrm{d}}$ in Eq. (F.63). We are then left with a derivative of the function $\widetilde{M}(\boldsymbol{k})$ [see Eq. (6.29)] which depends on s_γ because of Eq. (F.66). Introducing

$$\widetilde{Q}(\boldsymbol{k}) \equiv \sum_{i=1}^{N} (\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_\gamma) (\boldsymbol{k} \cdot \widehat{\boldsymbol{e}}_\gamma) \exp(i\boldsymbol{k} \cdot \boldsymbol{r}_i) \tag{F.92}$$

one obtains

$$\tau^{3d}_{\gamma\gamma,DF} = -\frac{2\pi}{V^2}\left\langle \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{1}{k^2}\exp\left(-\frac{k^2}{4\alpha^2}\right)\left\{\left[1-\left(\frac{2}{k^2}+\frac{1}{2\alpha^2}\right)\right](\boldsymbol{k}\cdot\widehat{\boldsymbol{e}}_\gamma)^2 \times\left|\widetilde{M}(\boldsymbol{k})\right|^2 + \widetilde{Q}(\boldsymbol{k})\,\widetilde{M}^*(\boldsymbol{k}) + \widetilde{Q}^*(\boldsymbol{k})\,\widetilde{M}(\boldsymbol{k})\right\}\right\rangle \tag{F.93}$$

Finally, the long-range contribution to the energy [see Eq. (6.27c)] gives rise to a stress contribution

$$\tau_{\gamma\gamma,DLR} = -\frac{1}{V^2}\frac{2\pi}{2\epsilon'+1}\left\langle M^2\right\rangle \tag{F.94}$$

The reader should appreciate the difference between the previous expression and the last term on the right side of Eq. (F.71). This difference arises because, for a dipolar system, $M_\gamma = \sum_{i=1}^{N}\boldsymbol{\mu}_i\cdot\widehat{\boldsymbol{e}}_\gamma$ is independent of s_γ, whereas for a Coulomb system, M_γ depends on s_γ as one can verify from Eq. (F.69). The diagonal component of the *total* stress tensor is then obtained by adding the three contributions given in Eqs. (F.91), (F.93), and (F.94) [see Eqs. (F.89) and (F.90)].

F.3 Slab geometry

F.3.1 Rigorous expressions

F.3.1.1 Point charges

To derive Eq. (6.34) for a system of point charges in slab geometry, we proceed in a fashion analogous to the one employed for bulk systems in Section 6.2.1 and Appendix F.1. In other words, we divide the original charge density related to Eq. (6.33)

$$\rho_i(\boldsymbol{r}') = \sum_{\boldsymbol{n}_\parallel}{}' \sum_{j=1}^{N} q_j\delta(z'-z_j)\,\delta\left(\boldsymbol{R}'-\boldsymbol{R}_j+\boldsymbol{n}_\parallel\right) \tag{F.95}$$

into three contributions corresponding to a set of screened charges $\rho_i^{(1)}(\boldsymbol{r}')$, a periodic set of charge clouds screening those original ones $\rho^{(2)}(\boldsymbol{r}')$, and a self-contribution $\rho_i^{(3)}(\boldsymbol{r}')$ describing the interaction of each charge cloud with itself. We choose the charge clouds to be spherical Gaussians[2] such that the

[2]See Ref. 248 for other choices.

three contributions of the charge distribution are

$$\rho_i^{(1)}(\boldsymbol{r}') = \rho_i(\boldsymbol{r}') - \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \sum_{\boldsymbol{n}_\parallel}{}' \sum_{j=1}^{N} q_j \exp\left[-\alpha^2 (z' - z_j)^2\right] \times \exp\left[-\alpha^2 \left(\boldsymbol{R}' - \boldsymbol{R}_j + \boldsymbol{n}_\parallel\right)^2\right] \tag{F.96a}$$

$$\rho^{(2)}(\boldsymbol{r}') = \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \sum_{\boldsymbol{n}_\parallel} \sum_{j=1}^{N} q_j \exp\left[-\alpha^2 (z' - z_j)^2\right] \times \exp\left[-\alpha^2 \left(\boldsymbol{R}' - \boldsymbol{R}_j + \boldsymbol{n}_\parallel\right)^2\right] \tag{F.96b}$$

$$\rho_i^{(3)}(\boldsymbol{r}') = -q_i \left(\frac{\alpha}{\sqrt{\pi}}\right)^3 \exp\left[-\alpha^2 (z' - z_i)^2\right] \times \exp\left[-\alpha^2 (\boldsymbol{R}' - \boldsymbol{R}_i)^2\right] \tag{F.96c}$$

which is completely analogous to the bulk expressions given in Eqs. (6.7), (6.10a), and (6.10b), respectively. Thus, we can immediately write down expressions for the potentials related to $\rho_i^{(1)}(\boldsymbol{r}')$ and $\rho_i^{(3)}(\boldsymbol{r}')$ [see Eqs. (6.8) and (6.14)]; that is,

$$\Phi^{(1)}(\boldsymbol{r}_i) = \sum_{\boldsymbol{n}}{}' \sum_{j=1}^{N} q_j \frac{\operatorname{erfc}(\alpha |\boldsymbol{r}_{ij} + \boldsymbol{n}|)}{|\boldsymbol{r}_{ij} + \boldsymbol{n}|} \tag{F.97a}$$

$$\Phi^{(3)}(\boldsymbol{r}_i) = -q_i \frac{2\alpha}{\sqrt{\pi}}, \tag{F.97b}$$

where in Eq. (F.97a), $\boldsymbol{n} = (\boldsymbol{n}_\parallel, 0)$.

However, the potential $\Phi^{(2)}(\boldsymbol{r}')$ related to $\rho^{(2)}(\boldsymbol{r}')$ differs from its bulk counterpart [see Eq. (6.14)] because the basic simulation cell of the current slab system is repeated in only two (of the three) spatial dimensions. Nevertheless, we can still apply our basic strategy detailed in Appendix F.1.1.2 to find the explicit expression for $\Phi^{(2)}(\boldsymbol{r}')$.

We start by expanding the potential in Fourier space according to

$$\Phi^{(2)}(\boldsymbol{r}) = \frac{s_z}{2\pi} \sum_{\boldsymbol{k}_\parallel} \exp\left[i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}\right] \int_{-\infty}^{\infty} \mathrm{d}k_z \widetilde{\Phi}^{(2)}(\boldsymbol{k}) \exp\left[ik_z z\right] \tag{F.98}$$

where $\boldsymbol{k}_\parallel = (2\pi m_x/s_x, 2\pi n_y/s_y)$ are two-dimensional reciprocal lattice vectors (i.e., $\exp\left[i\boldsymbol{k}_\parallel \cdot \boldsymbol{n}_\parallel\right] = 1$), whereas the vectors $\boldsymbol{k}$ appearing as arguments of the coefficients $\widetilde{\Phi}^{(2)}(\boldsymbol{k})$ are still three-dimensional. Equation (F.98) follows from its three-dimensional counterpart (F.19b) if we replace in the full

sum $\sum_{\boldsymbol{k}} \ldots = \sum_{k_x} \sum_{k_y} \sum_{k_z} \ldots$ the partial summation over the discrete variable k_z by an integration, that is $\sum_{k_z} \ldots \to (\Delta k_z)^{-1} \int_{-\infty}^{\infty} \mathrm{d}k_z \ldots$ with $\Delta k_z = 2\pi/s_z$. This is consistent with viewing the system in slab geometry as three-dimensional with a basic cell becoming *infinitely* large in the z-direction (i.e., $s_z \to \infty$) such that $\Delta k_z \to 0$.

The Fourier coefficients $\tilde{\Phi}^{(2)}(\boldsymbol{k})$ appearing in Eq. (F.98) are linked to the corresponding coefficients of the charge density via the Fourier-transformed Laplace equation [see Eq. (F.21)]

$$\begin{aligned} \tilde{\rho}^{(2)}(\boldsymbol{k}) &= \frac{1}{V_{\mathrm{sys}}} \int \mathrm{d}\boldsymbol{r} \exp(-i\boldsymbol{k}\cdot\boldsymbol{r})\, \rho^{(2)}(\boldsymbol{r}) \\ &= \frac{1}{V} \exp\left(-\frac{k_\parallel^2 + k_z^2}{4\alpha^2}\right) \sum_{j=1}^{N} q_j \exp(-ik_z z_j) \exp\left(-i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_j\right) \end{aligned} \tag{F.99}$$

where we have inserted Eq. (F.96b) to obtain the second line of Eq. (F.99). Combining Eqs. (F.99) and (F.21) and inserting the resulting Fourier coefficients $\tilde{\Phi}^{(2)}(\boldsymbol{k})$ into the expansion in Eq. (F.98), we find

$$\begin{aligned} \Phi^{(2)}(\boldsymbol{r}) &= \frac{2}{A} \sum_{j=1}^{N} \sum_{\boldsymbol{k}_\parallel \neq \boldsymbol{0}} q_j \exp\left[i\boldsymbol{k}_\parallel \cdot (\boldsymbol{R} - \boldsymbol{R}_j)\right] \int_{-\infty}^{\infty} \mathrm{d}k_z \frac{1}{k_\parallel^2 + k_z^2} \\ &\quad \times \exp\left[-\frac{k_\parallel^2 + k_z^2}{4\alpha^2} + ik_z(z - z_j)\right] + \Phi^{(2)}_{\boldsymbol{k}_\parallel \to \boldsymbol{0}}(z - z_j) \end{aligned} \tag{F.100}$$

where the sum in the first line is restricted to nonzero wavevectors $\boldsymbol{k}_\parallel$ and $\Phi^{(2)}_{\boldsymbol{k}_\parallel \to \boldsymbol{0}}$ contains contributions from the long-wavelength limit (see below). In Eq. (F.100), the integral over the continuous variable k_z gives [248]

$$\int_{-\infty}^{\infty} \mathrm{d}k_z \frac{1}{k_\parallel^2 + k_z^2} \exp\left[-\frac{k_\parallel^2 + k_z^2}{4\alpha^2} + ik_z(z - z_j)\right] = \frac{\pi}{2k_\parallel} f\left(k_\parallel, z - z_j, \alpha\right) \tag{F.101}$$

where the function $f\left(k_\parallel, z - z_j, \alpha\right)$ has been defined in Eq. (6.36).

From Eqs. (F.100) and (F.101) it follows that $\Phi^{(2)}_{\boldsymbol{k}_\parallel \to \boldsymbol{0}}(z - z_j)$ is defined as

$$\Phi^{(2)}_{\boldsymbol{k}_\parallel \to \boldsymbol{0}}(z - z_j) \equiv \frac{\pi}{Ak_\parallel} \sum_{j=1}^{N} \lim_{k_\parallel \to 0} f\left(k_\parallel, z - z_j, \alpha\right) \tag{F.102}$$

Thus, we consider the behavior of the function $f(k_\parallel, z - z_j, \alpha)$ for small wavenumbers $k_\parallel$. To this end we perform a Taylor expansion of both the

exponentials and the complementary error functions appearing on the right side of Eq. (6.36). In this expansion, the lowest-order Taylor coefficients of $\mathrm{erfc}(y) = 1 - \mathrm{erf}(y)$ follow immediately from Eq. (F.49). We also note the relation $\mathrm{erf}(-y) = -\mathrm{erf}(y)$, which follows from the definition of the error function in Eq. (F.9). Expanding $f\left(k_\parallel, z - z_j, \alpha\right)$ [see Eq. (6.36)] around $k_\parallel = 0$, we obtain

$$\begin{aligned} f\left(k_\parallel, z - z_j, \alpha\right) &= 2 - 2k_\parallel \left(z - z_j\right) \mathrm{erf}\left[\alpha\left(z - z_j\right)\right] \\ &\quad - \frac{2}{\alpha\sqrt{\pi}} k_\parallel \exp\left[-\alpha^2 \left(z - z_j\right)^2\right] + \mathcal{O}\left(k_\parallel^2\right) \end{aligned} \tag{F.103}$$

where we retain only linear terms in $k_\parallel$. Combining the previous expression with Eq. (F.102) yields

$$\begin{aligned} \Phi^{(2)}_{k_\parallel \to 0}\left(z - z_j\right) &= \frac{2}{A} \sum_{j=1}^{N} q_j \lim_{k_\parallel \to 0} \frac{\pi}{2k_\parallel} \left\{2 - 2k_\parallel \left(z - z_j\right) \mathrm{erf}\left[\alpha\left(z - z_j\right)\right]\right. \\ &\quad \left. - \frac{2}{\alpha\sqrt{\pi}} k_\parallel \exp\left[-\alpha^2 \left(z - z_j\right)^2\right] + \mathcal{O}\left(k^2\right)\right\} \end{aligned} \tag{F.104}$$

Inspecting the right side of Eq. (F.104) we see that the first term in parentheses is constant. This term is irrelevant because of global charge neutraliy (i.e., $\sum_{i=1}^{N} q_i = 0$). We therefore obtain from Eqs. (F.100) and (F.104) as a final expression for the potential from the set of Gaussians

$$\begin{aligned} \Phi^{(2)}\left(\boldsymbol{r}\right) &= \frac{\pi}{A} \sum_{j=1}^{N} \sum_{\boldsymbol{k}_\parallel \neq \boldsymbol{0}} q_j \frac{\exp\left[i\boldsymbol{k}_\parallel \cdot \left(\boldsymbol{R} - \boldsymbol{R}_j\right)\right]}{k_\parallel} f(k_\parallel, z, \alpha) \\ &\quad - \frac{2\sqrt{\pi}}{A} \sum_{j=1}^{N} q_j \frac{\exp[-\alpha^2 (z - z_j)^2]}{\alpha} \\ &\quad - \frac{2\pi}{A} \sum_{j=1}^{N} q_j \left(z - z_j\right) \mathrm{erf}\left[\alpha\left(z - z_j\right)\right] \end{aligned} \tag{F.105}$$

The corresponding contribution to the energy is

$$U_{\mathrm{CF}}^{\mathrm{2d}} = \frac{1}{2} \sum_{i=1}^{N} q_i \Phi^{(2)}\left(\boldsymbol{r}_i\right) \tag{F.106}$$

which coincides with Eq. (6.35).

F.3.1.2 Point dipoles

The rigorous Ewald sum for a slab-like system of point dipoles follows from the corresponding expression for Coulombic systems [see Eqs. (6.34) and (6.35)]. The derivation proceeds in a fashion similar to the one already discussed for bulk systems in Section 6.2.2. That is, we replace the charges q_i and q_j in the energy expressions by the operators $(\boldsymbol{\mu}_i \cdot \nabla_i)$ and $(\boldsymbol{\mu}_j \cdot \nabla_j)$. As a result,

$$U_{\mathrm{D}}^{\mathrm{2d}} = U_{\mathrm{DR}}^{\mathrm{2d}} + U_{\mathrm{DF}}^{\mathrm{2d}} + U_{\mathrm{DSF}}^{\mathrm{2d}} \tag{F.107}$$

where both real-space and self-part have the same form as in the three-dimensional case and are thus given by Eqs. (6.27a) and (6.32), respectively.

To evaluate the Fourier part, we start by considering the first sum on the right side of Eq. (6.35) involving nonzero wavevectors $\boldsymbol{k}_\parallel \neq \mathbf{0}$. For each pair i and j and each wavevector $\boldsymbol{k}_\parallel$, the replacement of the charge q_j by the operator $(\boldsymbol{\mu}_j \cdot \nabla_j)$ yields

$$\begin{aligned}
&(\boldsymbol{\mu}_j \cdot \nabla_j) \frac{\exp\left(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij}\right)}{k_\parallel} f\left(k_\parallel, z_{ij}, \alpha\right) \\
= \; & -i\left(\boldsymbol{\mu}_j \cdot \boldsymbol{k}_\parallel\right) \frac{\exp\left(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij}\right)}{k_\parallel} f\left(k_\parallel, z_{ij}, \alpha\right) \\
& + \left(\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_z\right) \frac{\exp\left(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij}\right)}{k_\parallel} d\left(k_\parallel, z_{ij}, \alpha\right)
\end{aligned} \tag{F.108}$$

where $\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j$, $z_{ij} = z_i - z_j$, the function $f(k_\parallel, z_{ij}, \alpha)$ is defined in Eq. (6.36), and

$$\begin{aligned}
d\left(k_\parallel, z_{ij}, \alpha\right) = \frac{\partial}{\partial z_j} f\left(k_\parallel, z_{ij}, \alpha\right) \; = \; & k_\parallel \exp\left(-k_\parallel z_{ij}\right) \operatorname{erfc}\left(\frac{k_\parallel}{2\alpha} - \alpha z_{ij}\right) \\
& -k_\parallel \exp\left(k_\parallel z_{ij}\right) \operatorname{erfc}\left(\frac{k_\parallel}{2\alpha} + \alpha z_{ij}\right)
\end{aligned} \tag{F.109}$$

Now we need to differentiate Eq. (F.108) one more time because of the second operator $(\boldsymbol{\mu}_i \cdot \nabla_i)$ replacing q_i in the original energy expression in Eq. (6.35),

which yields

$$
\begin{aligned}
&(\boldsymbol{\mu}_i \cdot \nabla_i)(\boldsymbol{\mu}_j \cdot \nabla_j) \frac{\exp(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij})}{k_\parallel} f(k_\parallel, z_{ij}, \alpha) \\
= \; &(\boldsymbol{\mu}_i \cdot \boldsymbol{k}_\parallel)(\boldsymbol{\mu}_j \cdot \boldsymbol{k}_\parallel) \frac{\exp(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij})}{k_\parallel} f(k_\parallel, z_{ij}, \alpha) \\
&+ i(\boldsymbol{\mu}_i \cdot \hat{\boldsymbol{e}}_z)(\boldsymbol{\mu}_j \cdot \boldsymbol{k}_\parallel) \frac{\exp(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij})}{k_\parallel} d(k_\parallel, z_{ij}, \alpha) \\
&+ i(\boldsymbol{\mu}_j \cdot \hat{\boldsymbol{e}}_z)(\boldsymbol{\mu}_i \cdot \boldsymbol{k}_\parallel) \frac{\exp(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij})}{k_\parallel} d(k_\parallel, z_{ij}, \alpha) \\
&+ (\boldsymbol{\mu}_i \cdot \hat{\boldsymbol{e}}_z)(\boldsymbol{\mu}_j \cdot \hat{\boldsymbol{e}}_z) \frac{\exp(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij})}{k_\parallel} e(k_\parallel, z_{ij}, \alpha)
\end{aligned}
\tag{F.110}
$$

where we have also used [see Eq. (F.109)]

$$
\frac{\partial}{\partial z_i} f(k_\parallel, z_{ij}, \alpha) = -\frac{\partial}{\partial z_j} f(k_\parallel, z_{ij}, \alpha) = -d(k_\parallel, z_{ij}, \alpha) \tag{F.111}
$$

and the function

$$
\begin{aligned}
e(k_\parallel, z_{ij}, \alpha) &= \frac{\partial}{\partial z_i} d(k_\parallel, z_{ij}, \alpha) \\
&= \frac{4\alpha k_\parallel}{\sqrt{\pi}} \exp\left(-\frac{k_\parallel^2}{4\alpha^2} - \alpha^2 z_{ij}^2\right) \\
&\quad - k_\parallel^2 \left[\exp(k_\parallel z_{ij}) \operatorname{erfc}\left(\frac{k_\parallel}{2\alpha} + \alpha z_{ij}\right)\right. \\
&\quad \left. + \exp(-k_\parallel z_{ij}) \operatorname{erfc}\left(\frac{k_\parallel}{2\alpha} - \alpha z_{ij}\right)\right]
\end{aligned}
\tag{F.112}
$$

Keeping in mind that the total Fourier energy involves a sum over *all* nonzero wavevectors $\boldsymbol{k}_\parallel \neq \boldsymbol{0}$ [see Eq. (6.35)], we may employ symmetry arguments to simplify the above expressions. For example, both $(\boldsymbol{\mu}_i \cdot \boldsymbol{k}_\parallel)(\boldsymbol{\mu}_j \cdot \boldsymbol{k}_\parallel)$ and the function $f(k_\parallel, z_{ij}, \alpha)$ appearing on the first line of the right side of Eq. (F.110) are invariant against inversion of the wavevectors, that is to say, a replacement of $\boldsymbol{k}_\parallel \rightarrow$ by $-\boldsymbol{k}_\parallel$. Therefore, only the real part of $\exp(i\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij})$ [i.e., $\cos(\boldsymbol{k}_\parallel \cdot \boldsymbol{R}_{ij})$] will contribute to the sum over all wavevectors. The same is true for the fourth term involving the product $(\boldsymbol{\mu}_i \cdot \hat{\boldsymbol{e}}_z)(\boldsymbol{\mu}_j \cdot \hat{\boldsymbol{e}}_z)$ and the function $e(k_\parallel, z_{ij}, \alpha)$, which is again invariant against inversion of $\boldsymbol{k}_\parallel$. However, the second and third terms on the right side of Eq. (F.110) are

linear in $\boldsymbol{k}_{\parallel}$ and therefore change sign upon inversion of the wavevector. As a consequence, we have

$$\begin{aligned} & i \sum_{\boldsymbol{k}_{\parallel} \neq \mathbf{0}} \left[\left(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_j \cdot \boldsymbol{k}_{\parallel} \right) + \left(\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_i \cdot \boldsymbol{k}_{\parallel} \right) \right] \\ & \times \frac{\exp\left(i \boldsymbol{k}_{\parallel} \cdot \boldsymbol{R}_{ij} \right)}{k_{\parallel}} d\left(k_{\parallel}, z_{ij}, \alpha \right) \\ = & - \sum_{\boldsymbol{k}_{\parallel} \neq \mathbf{0}} \left[\left(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_j \cdot \boldsymbol{k}_{\parallel} \right) + \left(\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_i \cdot \boldsymbol{k}_{\parallel} \right) \right] \\ & \times \frac{\sin\left(i \boldsymbol{k}_{\parallel} \cdot \boldsymbol{R}_{ij} \right)}{k_{\parallel}} d\left(k_{\parallel}, z_{ij}, \alpha \right) \end{aligned} \tag{F.113}$$

We now consider the remaining (second) sum in the Coulomb Fourier energy [see the right side of Eq. (6.35)] involving a double sum over pairs of dipoles i and j. Replacing the products q_i and q_j by the operators $(\boldsymbol{\mu}_i \cdot \nabla_i)$ and $(\boldsymbol{\mu}_j \cdot \nabla_j)$, respectively, as before yields

$$\begin{aligned} & \left(\boldsymbol{\mu}_i \cdot \nabla_i \right) \left(\boldsymbol{\mu}_j \cdot \nabla_j \right) \left[\frac{\exp\left(-\alpha^2 z_{ij}^2 \right)}{\alpha} + \sqrt{\pi} z_{ij} \operatorname{erf}\left(\alpha z_{ij} \right) \right] \\ = & \left(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_z \right) \frac{\exp\left(-\alpha^2 z_{ij}^2 \right)}{\alpha} \\ & \times \left(-4\alpha^2 z_{ij}^2 - 2\alpha + 4\alpha^2 z_{ij}^2 \right) \\ = & -2\alpha \exp\left(-\alpha^2 z_{ij}^2 \right) \left(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_z \right) \end{aligned} \tag{F.114}$$

Finally, putting all this together we arrive at the rigorous expression for the Fourier-space contribution to the total configurational energy of the dipolar system in slab geometry, namely

$$\begin{aligned} U_{\mathrm{DF}}^{\mathrm{2d}} = & \frac{\pi}{2A} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{\boldsymbol{k}_{\parallel} \neq \mathbf{0}} \left\{ \left(\boldsymbol{\mu}_i \cdot \boldsymbol{k}_{\parallel} \right) \left(\boldsymbol{\mu}_j \cdot \boldsymbol{k}_{\parallel} \right) \frac{\cos\left(\boldsymbol{k}_{\parallel} \cdot \boldsymbol{R}_{ij} \right)}{k_{\parallel}} f\left(k_{\parallel}, z_{ij}, \alpha \right) \right. \\ & - \left[\left(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_j \cdot \boldsymbol{k}_{\parallel} \right) + \left(\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_i \cdot \boldsymbol{k}_{\parallel} \right) \right] \\ & \times \frac{\sin\left(\boldsymbol{k}_{\parallel} \cdot \boldsymbol{R}_{ij} \right)}{k_{\parallel}} d\left(k_{\parallel}, z_{ij}, \alpha \right) \\ & \left. + \left(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_z \right) \frac{\cos\left(\boldsymbol{k}_{\parallel} \cdot \boldsymbol{R}_{ij} \right)}{k_{\parallel}} e\left(k_{\parallel}, z_{ij}, \alpha \right) \right\} \\ & + \frac{\sqrt{\pi}}{A} \sum_{i=1}^{N} \sum_{j=1}^{N} 2\alpha \exp\left(-\alpha^2 z_{ij}^2 \right) \left(\boldsymbol{\mu}_i \cdot \widehat{\boldsymbol{e}}_z \right) \left(\boldsymbol{\mu}_j \cdot \widehat{\boldsymbol{e}}_z \right) \end{aligned} \tag{F.115}$$

F.3.2 Force, torque, and stress in systems with slab geometry

F.3.2.1 Point charges

For ionic systems, the total Coulomb force acting on particle i within the slab-adapted three-dimensional Ewald sum [see Eq. (6.40)] can be cast as

$$\boldsymbol{F}_{\mathrm{C},i}^{\mathrm{slab}} = \boldsymbol{F}_{\mathrm{CR},i}^{\mathrm{slab}} + \boldsymbol{F}_{\mathrm{CF},i}^{\mathrm{slab}} + \boldsymbol{F}_{\mathrm{C,c},i}^{\mathrm{slab}} \tag{F.116}$$

where the first two contributions are identical to the corresponding ones in a truly three–dimensional system and are thus given by Eqs. (F.52a) and (F.52b), respectively. The last term in Eq. (F.116) arises from the correction term in the Ewald energy, $U_{\mathrm{C,c}}$ [see Eq. (6.39)]. One obtains

$$\boldsymbol{F}_{\mathrm{C,c},i}^{\mathrm{slab}} = -q_i \frac{4\pi}{V} \sum_{j=1}^{N} q_j z_j \widehat{\boldsymbol{e}}_{\mathrm{z}} = -q_i \frac{4\pi}{V} M_{\mathrm{z}} \widehat{\boldsymbol{e}}_{\mathrm{z}} \tag{F.117}$$

Regarding the stress tensor of the system, the (Coulomb) components corresponding to the two orthogonal directions parallel to the walls (i.e., $\gamma = x, y$) can be calculated exactly as in the three-dimensional case (see Appendix F.1.2.2). On the other hand, the normal component ($\gamma = z$) is given by

$$\tau_{\mathrm{C},zz}^{\mathrm{slab}} = \tau_{\mathrm{CR},zz}^{\mathrm{slab}} + \tau_{\mathrm{CF},zz}^{\mathrm{slab}} + \tau_{\mathrm{C,c},zz}^{\mathrm{slab}} \tag{F.118}$$

where only the real-space part $\tau_{\mathrm{CR},zz}^{\mathrm{slab}} = \tau_{\mathrm{CR},zz}^{\mathrm{3d}}$ [see Eq. (F.58)].

To evaluate the Fourier-space contribution, $\tau_{\mathrm{CF},zz}^{\mathrm{slab}}$, we note that, because of the *artificial* elongation of the basis cell in z-direction, neither the wavevectors involved in the Fourier contribution to the Ewald energy [see Eq. (6.18) with the wavevectors given in Eq. (6.41)] nor the volume V depend on s_{z}. The vectors $\boldsymbol{r}_i = (x_i, y_i, s_{\mathrm{z}}\widetilde{z}_i)$, on the other hand, depend on s_{z} if we employ scaled z-coordinates as indicated. Differentiation thus yields

$$\begin{aligned} \tau_{\mathrm{CF},zz}^{\mathrm{slab}} = \frac{1}{A_{\mathrm{z0}}} \left\langle \frac{\partial U_{\mathrm{CF}}^{\mathrm{3d}}}{\partial s_{\mathrm{z}}} \right\rangle &= -\frac{1}{2A_{\mathrm{z0}}s_{\mathrm{z}}} \frac{1}{V} \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{4\pi}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right) \\ &\quad \times \left\langle \widetilde{b}(\boldsymbol{k})\,\widetilde{a}^*(\boldsymbol{k}) + \widetilde{b}^*(\boldsymbol{k})\,\widetilde{a}(\boldsymbol{k}) \right\rangle \end{aligned} \tag{F.119}$$

where the quantity $\widetilde{a}(\boldsymbol{k})$ is defined in Eq. (6.19) and

$$\widetilde{b}(\boldsymbol{k}) = \sum_{i=1}^{N} i k_{\mathrm{z}} z_i \exp\left(-i\boldsymbol{k}\cdot\boldsymbol{r}_i\right) \tag{F.120}$$

Finally, as the energy correction term given in Eq. (6.39) depends on s_z only through the z-components of the position vectors $\boldsymbol{r}_i$, the expression for the corresponding stress in the direction normal to the confining substrates follows as

$$\tau_{\mathrm{C,c,zz}} = \frac{1}{A_{z0}} \left\langle \frac{\partial \widetilde{U}_{\mathrm{C}}}{\partial s_z} \right\rangle = \frac{1}{A_{z0} s_z} \frac{4\pi}{V} \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j z_i z_j \tag{F.121}$$

F.3.2.2 Point dipoles

For dipolar particles, all force contributions within the slab-adapted three-dimensional Ewald sum coincide with those for truly three-dimensional systems discussed in Appendix F.2.2. This result arises because the correction term to the total dipolar energy [see Eqs. (6.44) and (6.43)] is independent of particle positions. There is, however, a contribution to the total torque that we need to consider separately. The total torque can be cast as

$$\boldsymbol{T}_{\mathrm{D},i}^{\mathrm{slab}} = \boldsymbol{T}_{\mathrm{DR},i}^{\mathrm{slab}} + \boldsymbol{T}_{\mathrm{DF},i}^{\mathrm{slab}} + \boldsymbol{T}_{\mathrm{D,c},i}^{\mathrm{slab}} \tag{F.122}$$

where $\boldsymbol{T}_{\mathrm{DR},i}^{\mathrm{slab}}$ and $\boldsymbol{T}_{\mathrm{DF},i}^{\mathrm{slab}}$ are given by the bulk expressions [see Eqs. (F.88)], whereas

$$\boldsymbol{T}_{\mathrm{D,c},i}^{\mathrm{slab}} = -\boldsymbol{\mu}_i \times \left(\frac{4\pi}{V} M_z \widehat{\boldsymbol{e}}_z \right) \tag{F.123}$$

Turning next to the stress tensor we realize that its normal component within the slab-adapted three-dimensional Ewald formalism can be written as a sum of two contributions, namely

$$\tau_{\mathrm{D,zz}}^{\mathrm{slab}} = \tau_{\mathrm{DR,zz}}^{\mathrm{slab}} + \tau_{\mathrm{DF,zz}}^{\mathrm{slab}} \tag{F.124}$$

because the correction term to the total configurational potential energy in Eq. (6.43) does not depend on s_z (note that the V is the volume of the artificial cell *including* the vacuum space in the z-direction). The real-space part on the right side of Eq. (F.124) coincides with its three-dimensional analog given in Eq. (F.91). The Fourier part, $\tau_{\mathrm{DF,zz}}^{\mathrm{slab}}$, can be derived along the same lines already discussed below Eq. (F.118). We finally obtain with little ado the expression

$$\begin{aligned} \tau_{\mathrm{DF,zz}}^{\mathrm{slab}} = \frac{1}{A_{z0}} \left\langle \frac{\partial U_{\mathrm{CF}}^{\mathrm{3d}}}{\partial s_z} \right\rangle &= -\frac{1}{2A_{z0}s_z} \frac{1}{V} \sum_{\boldsymbol{k}\neq\boldsymbol{0}} \frac{4\pi}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right) \\ &\quad \times \left\langle \widetilde{V}(\boldsymbol{k}) \widetilde{M}^*(\boldsymbol{k}) + \widetilde{V}^*(\boldsymbol{k}) \widetilde{M}(\boldsymbol{k}) \right\rangle \end{aligned} \tag{F.125}$$

where the quantity $\widetilde{M}(\boldsymbol{k})$ is defined in Eq. (6.29) and

$$\widetilde{V}(\boldsymbol{k}) = \sum_{i=1}^{N} (\boldsymbol{\mu}_i \cdot \boldsymbol{k})\, ik_z z_i \exp(-i\boldsymbol{k} \cdot \boldsymbol{r}_i) \tag{F.126}$$

F.3.3 Metallic substrates

F.3.3.1 Point charges

Here we derive Eq. (6.66) linking the energy of a slab-like system of point charges between metallic walls to that of an extended system with three-dimensional periodicity.

The basic cell of the extended system contains N charges in the original cell plus the first set of images; that is, the N images resulting from the presence of just the lower wall. Positions and charges of these image particles are then given by the relations [see Eq. (6.59) with $n_z = 0$]

$$\boldsymbol{r}_{i+N} = \boldsymbol{r}_i - 2z_i\widehat{\boldsymbol{e}}_z, \quad i = 1, \ldots, N \tag{F.127a}$$

$$q_{i+N} = -q_i, \quad i = 1, \ldots, N \tag{F.127b}$$

Replicating the extended basic cell periodically in all three spatial directions, the total energy of the resulting system is given by

$$U_{\mathrm{C}}^{\mathrm{3d,ex}} = \frac{1}{2} \sum_{i=1}^{2N} \sum_{j=1}^{2N} {\sum_{\overline{\boldsymbol{n}}}}' \frac{q_i q_j}{|\boldsymbol{r}_{ij} + \overline{\boldsymbol{n}}|} \tag{F.128}$$

where the lattice vectors $\overline{\boldsymbol{n}}$ are specified in Eq. (6.64) and the prime at the sum indicates that the term related to $i = j$ is omitted for $\overline{\boldsymbol{n}} = \boldsymbol{0}$.

We now split the double sum in Eq. (F.128) into four terms containing

1. Particle particle contributions $\sum_{i=1}^{N} \sum_{j=1}^{N}$,
2. Image image contributions $\sum_{i=N+1}^{2N} \sum_{j=N+1}^{2N}$,
3. Particle image contributions $\sum_{i=1}^{N} \sum_{j=N+1}^{2N}$, and
4. Image particle contributions $\sum_{i=N+1}^{2N} \sum_{j=1}^{N}$.

Terms 1 and 2 give the same result as one may varify from the relations

$$\begin{aligned} q_{i+N}q_{j+N} &= (-q_i)(-q_j) = q_iq_j && \text{(F.129a)} \\ |\boldsymbol{r}_{i+N,j+N} + \overline{\boldsymbol{n}}| &= |\boldsymbol{r}_{ij} + \overline{\boldsymbol{n}} - 2z_{ij}\widehat{\boldsymbol{e}}_z| \\ &= \sqrt{(x_{ij} + s_xn_x)^2 + (y_{ij} + s_yn_y)^2 + (2s_zn_z - z_{ij})^2} \\ &= \sqrt{(x_{ij} + s_xn_x)^2 + (y_{ij} + s_yn_y)^2 + (z_{ij} - 2s_zn_z)^2} \\ &= |\boldsymbol{r}_{ij} + \overline{\boldsymbol{n}} - 4s_zn_z\widehat{\boldsymbol{e}}_z| && \text{(F.129b)} \end{aligned}$$

and the fact that we sum in Eq. (F.128) over an infinite set of lattice vectors $\{\overline{\boldsymbol{n}}\}$ such that the term $4s_zn_z\widehat{\boldsymbol{e}}_z$ on the right side of Eqs. (F.129) is irrelevant. By similar reasoning, terms 3 and 4 in the above decomposition give equivalent results because of

$$\begin{aligned} q_iq_{j+N} &= -q_iq_j = q_{i+N}q_j && \text{(F.130a)} \\ |\boldsymbol{r}_{i,j+N} + \overline{\boldsymbol{n}}| &= |\boldsymbol{r}_{ij} + 2z_j\widehat{\boldsymbol{e}}_z + \overline{\boldsymbol{n}}| \\ &= \sqrt{(x_{ij} + s_xn_x)^2 + (y_{ij} + s_yn_y)^2 + (z_i + z_j + 2s_zn_z)^2} \\ &= \sqrt{(x_{ij} + s_xn_x)^2 + (y_{ij} + s_yn_y)^2 + (-z_i - z_j - 2s_zn_z)^2} \\ &= |\boldsymbol{r}_{i+N,j} + \overline{\boldsymbol{n}} - 4s_zn_z\widehat{\boldsymbol{e}}_z| && \text{(F.130b)} \end{aligned}$$

Putting all this together, Eq. (F.128) can be rewritten as

$$U_{\mathrm{C}}^{\mathrm{3d,ex}} = \left[\sum_{i=1}^{N}\sum_{j=1}^{N}{\sum_{\overline{\boldsymbol{n}}}}' \frac{q_iq_j}{|\boldsymbol{r}_{ij} + \overline{\boldsymbol{n}}|} - \frac{q_iq_j}{|\boldsymbol{r}_{ij} + 2z_j\widehat{\boldsymbol{e}}_z + \overline{\boldsymbol{n}}|}\right] \qquad \text{(F.131)}$$

We therefore see that $U_{\mathrm{C}}^{\mathrm{3d,ex}}$ in Eq. (F.131) for a three-dimensional system with the extended basis cell is indeed exactly twice the energy U_{C} given in Eq. (6.65).

F.3.3.2 Point dipoles

To derive Eq. (6.68) for the total energy of an *infinite* slab of dipolar particles between metallic substrates, we go one step back and consider a situation where the central cell comprising N particles has not yet been replicated in the x- and y-directions. The corresponding energy can be written as

$$\widetilde{U}_{\mathrm{D}} = -\frac{1}{2}\sum_{i=1}^{N}\boldsymbol{\mu}_i \cdot \left(\boldsymbol{E}_i^{\mathrm{self}} + \boldsymbol{E}_i^{\mathrm{dis}}\right) \qquad \text{(F.132)}$$

where $\boldsymbol{E}_i^{\text{self}}$ and $\boldsymbol{E}_i^{\text{dis}}$ are the electrostatic fields arising from the images of particle i, on the one hand, and from the other particles j and their images, on the other hand. Using short-hand notation

$$\boldsymbol{e}_i(\boldsymbol{\mu}_j, \boldsymbol{r}_j) = \frac{3\boldsymbol{r}_{ij}(\boldsymbol{\mu}_j \cdot \boldsymbol{r}_{ij})}{r_{ij}^5} - \frac{\boldsymbol{\mu}_j}{r_{ij}^3} \tag{F.133}$$

the fields $\boldsymbol{E}_i^{\text{self}}$ and $\boldsymbol{E}_i^{\text{dis}}$ follow as

$$\boldsymbol{E}_i^{\text{self}} = \sum_{n_z=-\infty}^{\infty}{}^{*} \boldsymbol{e}_i(\boldsymbol{\mu}_i, \boldsymbol{r}_i + 2n_z s_z \widehat{\boldsymbol{e}}_z) + \sum_{n_z=-\infty}^{\infty} \boldsymbol{e}_i[\boldsymbol{\mu}_i', \boldsymbol{r}_i + 2(n_z s_z - z_i)\widehat{\boldsymbol{e}}_z] \tag{F.134a}$$

$$\boldsymbol{E}_i^{\text{dis}} = \sum_{j\neq i}^{N} \left\{ \boldsymbol{e}_i(\boldsymbol{\mu}_j, \boldsymbol{r}_j) + \sum_{n_z=-\infty}^{\infty}{}^{*} \boldsymbol{e}_i(\boldsymbol{\mu}_j, \boldsymbol{r}_j + 2n_z s_z \widehat{\boldsymbol{e}}_z) + \sum_{n_z=-\infty}^{\infty} \boldsymbol{e}_i[\boldsymbol{\mu}_j', \boldsymbol{r}_j + 2(n_z s_z - z_i)\widehat{\boldsymbol{e}}_z] \right\} \tag{F.134b}$$

where the asterisk attached to the sums indicates that terms corresponding to $n_z = 0$ have been omitted.

Replicating the original cell now in the x- and y- directions essentially implies that the sums over the integer variable n_z in Eq. (F.134a) have to be replaced by three-dimensional lattice sums over the vectors $\overline{\boldsymbol{n}}$ introduced in Eq. (6.64) [see the analogous procedure for charges described below Eq. (6.62a)]. Inserting the resulting field expressions into Eq. (F.132) and summarizing, one obtains Eq. (6.68) after some tedious but straightforward algebraic manipulations.

As a next step we now have to prove Eq. (6.69) where we again proceed as before in the Coulombic case. The basic cell of the extended dipolar system contains N dipoles in the original cell plus the first set of images, which are the N images resulting from the presence of just the lower wall. Positions and orientations of these N image particles are then given by

$$\boldsymbol{r}_{i+N} = \boldsymbol{r}_i - 2z_i\widehat{\boldsymbol{e}}_z, \quad i = 1, \ldots, N \tag{F.135a}$$

$$\boldsymbol{\mu}_{i+N} = \begin{pmatrix} -\mu_{i,x} \\ -\mu_{i,y} \\ \mu_{i,z} \end{pmatrix}, \quad i = 1, \ldots, N \tag{F.135b}$$

Replicating the basic cell periodically in all three spatial directions, we obtain

for the total configurational potential energy the expression

$$U_{\mathrm{D}}^{\mathrm{3d,ex}} = \frac{1}{2}\sum_{i=1}^{2N}\sum_{j=1}^{2N}{\sum_{\bar{\boldsymbol{n}}}}' \left\{ \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{|\boldsymbol{r}_{ij}+\bar{\boldsymbol{n}}|^3} - 3\frac{[\boldsymbol{\mu}_i \cdot (\boldsymbol{r}_{ij}+\bar{\boldsymbol{n}})]\,[\boldsymbol{\mu}_j \cdot (\boldsymbol{r}_{ij}+\bar{\boldsymbol{n}})]}{|\boldsymbol{r}_{ij}+\bar{\boldsymbol{n}}|^5} \right\} \tag{F.136}$$

where the lattice vectors $\bar{\boldsymbol{n}}$ are specified in Eq. (6.64) and the prime at the lattice sum indicates that $i = j$ is omitted for $\bar{\boldsymbol{n}} = 0$. Separating now the double sum in Eq. (F.136) into

1. Particle particle contributions $\sum_{i=1}^{N}\sum_{j=1}^{N}$,
2. Image image contributions $\sum_{i=N+1}^{2N}\sum_{j=N+1}^{2N}$,
3. Particle image contributions $\sum_{i=1}^{N}\sum_{j=N+1}^{2N}$, and
4. Image particle contributions $\sum_{i=N+1}^{2N}\sum_{j=1}^{N}$

one finds that terms 1 and 2 give the same result after performing the lattice sum. Indeed, one can easily show that

$$\boldsymbol{\mu}_{i+N} \cdot \boldsymbol{\mu}_{j+N} = \boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \tag{F.137a}$$

$$|\boldsymbol{r}_{i+N,j+N} + \bar{\boldsymbol{n}}| = |\boldsymbol{r}_{ij} + \bar{\boldsymbol{n}} - 4n_z s_z \hat{\boldsymbol{e}}_z| \tag{F.137b}$$

where Eq. (F.137b) is identical with Eq. (F.129b) and

$$\begin{aligned} &[\boldsymbol{\mu}_{i+N} \cdot (\boldsymbol{r}_{i+N,j+N} + \bar{\boldsymbol{n}})]\,[\boldsymbol{\mu}_{j+N} \cdot (\boldsymbol{r}_{i+N,j+N} + \bar{\boldsymbol{n}})] \\ = \;& [\boldsymbol{\mu}_i \cdot (\boldsymbol{r}_{ij} + \bar{\boldsymbol{n}} - 4n_z s_z \hat{\boldsymbol{e}}_z)]\,[\boldsymbol{\mu}_j \cdot (\boldsymbol{r}_{ij} + \bar{\boldsymbol{n}} - 4n_z s_z \hat{\boldsymbol{e}}_z)] \end{aligned} \tag{F.138}$$

where we recall that the terms with $4n_z s_z \hat{\boldsymbol{e}}_z$ are irrelevant because we sum over an infinite set of lattice vectors in Eq. (F.136). Moreover, terms 3 and 4 in the above decomposition are also equivalent because of the relations [see also Eq. (F.130b)]

$$\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_{j+N} = \boldsymbol{\mu}_{i+N} \cdot \boldsymbol{\mu}_j \tag{F.139a}$$

$$|\boldsymbol{r}_{i,j+N} + \bar{\boldsymbol{n}}| = |\boldsymbol{r}_{i+N,j} + \bar{\boldsymbol{n}} - 4n_z s_z \hat{\boldsymbol{e}}_z| \tag{F.139b}$$

and

$$\begin{aligned} &[\boldsymbol{\mu}_i \cdot (\boldsymbol{r}_{i,j+N} + \bar{\boldsymbol{n}})]\,[\boldsymbol{\mu}_{j+N} \cdot (\boldsymbol{r}_{i,j+N} + \bar{\boldsymbol{n}})] \\ = \;& [\boldsymbol{\mu}_{i+N} \cdot (\boldsymbol{r}_{i+N,j} + \bar{\boldsymbol{n}} - 4n_z \hat{\boldsymbol{e}}_z)]\,[\boldsymbol{\mu}_j \cdot (\boldsymbol{r}_{i+N,j} + \bar{\boldsymbol{n}} - 4n_z \hat{\boldsymbol{e}}_z)] \end{aligned} \tag{F.140}$$

We therefore see that the energy $U_{\mathrm{D}}^{\mathrm{3d,ex}}$ [see Eq. (F.136)] is indeed exactly twice the energy U_{D} given in Eq. (6.68).