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**Effects of Periodic Boundary Conditions on the  
Static Properties of Charged Fluids**

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**Effects of Periodic Boundary Conditions on the  
Static Properties of Charged Fluids**

by

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*to the memory of C. A. Floudas*

# Effects of Periodic Boundary Conditions on the Static Properties of Charged Fluids

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I investigate the system-size dependence of the thermodynamic properties of classical Coulomb systems in three dimensions with periodic boundary conditions. The system of interest—at given density, composition, and temperature—is assumed to behave as a conductor in the thermodynamic limit  $V \rightarrow \infty$ , where  $V$  is the volume of the unit cell. The leading-order finite-size correction to the Coulomb energy per unit volume is shown to be  $\frac{1}{2}k_B T/V$  (with  $k_B T$  the thermal energy). This correction is the classical analog of the correction to the potential energy of the electron gas at zero temperature derived by Chiesa et al. [Phys. Rev. Lett. **97**, 076404 (2006)]. Also considered is the system-size dependence of the change in free energy due to the insertion of a localized charge distribution of net charge  $Q \neq 0$ , which serves as a prototype for the size dependence of the chemical potential of an ion. It is found that the finite-size correction to the charging free energy is of order  $1/V$ . If the response of the system is linear, the leading-order correction is given by  $\frac{1}{2}aQ^2\chi^{(4)}/V$ , where  $\chi^{(4)}$  is the fourth moment of the static charge response function of the bulk fluid, and  $a$  is a constant that depends on the choice of units. This formula may provide a useful estimate of the system-size dependence of charging free energies (or ionic chemical potentials) when paired with an approximate theory that gives a closed-form expression for  $\chi^{(4)}$ . Finite-size corrections to excess thermodynamic properties obtained from the linearized Debye–Hückel theory are reviewed; these analytic expressions are valid for ionic systems in the low-density limit. A subset of the theoretical results are compared with computer simulation data for two simple models: the classical one-component plasma and a symmetric primitive-model electrolyte solution. This work may have methodological implications for simulation studies of various models of charged fluids.

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Lists, such as contents pages and recipes, are opportunities to build architectural structures in which the space between the elements both separates and binds. The two favorite ways of destroying such an opportunity are setting great chasms of space that the eye cannot leap without help from the hand, and setting unenlightening rows of dots (*dot leaders*, they are called) that force the eye to walk the width of the page like a prisoner being escorted back to its cell. — ROBERT BRINGHURST

# 1

## Introduction

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Fluids composed of charged particles interacting via long-range Coulomb forces, such as plasmas and ionic solutions, are ubiquitous in nature and integral to numerous industrial processes. Along with experimental and theoretical approaches, computer simulations are instrumental in understanding the properties of such systems. Monte Carlo simulations of classical Coulomb systems were first carried out in the 1960s. Arguably the most influential of these works is that of Brush, Sahlin, and Teller [1], who studied the equilibrium properties of the one-component plasma (OCP), a system consisting of identical point-like ions embedded in a uniform neutralizing background. In the half century since their work was published, advances in both hardware and algorithms have enabled simulations of increasingly complex models of charged fluids, along with more exhaustive sampling of configuration (or phase) space. Still, in the case that periodic boundary conditions are imposed on the simulated system to avoid surface effects, it remains common to compute the electrostatic potential energy by the method laid out in Ref. [1] (and introduced independently by Barker [2]). In this method, the electrostatic potential due to all periodic images of the particles in the simulation cell is evaluated by Ewald summation [3] or an equivalent numerical scheme. The present work deals exclusively with periodic systems in which the electrostatic interactions are treated in such a self-consistent<sup>1</sup> manner.

Computational feasibility dictates the number of particles  $N$  contained in the unit cell of a simulated periodic system. In the study of bulk matter, the restriction of finite  $N$  may lead to systematic differences between the observed properties of the model system and those of the bulk system that the model is meant to represent.

<sup>1</sup>In Caillol's [4] words: "It must be stressed that most of the macroscopic electric properties of a conductive or a dielectric liquid are, more or less, a consequence of the harmonicity of the Coulomb potential. Therefore, in order to perform a reliable computer simulation of such fluids, it is of prime importance to consider interactions obeying the fundamental laws of electrostatics in the considered geometry. In that sense, using truncated  $1/r$  potentials in a  $C_3$  [periodic] system—rather than Ewald potentials—is heretic and can lead to seriously erroneous results."

Properly accounting and, if necessary, correcting for such systematic errors is thus a fundamental task in the calculation of bulk properties from simulations. In the case of periodic Coulomb systems, the issue of system-size dependence received special attention in many early studies of the OCP [1, 5–8]. Yet no firm theoretical basis for selecting a value of  $N$  for a given calculation, or for extrapolating results to the thermodynamic limit  $N \rightarrow \infty$  (at fixed density), was proposed. Hansen [5] concluded empirically that “even for Coulomb systems, a system size of a few hundred particles is sufficient to predict energy values close to their thermodynamic limit ...” and observed, “This apparent paradox is due to the well-known screening effect which strongly reduces the long range of the Coulomb forces.” (This qualitative observation is given a quantitative foundation in the developments of this work.) Meanwhile, Slattery, Doolen, and DeWitt [7] concluded their 1982 report “ $N$  dependence in the classical one-component plasma Monte Carlo calculations” with the following:

“What is the exact form of the  $N$ -dependence?” The term given earlier [for the  $N$  dependence of the internal energy per particle] gives the best fit to our data, but there is no rigorous theory to guide us.

More than 30 years later, such a rigorous theory for the system-size dependence of the thermodynamic properties of a three-dimensional, classical Coulomb system with periodic boundary conditions seemed still to be lacking. This apparent gap in knowledge prompted the work reported in this thesis.

Practical motivation was provided by several recent simulation studies [9–15] of the thermodynamic properties of explicit-solvent models of aqueous electrolyte solutions. (See Ref. [16] for extensive review.) Common to these studies is the use of systems that might, particularly if the solvent were suddenly replaced by a continuous medium, be recognized as being rather small for the task of modeling the ion–ion correlations and screening behavior of a bulk solution at finite salt concentration. This is especially true at low concentration, where the large solvent-to-salt ratio makes simulation cells containing more than a few ions impractical for precise calculations of such quantities as the electrolyte chemical potential. It has been recognized [16] that the possible system-size dependence of the results of such simulations is worth investigating. Note that in the above-mentioned studies, the negligibility of finite-size effects has at times been supported empirically—for example by agreement, within statistical error, of results from two systems with

values of  $N$  differing by a factor of ten [9]. The aim of this work is to develop some theoretical results that might not only facilitate these sort of assessments, but also yield correction formulas for extrapolation of results to the thermodynamic limit. Such expressions may also, of course, provide guidelines for the choice of system size at the outset of a calculation.

## 1.1 SCOPE AND RELATED WORK

Attention is restricted to classical systems in three dimensions with periodic boundary conditions. The system of interest is assumed to contain mobile charges and, in the bulk limit  $N \rightarrow \infty$ , to behave as a conductor (in a sense to be made precise in the next chapter). The system is furthermore assumed to be at an “ordinary” point [17] in macroscopic state space, away from criticality or a phase transition. In the absence of an external field, the system is uniform. The focus is on the  $N$  dependence of static properties that are related to fluctuations in charge density or electrostatic potential, and which may be considered without a detailed specification of the short-range interaction potential between particles.<sup>2</sup>

There are two closely related problems should be mentioned. The first deals with the effect of periodic boundary conditions on the calculation of the electrostatic energy of an isolated charged “solute” in a non-conducting phase—e.g., an ion in pure solvent or a charged defect in a crystalline solid [19–24]. In such systems, the solute charge distribution is not completely shielded; correspondingly, the average electrostatic potential at large distance  $r$  from the solute decays as  $1/r$ , that is, as the bare Coulomb potential. The leading term in the finite-size correction to the energy is thus of order  $1/V^{1/3}$ , where  $V$  is the volume of the unit cell. It is demonstrated in what follows that for a system with a nonzero density of mobile charges (which completely screens a localized external charge density), the leading correction to the electrostatic energy of a charged particle is instead of order  $1/V$ .

The second problem is quantifying system-size effects in quantum Monte Carlo calculations for electronic systems at zero temperature [25–28]. Chiesa et al. [26]

<sup>2</sup>Given this model-agnostic perspective, it is convenient to adopt the volume  $V$  of the unit cell, rather than the particle number  $N$ , as the extensive variable by which the system size is characterized. (These two variables are simply proportional in the case that the density  $n = N/V$  is fixed, as will be assumed in what follows.) Note that this convention, along with some of the notation used in this manuscript, differs from that of a paper [18] in which part of the following work is published.

showed that an exact expression for the leading-order finite-size correction to the potential energy of the uniform electron gas<sup>3</sup> may be obtained by considering the long-wavelength behavior of the static structure factor. As will be seen in Chapter 5, the same approach may be used to derive the leading correction to the Coulomb energy of a classical charged fluid—provided that one uses the second-moment sum rule [29, 30] for the charge–charge structure factor appropriate to a classical system.

## 1.2 OUTLINE

The next two chapters establish some necessary background: Chapter 2 reviews the fundamental constraints (sum rules) satisfied by the charge–charge correlation function of a uniform classical fluid containing free charges, while Ch. 3 outlines how electrostatic interactions are treated in a periodic system.

In Chapter 4, the adaptation of the Debye–Hückel theory to a periodic system is discussed, along with the resulting approximate finite-size corrections to the thermodynamic properties of an ionic fluid at low density.

Chapter 5, which contains the main results of this work, is concerned with establishing the asymptotic form of the system-size dependence of some thermodynamic properties of a classical charged system with periodic boundary conditions.

Lastly, Chapter 6 compares some of the theoretical expressions with simulation data for two simple models: the OCP and a primitive-model electrolyte.

<sup>3</sup>That is, the jellium model or quantum OCP.

# 2

## Screening and sum rules

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As we will see in Chapter 3, the long range of the Coulomb potential—that is, its slow  $1/r$  decay with increasing distance  $r$  between charges—presents some complications in the mathematical treatment of systems of charged particles. Yet this same feature of the Coulomb potential gives rise in charged fluids to characteristic physical behavior, absent in systems comprising only neutral particles [31]. This behavior is embodied in the fact that the charge–charge correlations of such systems obey specific constraints, which in turn imply conditions on certain linear combinations of the particle distribution functions [29, 30]. Here the most basic of these sum rules are reviewed, with focus limited to the static correlations of a uniform classical fluid. Martin [32] provides an excellent—and extensive—review of sum rules in a more general context, covering time-displaced correlations as well as nonuniform and quantum fluids.

The presentation here, based on that of Hansen and McDonald [31], follows the phenomenological approach of Stillinger and Lovett [29, 30]. Specifically, the sum rules appear as a result of the assumption, grounded in empirical knowledge, that a localized external charge distribution is completely screened by the free charges of a conducting fluid.<sup>1</sup> As shown by Martin and Gruber [33], the Stillinger–Lovett sum rules for an ionic fluid or an ion–dipole mixture<sup>2</sup> may also be derived under a “clustering” hypothesis for the  $k$ -particle distribution functions ( $k = 2, 3, \dots$ ). Another route is to assume that the ion–ion direct correlation functions (of the Ornstein–Zernike relations) decay like the Coulomb potential<sup>3</sup> at large  $r$  [34].

Consider a fluid in equilibrium in the presence of a localized external charge

<sup>1</sup>As Stillinger and Lovett [29] put it: “The electrolyte can do a perfect job of shielding if it is given enough room in which to perform the task.”

<sup>2</sup>Though only pure ionic systems and ion–dipole mixtures are considered explicitly by Martin and Gruber [33], one expects that their proof may be generalized to more complex models of ionic solutions—for example, those in which the solvent particles carry higher-order multipoles or have charge densities described by multiple discrete charges (i.e., interaction-site models).

<sup>3</sup>See for example Eq. (4.8).

density  $\rho^{\text{ext}}(\mathbf{r})$ . It is assumed for convenience that the system contains no point multipoles. The charge response of the system to the field produced by the external charge is characterized by the mean induced charge density

$$\rho^{\text{ind}}(\mathbf{r}) = \langle \rho(\mathbf{r}) \rangle_{\text{ext}}, \quad (2.1)$$

where  $\rho(\mathbf{r})$  is the microscopic charge density<sup>4</sup> of the system at point  $\mathbf{r}$ , and  $\langle \cdots \rangle_{\text{ext}}$  indicates a thermal average in the presence of the external field. The system has the *complete shielding property* [33] if, for an arbitrary external charge distribution, the total charge density satisfies

$$\int d^3\mathbf{r} [\rho^{\text{ind}}(\mathbf{r}) + \rho^{\text{ext}}(\mathbf{r})] = 0, \quad (2.2)$$

where the integral is over all space. Unless noted otherwise, it is assumed in what follows that condition (2.2) holds for the bulk system of interest, at least for the sort of external charges that we wish to subject it to.

If an arbitrary external charge density is perfectly screened, then so must be an infinitesimal one. In this case, the response of the system may be assumed to be linear. Let

$$\phi^{\text{ext}}(\mathbf{r}) = \int d^3\mathbf{r}' \frac{\rho^{\text{ext}}(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|} \quad (2.3)$$

be the electrostatic potential due to  $\rho^{\text{ext}}(\mathbf{r})$ , with  $\epsilon_0$  the vacuum permittivity. A first-order functional Taylor expansion of the mean induced charge density in powers of  $\phi^{\text{ext}}$  yields<sup>5</sup>

$$\rho^{\text{ind}}(\mathbf{r}) = \int d^3\mathbf{r}' \chi(|\mathbf{r} - \mathbf{r}'|) \phi^{\text{ext}}(\mathbf{r}'), \quad (2.4)$$

where  $\chi(\mathbf{r}, \mathbf{r}') = \chi(|\mathbf{r} - \mathbf{r}'|)$  is the charge response function of the (homogeneous and isotropic) unperturbed system. Defining the static charge–charge correlation

<sup>4</sup>E.g., for a system of spherical particles, in which each of the  $N_\alpha$  particles of species  $\alpha$  carries a point charge  $q_\alpha$ , the microscopic charge density is

$$\rho(\mathbf{r}) = \sum_{\alpha} q_{\alpha} \sum_{i=1}^{N_{\alpha}} \delta(\mathbf{r} - \mathbf{r}_{i\alpha}),$$

where the first sum runs over all species, and  $\mathbf{r}_{i\alpha}$  is the position of the  $i$ th particle of species  $\alpha$ .

<sup>5</sup>See for example Hansen & McDonald [31], §§ 3.6 and 10.2.

function

$$S(|\mathbf{r} - \mathbf{r}'|) = \langle \rho(\mathbf{r})\rho(\mathbf{r}') \rangle, \quad (2.5)$$

with  $\langle \dots \rangle$  an average in the absence of the external field, the response function may—for a classical system [32]—be expressed as

$$\chi(r) = -\beta S(r), \quad (2.6)$$

where  $\beta^{-1} = k_{\text{B}}T$ , with  $k_{\text{B}}$  the Boltzmann constant and  $T$  the temperature.

In Fourier space, Eqs. (2.2)–(2.4) take the forms (respectively)

$$\lim_{\mathbf{k} \rightarrow \mathbf{0}} [\hat{\rho}^{\text{ind}}(\mathbf{k}) + \hat{\rho}^{\text{ext}}(\mathbf{k})] = 0, \quad (2.7)$$

$$\hat{\phi}^{\text{ext}}(\mathbf{k}) = \frac{\hat{\rho}^{\text{ext}}(\mathbf{k})}{\epsilon_0 k^2}, \quad (2.8)$$

$$\hat{\rho}^{\text{ind}}(\mathbf{k}) = \hat{\chi}(k) \hat{\phi}^{\text{ext}}(\mathbf{k}), \quad (2.9)$$

where the circumflex indicates the Fourier transform

$$\hat{f}(\mathbf{k}) = \int d^3\mathbf{r} f(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}), \quad (2.10)$$

with  $r = |\mathbf{r}|$  and  $k = |\mathbf{k}|$  for radial functions, and  $1/\epsilon_0 k^2$  is the transform of the Coulomb potential  $1/4\pi\epsilon_0 r$ . Using Eqs. (2.6) and (2.8), Eq. (2.9) may be written as

$$\hat{\rho}^{\text{ind}}(\mathbf{k}) = -\beta \frac{\hat{S}(k)}{\epsilon_0 k^2} \hat{\rho}^{\text{ext}}(\mathbf{k}). \quad (2.11)$$

Adding  $\hat{\rho}^{\text{ext}}(\mathbf{k})$  to both sides, taking the limit  $\mathbf{k} \rightarrow \mathbf{0}$ , and using the perfect screening condition (2.7) yields

$$0 = Q \lim_{\mathbf{k} \rightarrow \mathbf{0}} \left[ 1 - \beta \frac{\hat{S}(k)}{\epsilon_0 k^2} \right], \quad (2.12)$$

where  $Q = \hat{\rho}^{\text{ext}}(\mathbf{0})$  is the net charge of the external charge density. For Eq. (2.12) to be true in general (i.e., for arbitrary  $Q$ ), we must have

$$\beta \lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{\hat{S}(k)}{\epsilon_0 k^2} = 1. \quad (2.13)$$

It is assumed that  $S(r)$  is integrable. Then its Fourier transform—the charge structure factor  $\hat{S}(k)$ —has the small- $k$  expansion

$$\hat{S}(k) = S^{(0)} + S^{(2)}k^2 + S^{(4)}k^4 + \dots, \quad k \rightarrow 0, \quad (2.14)$$

with moments defined for  $n = 0, 2, \dots$  by<sup>6</sup>

$$S^{(n)} = \frac{(-1)^{n/2}}{(n+1)!} \int d^3\mathbf{r} r^n S(r). \quad (2.15)$$

Using this expansion, it is seen that Eq. (2.13) implies the moment conditions

$$S^{(0)} = \int d^3\mathbf{r} S(r) = 0, \quad (2.16)$$

$$S^{(2)} = -\frac{1}{6} \int d^3\mathbf{r} r^2 S(r) = \varepsilon_0 k_B T. \quad (2.17)$$

The zeroth-moment condition (2.16) expresses the constraint of local electroneutrality. Since any of the system’s particles may be regarded, logically, as the source of an external field in which the remaining particles move, this constraint “can be interpreted as the shielding of test particles of the same species as those which constitute the system itself” [32]. Consider for example a mixture of spherical ions of species  $\alpha = 1, \dots, s$  carrying charges  $q_\alpha$ . Here  $S(r)$  is given by

$$S(r) = \sum_\alpha \sum_\gamma n_\alpha n_\gamma q_\alpha q_\gamma h_{\alpha\gamma}(r) + \delta(r) \sum_\alpha n_\alpha q_\alpha^2, \text{ constraints} \quad (2.18)$$

where  $n_\alpha$  is the number density of species  $\alpha$ , and  $h_{\alpha\gamma}(r)$  are the usual pair correlation functions. The latter may be expressed as

$$n_\alpha n_\gamma h_{\alpha\gamma}(|\mathbf{r} - \mathbf{r}'|) = \langle \delta n_\alpha(\mathbf{r}) \delta n_\gamma(\mathbf{r}') \rangle - n_\alpha \delta_{\alpha\gamma} \delta(\mathbf{r} - \mathbf{r}'), \quad (2.19)$$

where  $\delta_{\alpha\gamma}$  is the Kronecker delta, and  $\delta n_\alpha(\mathbf{r}) = n_\alpha(\mathbf{r}) - n_\alpha$  is the deviation in the

<sup>6</sup>The odd moments of a radial function vanish by symmetry.

microscopic number density

$$n_\alpha(\mathbf{r}) = \sum_{\alpha=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_{i\alpha}) \quad (2.20)$$

of species  $\alpha$  at point  $\mathbf{r}$  from its average  $n_\alpha = \langle n_\alpha(\mathbf{r}) \rangle$ . For this system, Eq. (2.16) is a linear combination of  $s$  neutrality constraints

$$\int d^3\mathbf{r} \sum_Y n_Y q_Y h_{\alpha Y}(r) = -q_\alpha \quad (\alpha = 1, \dots, s), \quad (2.21)$$

which express the fact that the mean charge density around a particle—its screening cloud—must exactly cancel its charge.

The second-moment condition (2.17) is due to Stillinger and Lovett, who derived it first for the primitive-model electrolyte [29] and then for general solutions of ions in a molecular solvent [30].<sup>7</sup> Qualitatively, condition (2.17) gives an exact constraint on the second radial moment of the “average” screening cloud, the average being weighted by the charge at each cloud’s center. For the simple ionic system with  $S(r)$  given by Eq. (2.18), this sum rule takes the form

$$\sum_\alpha n_\alpha q_\alpha \int d^3\mathbf{r} r^2 \sum_Y n_Y q_Y h_{\alpha Y}(r) = -6\epsilon_0 k_B T = -6\lambda_D^2 \sum_\alpha n_\alpha q_\alpha^2, \quad (2.22)$$

where in the last equality,

$$\lambda_D = \left( \beta \sum_\alpha n_\alpha q_\alpha^2 / \epsilon_0 \right)^{-1/2} \quad (2.23)$$

is the Debye length.

<sup>7</sup>The charge–charge correlation function of an ionic solution may be separated into ion–ion, ion–solvent, and solvent–solvent parts:

$$S(r) = S_{ii}(r) + S_{is}(r) + S_{ss}(r).$$

Strictly speaking, the second-moment condition derived by Stillinger and Lovett in Ref. [30] was on the ion–ion part  $S_{ii}(r)$ . It takes the form [cf. Eq. (2.17)]

$$S_{ii}^{(2)} = \epsilon_{\text{eff}} k_B T,$$

where  $\epsilon_{\text{eff}}$  is the composition-dependent dielectric constant discussed in Refs. [35–37].

# 3

## Electrostatics in periodic systems

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It is a remarkable fact that our proof of the stability of matter, after such a tremendous detour via dissections of space and other artificial tricks, boils down in the end to an estimate of the binding energy of a single electron in a periodic Coulomb potential.

— A. LENARD & F. J. DYSON [38]

Before discussing the thermodynamic properties of charged systems with periodic boundary conditions, it will be useful to review how to “build electrostatics” [39] in a periodic space. Here the required periodicity of the electric field deprives the unit point charge of its usual status as the elementary building block [39]. Moreover, the long range of the Coulomb potential gives rise to conditionally convergent series in naive expressions of the electrostatic potential. Overcoming the latter difficulty—or rather, ordering such series to yield values consistent with a well-defined physical picture [1]—requires certain mathematical tricks. Unsurprisingly, these tricks originated largely in the study of *real* periodic matter (e.g., ionic crystals), in contrast to the sort of model systems considered here (in which periodicity is an artifact imposed by computational necessity). The Ewald summation method, initially devised<sup>1</sup> for calculating Madelung energies, was first applied to simulations of classical plasmas in the mid-1960s by Barker [2] and by Brush, Sahlin, and Teller [1]. de Leeuw, Perram, and Smith [40] gave more rigorous foundation to the Hamiltonian of a Coulomb system in periodic boundary conditions.<sup>2</sup> Importantly, they discussed how the potential energy depends on the dielectric properties of the medium imagined to surround the infinite array of periodic replicas of the unit cell. The necessity of accounting for the properties of the surrounding medium is, again, a result of the long range of the Coulomb force [42]. It should be stressed that the concepts outlined below are well established, and numerous works address them

<sup>1</sup>With the help of some advice from Debye. See H.J. Juretschke and H.K. Wagenfeld, *Current Contents/Phys., Chem. & Earth Sci.* No. 49, 20 (1985).

<sup>2</sup>An ambiguity in Ref. [40] regarding the proper definition of the net dipole moment of an ionic system was later resolved by Caillol [41].

in detail. They are presented here with the aim of facilitating the developments in later chapters. For further background, the reader is referred to Refs. [40–45].

In considering a system under periodic boundary conditions, it is often convenient to focus not on the finite sample surrounded on all sides by periodic copies of itself, but rather on the infinite system comprising all such copies. This infinite system is periodic on some Bravais lattice with fundamental translation vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$ , which define a unit cell  $\mathcal{C} \subset \mathbb{R}^3$  of volume  $V = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$ . The boundary conditions imply that the microscopic charge density  $\rho(\mathbf{r})$  and electric field  $\mathbf{e}(\mathbf{r})$  are periodic functions, satisfying

$$\rho(\mathbf{r}) = \rho(\mathbf{r} + \mathbf{R}) \quad \text{and} \quad \mathbf{e}(\mathbf{r}) = \mathbf{e}(\mathbf{r} + \mathbf{R}) \quad (3.1)$$

for all lattice vectors  $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ , where  $(n_1, n_2, n_3) \in \mathbb{Z}^3$  are integer coordinates. Since the field and charge density are related by Gauss's law

$$\nabla \cdot \mathbf{e}(\mathbf{r}) = \varepsilon_0^{-1} \rho(\mathbf{r}), \quad (3.2)$$

periodicity of  $\mathbf{e}(\mathbf{r})$  requires that the unit cell be electroneutral:<sup>3</sup>

$$\int_{\mathcal{C}} d^3\mathbf{r} \rho(\mathbf{r}) = 0. \quad (3.3)$$

The periodic system is understood to be an infinite ellipsoidal array of replicas of the basic cell, surrounded by a continuous medium of permittivity  $\varepsilon'$  [40, 42]. Given a charge density satisfying conditions (3.1) and (3.3), the field is determined up to a uniform macroscopic contribution [42]

$$\mathbf{e}_0 = \frac{1}{V} \int_{\mathcal{C}} d^3\mathbf{r} \mathbf{e}(\mathbf{r}). \quad (3.4)$$

The choice  $\mathbf{e}_0 = \mathbf{0}$  amounts to assuming that the surrounding medium is a perfect conductor ( $\varepsilon' = \infty$ ). If instead the external medium is has a finite permittivity  $\varepsilon'$ , the polarization of the medium in response to the net polarization of the enclosed system leads to a nonvanishing value of  $\mathbf{e}_0$ . Only conducting boundary conditions

<sup>3</sup>As mentioned in Refs. [39, 45, 46] and elsewhere, this may be seen by integrating Eq. (3.2) over the cell and using the divergence theorem along with the periodicity of  $\mathbf{e}(\mathbf{r})$ , the latter implying that the electric flux going out one face of the cell equals that coming in the opposite face.

(i.e.,  $\varepsilon' = \infty$ , also called tinfoil or metallic boundary conditions) are considered in the present work. In this case, the system is “electrically closed on itself” [47] and may be mapped onto a torus in the same way as a system with only short-range interactions [41].

With  $\mathbf{e}_0 = \mathbf{0}$ , the electrostatic potential  $\varphi(\mathbf{r})$  associated with the field  $\mathbf{e}(\mathbf{r})$  is also a periodic function. It is given up to an arbitrary constant by

$$\varphi(\mathbf{r}) = (4\pi\varepsilon_0)^{-1} \int_{\mathcal{C}} d^3\mathbf{r}' \psi(\mathbf{r} - \mathbf{r}'; \mathcal{C}) \rho(\mathbf{r}'), \quad (3.5)$$

where  $\psi(\mathbf{r}; \mathcal{C})$  is a periodic solution of the Poisson equation

$$\nabla^2 \psi(\mathbf{r}; \mathcal{C}) = -4\pi \left[ \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R}) - \frac{1}{V} \right], \quad (3.6)$$

with the sum in brackets running over all lattice vectors. Noting that the source term in Eq. (3.6) is the charge density of a periodic array of point charges embedded in a uniform neutralizing background—i.e., a Wigner lattice—Cichoki, Felderhof, and Hinsien [42] termed  $\psi(\mathbf{r}; \mathcal{C})$  the Wigner potential. Lenard and Dyson [38] called it simply the *periodic Coulomb potential*, the term that will be used here. Equation (3.6) suggests that the Wigner lattice<sup>4</sup>

$$\sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R}) - 1/V, \quad (3.7)$$

rather than the unit point charge  $\delta(\mathbf{r})$ , be treated as the basic electrostatic entity in a periodic space [4, 42].

An attempt to solve Eq. (3.6) by integration in direct space yields the conditionally convergent integral

$$\psi(\mathbf{r}; \mathcal{C}) = \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left[ \sum_{\mathbf{R}} \delta(\mathbf{r}' - \mathbf{R}) - \frac{1}{V} \right]. \quad (3.8)$$

The integral may be evaluated using a generalization of Ewald’s method (see for example Ref. [48]). In this approach, the Coulomb potential  $1/r$  is split into two parts: a short-range (integrable) part that contains the singularity at  $r = 0$ , and

<sup>4</sup>Or “pseudocharge” [4] or “C + B charge” [23] (C = charge, B = background).

a long-range, slowly varying part that is well represented by its first few Fourier components. The common choice

$$1/r = (1/r) \operatorname{erfc}(\eta r) + (1/r) \operatorname{erf}(\eta r), \quad (3.9)$$

with  $\operatorname{erfc}(x) \equiv 1 - \operatorname{erf}(x)$  the complementary error function and  $\eta$  a positive convergence parameter, gives the Ewald sum

$$\psi(\mathbf{r}; \mathcal{C}) = \sum_{\mathbf{R}} \frac{\operatorname{erfc}(\eta|\mathbf{r} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{R}|} + \frac{1}{V} \sum_{\mathbf{G} \neq 0} \frac{4\pi}{|\mathbf{G}|^2} \exp(-|\mathbf{G}|^2/4\eta^2) \exp(i\mathbf{G} \cdot \mathbf{r}) - \frac{\pi}{\eta^2 V}, \quad (3.10)$$

where the second sum runs over nonzero reciprocal lattice vectors  $\mathbf{G}$  [satisfying  $\exp(i\mathbf{G} \cdot \mathbf{R}) = 1$  for all  $(\mathbf{R}, \mathbf{G})$ ]. Note that this potential satisfies the arbitrary but mathematically convenient [44] normalization condition

$$\int_{\mathcal{C}} d^3\mathbf{r} \psi(\mathbf{r}; \mathcal{C}) = 0. \quad (3.11)$$

For a system of  $N$  particles with periodic boundary conditions, the microscopic charge density may be expressed as

$$\begin{aligned} \rho(\mathbf{r}) &= \int d^3\mathbf{r}' \sum_{i=1}^N \rho_i(\mathbf{r}') \left[ \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{r}' - \mathbf{R}) - \frac{1}{V} \right] \\ &= \sum_{\mathbf{R}} \sum_{i=1}^N \rho_i(\mathbf{r} - \mathbf{R}) - \frac{1}{V} \sum_{i=1}^N \int d^3\mathbf{r}' \rho_i(\mathbf{r}'), \end{aligned} \quad (3.12)$$

where  $\rho_i(\mathbf{r})$  is the charge density of a single copy of particle  $i$  [e.g.,  $\rho_i(\mathbf{r}) = q\delta(\mathbf{r} - \mathbf{r}_i)$  if particle  $i$  is a point ion of charge  $q$ ]. The uniform background charge density described by the last term of Eq. (3.12) ensures that the unit cell is electroneutral in the case that the particles have a nonzero net charge. If  $\rho(\mathbf{r})$  is continuous, the total electrostatic potential energy of the  $N$  particles can be written as

$$V_N^{\text{el}} = \frac{1}{2} \int_{\mathcal{C}} d^3\mathbf{r} \rho(\mathbf{r}) \varphi(\mathbf{r}), \quad (3.13)$$

where  $\varphi(\mathbf{r})$  is the microscopic electric potential (3.5). Alternatively, if the system is composed of  $N$  point charges  $q_1, \dots, q_N$ , subtracting out the infinite self-energy

terms leaves

$$(4\pi\epsilon_0)V_N^{\text{el}} = \sum_{i=1}^N \sum_{j>i}^N q_i q_j \psi(\mathbf{r}_i - \mathbf{r}_j; \mathcal{C}) + \frac{1}{2} \sum_{i=1}^N q_i^2 \lim_{r \rightarrow 0} [\psi(\mathbf{r}; \mathcal{C}) - 1/r]. \quad (3.14)$$

The last term in Eq. (3.14) accounts for self-interactions of each charge  $q_i$  with its own images and neutralizing background charge density  $-q_i/V$ . These *individual* background charges are implied by the source term in Eq. (3.6). When superposed, the individual background charges may in certain cases (e.g., in models of electrolyte solutions) lead to a vanishing *net* background charge density  $-\sum_{i=1}^N q_i/V$ . Defining the Madelung constant<sup>5</sup>

$$\xi = V^{1/3} \lim_{r \rightarrow 0} [\psi(\mathbf{r}; \mathcal{C}) - 1/r] \leq 0, \quad (3.15)$$

the final term of Eq. (3.14) may be written as

$$\frac{\xi}{2V^{1/3}} \sum_{i=1}^N q_i^2. \quad (3.16)$$

The self-term (3.16) depends on the volume and shape of the cell but is independent of the particle coordinates; it thus has no effect on the sampling of phase space as long as the primitive vectors  $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$  remain fixed. Still, based on a heuristic argument, Caillol [49] suggested that retaining this term in the Coulomb energy  $V_N^{\text{el}}$  should lead to better convergence of the energy per particle  $\langle V_N^{\text{el}}/N \rangle_V$  (with  $\langle \cdot \cdot \rangle_V$  an average over configurations of the periodic system) to its thermodynamic limit—i.e., its limit as  $\mathcal{C} \rightarrow \mathbb{R}^3$  (and  $V \rightarrow \infty$ ) at fixed density  $N/V$ . In his words: “All what we can hope is that ... the convergence towards the thermodynamic limit is [then] ‘optimum’ in a sense which remains to be precised.” We will see in what follows how this sense may indeed be made precise.

<sup>5</sup>For a cubic cell,  $\xi = -2.837\,297\dots$  [48].

# 4

## Debye–Hückel theory

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The goal of this and the next chapter is to determine the dependence of intensive properties of a “periodic fluid” [50] on the volume  $V$  of the unit cell  $\mathcal{C} \subset \mathbb{R}^3$ , given fixed values of the temperature  $T$  and number densities  $n_\alpha = N_\alpha/V$  of all species  $\alpha$ . It is assumed that the cell scales in some well behaved manner (e.g., isotropically) with changes in volume, so that the limit  $V \rightarrow \infty$  implies  $\mathcal{C} \rightarrow \mathbb{R}^3$ . The focus is limited to static properties that depend solely on fluctuations in charge density (e.g., the Coulomb part of the excess internal energy per unit volume) or electrostatic potential (e.g., the free-energy change caused by the presence of a test charge). The system in the bulk limit is assumed to be in a conducting phase and, correspondingly, to satisfy the complete shielding property (2.2).

### 4.1 LINEARIZED POISSON–BOLTZMANN EQUATION

To get a sense of how periodic boundary conditions affect the static properties of a classical plasma or ionic fluid in the low-density limit, one may derive the Debye–Hückel theory for a periodic system [18, 51]. Hünenberger and McCammon [23] considered basically this approach. They proposed solving the linearized Poisson–Boltzmann equation with periodic boundary conditions to estimate the  $V$  dependence of the solvation free energy of an ion in solution. In their approach, the central ion was modeled by one or more fixed charges inside a cavity bounded by a sharp dielectric interface, while its ion atmosphere consisted of mobile point ions embedded in the surrounding continuous dielectric medium. This asymmetric description reduced to a Born-like picture in the limit of zero density of mobile ions. Since, for a finite cavity size, this system is inhomogeneous with a position-dependent permittivity  $\varepsilon(\mathbf{r})$ , only numerical solution of the linearized Poisson–Boltzmann equation was considered in Ref. [23]. This equation may be solved analytically in the case of uniform  $\varepsilon(\mathbf{r})$ , and Liang, Xu, and Xing [51] did so to derive an approximation for the system-size dependence of the internal energy per

particle of a primitive-model electrolyte solution.

The same fundamental equation

$$(\nabla^2 - \kappa^2)\psi_\kappa(\mathbf{r}; \mathcal{C}) = -4\pi \left[ \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R}) - \frac{1}{V} \right] \quad (\kappa > 0) \quad (4.1)$$

for the screened Coulomb potential  $\psi_\kappa(\mathbf{r}; \mathcal{C})$  due to a periodically replicated point charge with a canceling background<sup>1</sup> was considered earlier in a different context—namely, the simulation of Yukawa systems [52–54]. (Here  $\kappa$  is an inverse screening length.) In the limit  $\kappa \rightarrow 0$ , Eq. (4.1) reduces to the Poisson equation (3.6). In contrast to that equation, Eq. (4.1) for  $\kappa > 0$  may be solved at once by convolution of the free-space Green’s function (the familiar screened Coulomb potential)

$$\psi_\kappa(\mathbf{r}; \mathbb{R}^3) = \frac{\exp(-\kappa r)}{r} \quad (4.2)$$

with the source term  $\sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R}) - 1/V$ . The result is

$$\psi_\kappa(\mathbf{r}; \mathcal{C}) = \sum_{\mathbf{R}} \frac{\exp(-\kappa|\mathbf{r} - \mathbf{R}|)}{|\mathbf{r} - \mathbf{R}|} - \frac{4\pi}{\kappa^2 V}, \quad (4.3)$$

where the last term arises from the background charge.

## 4.2 ENERGY AND PRESSURE

Consider the simple ionic mixture introduced in Chapter 2 (see p. 8), consisting of  $s$  species of spherical ions with number densities  $n_\alpha$  and charges  $q_\alpha$  ( $\alpha = 1, \dots, s$ ). Though not made explicit earlier, the net charge  $\sum_\alpha n_\alpha q_\alpha$  of the ions need not be zero; in the general case, the charge of the particles is neutralized by including in the microscopic charge density  $\rho(\mathbf{r})$  a fixed uniform background term

$$\rho_b = - \sum_{\alpha} n_{\alpha} q_{\alpha}. \quad (4.4)$$

Thus, for instance, the model reduces to the one-component plasma when  $s = 1$ . Note that in the capacity of this model as a primitive model of an ionic solution, the

<sup>1</sup>Recall from Ch. 3 that when a point charge  $q$  is fixed at the origin in the periodic system, the total fixed charge density is  $\sum_{\mathbf{R}} q\delta(\mathbf{r} - \mathbf{R}) - q/V$ .

quantity  $\epsilon_0$  appearing below (i.e., the vacuum permittivity) should be interpreted as the permittivity of the continuum solvent.

The truncated charge–charge correlation function  $S(|\mathbf{r} - \mathbf{r}'|) = \langle \rho(\mathbf{r})\rho(\mathbf{r}') \rangle$  of the bulk fluid is given by Eq. (2.18), rewritten here as

$$S(r) = \sum_{\alpha} \sum_{\gamma} n_{\alpha} n_{\gamma} q_{\alpha} q_{\gamma} h_{\alpha\gamma}(r) + nq^2 \delta(\mathbf{r}), \quad (4.5)$$

where  $n = \sum_{\alpha} n_{\alpha}$  is the total number density, and

$$q^2 = n^{-1} \sum_{\alpha} n_{\alpha} q_{\alpha}^2 \quad (4.6)$$

is introduced for convenience. The pair correlation functions  $h_{\alpha\gamma}(r)$  solve the set of Ornstein–Zernike equations

$$h_{\alpha\gamma}(r) = c_{\alpha\gamma}(r) + \sum_{\lambda} n_{\lambda} \int d^3\mathbf{r}' c_{\alpha\lambda}(|\mathbf{r} - \mathbf{r}'|) h_{\lambda\gamma}(r'), \quad (4.7)$$

where  $c_{\alpha\gamma}(r)$  are the direct correlation functions. In the linearized Debye–Hückel theory, valid in the limit of vanishing densities (all  $n_{\alpha} \rightarrow 0$ ), the closure to the set of integral equations (4.7) is given by

$$c_{\alpha\gamma}(r) = \frac{-\beta q_{\alpha} q_{\gamma}}{4\pi\epsilon_0 r}. \quad (4.8)$$

That is, the direct correlation function  $c_{\alpha\gamma}(r)$  is approximated by its  $r \rightarrow \infty$  limit for all interparticle distances  $r$ . Using Eq. (4.8) in Eq. (4.7) leads to

$$h_{\alpha\gamma}(r) = \frac{-\beta q_{\alpha} q_{\gamma}}{4\pi\epsilon_0 r} \exp(-k_D r), \quad (4.9)$$

where

$$k_D = (\beta n q^2 / \epsilon_0)^{1/2} = 1/\lambda_D \quad (4.10)$$

is the Debye wavenumber—the inverse of the Debye length (6.4). Substituting this expression for  $h_{\alpha\gamma}(r)$  into Eq. (4.5) gives

$$S(r) = nq^2 \left[ \delta(\mathbf{r}) - \frac{k_D^2}{4\pi r} \exp(-k_D r) \right]. \quad (4.11)$$

It is convenient to define the function

$$\Psi(r) = (4\pi\epsilon_0)^{-1} \int d^3\mathbf{r}' |\mathbf{r} - \mathbf{r}'|^{-1} S(r'). \quad (4.12)$$

For the simple model considered here,  $\Psi(r)$  may be expressed as the linear combination

$$\Psi(r) = \sum_{\alpha} n_{\alpha} q_{\alpha} \phi_{\alpha}(r), \quad (4.13)$$

where

$$\phi_{\alpha}(r) = \frac{q_{\alpha}}{4\pi\epsilon_0 r} + \sum_{\gamma} n_{\gamma} q_{\gamma} \int d^3\mathbf{r}' \frac{h_{\alpha\gamma}(r')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} \quad (4.14)$$

is the change in the average electrostatic potential at point  $\mathbf{r}$  upon fixing an ion of species  $\alpha$  at the origin. Carnie and Chan [55] called  $\phi_{\alpha}(r)$  the fluctuation potential. Given relation (4.13),  $\Psi(r)$  may be termed the *mean fluctuation potential*.<sup>2</sup> This term is used in what follows for the quantity defined by Eq. (4.12), even in the case (e.g., for more complex models) that it is not given simply by Eqs. (4.13) and (4.14). In terms of the mean fluctuation potential, the Coulomb contribution  $u^{\text{el}} = \langle V_N^{\text{el}}/V \rangle$  to the excess internal energy per unit volume—i.e., the Coulomb energy density—may be written as

$$u^{\text{el}} = \frac{1}{2} \lim_{r \rightarrow 0} [\Psi(r) - nq^2/4\pi\epsilon_0 r], \quad (4.15)$$

where the second (generally model-dependent) term inside brackets serves here to cancel the infinite self-energy of the point charges. Substituting the Debye–Hückel expression (4.11) for  $S(r)$  into Eq. (4.12) results in

$$\Psi(r) = \frac{nq^2}{4\pi\epsilon_0 r} \exp(-k_{\text{D}}r), \quad (4.16)$$

which when used in Eq. (4.15) gives the familiar limiting law  $\beta u^{\text{el}} = -k_{\text{D}}^3/8\pi$ .

Consider now the periodic system of finite cell volume  $V$ . Its charge–charge correlation function

$$S_V(\mathbf{r} - \mathbf{r}') = \langle \rho(\mathbf{r})\rho(\mathbf{r}') \rangle_V, \quad (4.17)$$

with  $\langle \cdots \rangle_V$  denoting a canonical average under periodic boundary conditions, is pe-

<sup>2</sup>The term “mean fluctuation potential” appears in the abstract of Ref. [55]; there, is not entirely clear whether it refers to  $\phi_{\alpha}(r)$  or to the charge-weighted linear combination  $\Psi(r)$ .

riodic and, consequently, nonspherical. At the mean-field level of the Debye–Hückel approximation,  $S_V(\mathbf{r})$  is related to its bulk-system counterpart  $S(r)$  by periodic summation (i.e., superposition):

$$S_V(\mathbf{r}) = \sum_{\mathbf{R}} S(|\mathbf{r} - \mathbf{R}|). \quad (4.18)$$

Making use of the local neutrality condition (2.16) and the property

$$\int_{\mathcal{C}} d^3\mathbf{r} \sum_{\mathbf{R}} f(\mathbf{r} - \mathbf{R}) = \int d^3\mathbf{r} f(\mathbf{r}) \quad (4.19)$$

for an integrable function  $f(\mathbf{r})$ , one readily checks that the expression for  $S_V(\mathbf{r})$  given by Eq. (4.18) satisfies the neutrality constraint

$$\int_{\mathcal{C}} d^3\mathbf{r} S_V(\mathbf{r}) = 0. \quad (4.20)$$

Defining by analogy with Eq. (4.12) the mean fluctuation potential

$$\Psi_V(\mathbf{r}) = (4\pi\epsilon_0)^{-1} \int_{\mathcal{C}} d^3\mathbf{r}' \psi(\mathbf{r} - \mathbf{r}'; \mathcal{C}) S_V(\mathbf{r}'), \quad (4.21)$$

where  $\psi(\mathbf{r}; \mathcal{C})$  is the periodic Coulomb potential (3.10), the Coulomb energy density may be expressed as

$$u_V^{\text{el}} = \frac{1}{2} \lim_{r \rightarrow 0} [\Psi_V(\mathbf{r}) - nq^2/4\pi\epsilon_0 r]. \quad (4.22)$$

The quantity  $u_V^{\text{el}}$  is related to its large- $V$  limit by

$$u_V^{\text{el}} = u^{\text{el}} + \frac{1}{2} \lim_{r \rightarrow 0} [\Psi_V(\mathbf{r}) - \Psi(r)]. \quad (4.23)$$

Substituting Eq. (4.18) into Eq. (4.21), one finds

$$\begin{aligned}
\Psi_V(\mathbf{r}) &= \int_{\mathcal{C}} d^3\mathbf{r}' \psi(\mathbf{r} - \mathbf{r}'; \mathcal{C}) S_V(\mathbf{r}') \\
&= \int d^3\mathbf{r}' \psi(\mathbf{r} - \mathbf{r}'; \mathcal{C}) S(\mathbf{r}') \\
&= \sum_{\mathbf{R}} \Psi(|\mathbf{r} - \mathbf{R}|) - \frac{1}{V} \int d^3\mathbf{r}' \Psi(\mathbf{r}'), \tag{4.24}
\end{aligned}$$

where the last equality may be obtained by expressing  $\psi(\mathbf{r}; \mathcal{C})$  as the  $\kappa \rightarrow 0$  limit of the screened potential  $\psi_\kappa(\mathbf{r}; \mathcal{C})$  defined by Eq. (4.3). Note that Eq. (4.24) is true in general when  $S_V(\mathbf{r})$  and  $S(\mathbf{r})$  are related by Eq. (4.18).

Using the Debye–Hückel expression (4.16) for  $\Psi(\mathbf{r})$  in Eq. (4.24) yields [51]

$$\Psi_V(\mathbf{r}) = \frac{nq^2}{4\pi\epsilon_0} \psi_{k_D}(\mathbf{r}; \mathcal{C}), \tag{4.25}$$

where  $\psi_\kappa(\mathbf{r}; \mathcal{C})$  is the screened Coulomb potential (4.3) of a periodically replicated unit charge in a neutralizing background. Combining Eqs. (4.16), (4.23), and (4.25), one obtains the approximation of Ref. [51] for the system-size dependence of the Coulomb energy:<sup>3</sup>

$$u_V^{\text{el}} = u^{\text{el}} + \frac{nq^2}{8\pi\epsilon_0} \left[ \sum_{\mathbf{R} \neq 0} \frac{\exp(-k_D|\mathbf{R}|)}{|\mathbf{R}|} - \frac{4\pi}{k_D^2 V} \right], \tag{4.26}$$

which expresses the Debye–Hückel limiting law for the finite-size error  $u_V^{\text{el}} - u^{\text{el}}$ . Liang, Xu, and Xing [51] note that relative error in  $u_V^{\text{el}}$  is given at large  $V$  by

$$\frac{|u_V^{\text{el}} - u^{\text{el}}|}{u^{\text{el}}} \simeq \frac{4\pi}{k_D^3 V}. \tag{4.27}$$

Perhaps more striking is the asymptotic behavior of the absolute error,

$$u_V^{\text{el}} \simeq u^{\text{el}} - \frac{1}{2} k_B T / V, \tag{4.28}$$

which, hindsight bias notwithstanding, seems to suggest a universal scaling relation.

<sup>3</sup>Up to a small difference in how the Debye length was defined in Ref. [51].

(Note that the coefficient  $\frac{1}{2}k_B T$  is independent of the details of the model.) It will be shown in the next chapter that the leading-order correction given by Eq. (4.28) holds in general, provided that the system obeys classical statistical mechanics and is in a conducting phase.

In many cases of interest, the total potential energy  $V_N$  includes, in addition to the Coulomb energy  $V_N^{\text{el}}$ , a short-range part  $V_N^{\text{sr}} = V_N - V_N^{\text{el}}$ . For classical systems in three dimensions, a repulsive core interaction between point charges of opposite sign is necessary to prevent collapse [32]. More generally,  $V_N^{\text{sr}}$  may account for attractive (e.g., dispersion) as well as repulsive interactions. At very low densities where the Debye–Hückel theory is valid, short-range contributions to the excess internal energy per unit volume  $u_V^{\text{ex}} = \langle V_N/V \rangle_V$  may be neglected. Then  $u_V^{\text{ex}}$  reduces to the Coulomb energy per unit volume  $u_V^{\text{el}}$ , and the finite-size correction to  $u_V^{\text{el}}$  may be taken as the correction to  $u_V^{\text{ex}}$ .

One may consider also the system-size dependence of the excess pressure

$$p_V^{\text{ex}} = p_V - nk_B T, \quad (4.29)$$

with  $p_V$  the total pressure and  $nk_B T$  the pressure in the ideal-gas reference state. The excess pressure may be expressed as

$$p_{V'}^{\text{ex}} = -\langle \partial V_N / \partial V \rangle_{V'}, \quad (4.30)$$

where  $V_N$  is the total potential energy of the  $N$  particles in the cell  $\mathcal{C}$ . Here infinitesimal volume changes, accompanied by scaling of the particle positions, are understood to be isotropic. The excess pressure (4.30) may be separated into short-range and electrostatic contributions, with the latter given by

$$p_{V'}^{\text{el}} = -\langle \partial V_N^{\text{el}} / \partial V \rangle_{V'} = \frac{1}{3} \langle V_N^{\text{el}} / V \rangle_{V'} \equiv \frac{1}{3} u_{V'}^{\text{el}}. \quad (4.31)$$

The second equality follows from the fact that the Coulomb energy, a homogeneous function of degree  $-1$  in the particle coordinates, may be written as

$$V_N^{\text{el}} = V^{-1/3} \tilde{V}_N^{\text{el}}, \quad (4.32)$$

where the quantity  $\tilde{V}_N^{\text{el}}$  is independent of isotropic volume changes [56]. Clearly

the finite-size correction to  $p_V^{\text{el}}$  is just one third of the correction to the Coulomb energy density—with the latter given in the low-density limit by Eq. (4.26).

### 4.3 CHEMICAL POTENTIAL

Consider now the change in free energy due to the introduction of a fixed point charge  $Q$  into the system. In the low-density limit, this quantity may be identified<sup>4</sup> with the excess chemical potential of an ion of charge  $Q$ .

For convenience, the test charge is assumed to be fixed at the origin. In the periodic system, the charge brings with it its images and canceling background, which together have a charge density of

$$\sum_{\mathbf{R} \neq \mathbf{0}} Q \delta(\mathbf{r} - \mathbf{R}) - Q/V. \quad (4.33)$$

The change  $\phi_V(\mathbf{r}; Q)$  in the average electrostatic potential at  $\mathbf{r}$  upon insertion of the charge is approximated by the solution of the linearized Poisson–Boltzmann equation

$$(\nabla^2 - k_D^2) \phi_V(\mathbf{r}; Q) = -\frac{Q}{\epsilon_0} \left[ \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R}) - 1/V \right], \quad (4.34)$$

which as we we have seen above is given by

$$\phi_V(\mathbf{r}; Q) = \frac{Q}{4\pi\epsilon_0} \psi_{k_D}(\mathbf{r}; \mathcal{C}). \quad (4.35)$$

The reversible introduction of the charge into the system is accompanied by a change in the total free energy per cell given by

$$\Delta F_V = \int_0^Q dQ' \lim_{r \rightarrow 0} [\phi_V(\mathbf{r}; Q') - Q'/4\pi\epsilon_0 r] = \frac{Q^2}{8\pi\epsilon_0} \lim_{r \rightarrow 0} [\psi_{k_D}(\mathbf{r}; \mathcal{C}) - 1/r], \quad (4.36)$$

where the second equality follows from the approximation (4.35). Note that in the bracketed term of Eq. (4.36), the electrostatic potential due to the isolated charge  $Q\delta(\mathbf{r})$  is subtracted out—rather than the potential  $(4\pi\epsilon_0)^{-1}Q\psi(\mathbf{r}; \mathcal{C})$  due to the charge plus its images and background. In this picture, the appearance of the

<sup>4</sup>Up to a term  $Q\langle\varphi(\mathbf{r})\rangle$  that depends on the arbitrary definition of the zero of the electrostatic potential  $\varphi(\mathbf{r})$ .

charge density (4.33) may be viewed as part of the *system's* response, albeit an implicit one demanded by the periodic boundary conditions.<sup>5</sup>

The finite-size correction to  $\Delta F_V$  is given by

$$\Delta F_V = \Delta F + \frac{Q^2}{8\pi\epsilon_0} \lim_{r \rightarrow 0} \left[ \psi_{k_D}(\mathbf{r}; \mathcal{C}) - \frac{\exp(-k_D r)}{r} \right], \quad (4.37)$$

where the term in brackets is identical to the bracketed term in Eq. (4.26). In the case of  $Q^2 = q^2$ , this formula gives an approximation for the correction to the mean excess chemical potential

$$\mu_V^{\text{ex}} = n^{-1} \sum_{\alpha} n_{\alpha} \tilde{\mu}_{\alpha;V}^{\text{ex}}, \quad (4.38)$$

where  $\tilde{\mu}_{\alpha;V}^{\text{ex}}$  is the excess electrochemical potential of species  $\alpha$ . That is, in the low-density limit,

$$\mu_V^{\text{ex}} = \mu^{\text{ex}} + \frac{q^2}{8\pi\epsilon_0} \lim_{r \rightarrow 0} \left[ \psi_{k_D}(\mathbf{r}; \mathcal{C}) - \frac{\exp(-k_D r)}{r} \right]. \quad (4.39)$$

#### 4.4 PRACTICAL NOTE

The approximate correction formulas in this chapter all involve the basic expression

$$\lim_{r \rightarrow 0} \left[ \psi_{\kappa}(\mathbf{r}; \mathcal{C}) - \frac{\exp(-\kappa r)}{r} \right] = \sum_{\mathbf{R} \neq 0} \frac{\exp(-\kappa |\mathbf{R}|)}{|\mathbf{R}|} - \frac{4\pi}{\kappa^2 V}. \quad (4.40)$$

By analogy with Eq. (3.15), one may define [54] a “screened Madelung constant”

$$\xi_{\bar{\kappa}} = V^{1/3} \lim_{r \rightarrow 0} \left[ \psi_{\kappa}(\mathbf{r}; \mathcal{C}) - \frac{\exp(-\kappa r)}{r} \right], \quad (4.41)$$

<sup>5</sup>In the terminology of Figueirido, Del Buono, and Levy [21], the quantity (4.36) is a *total* free energy of charging. That is, it may be obtained by integrating  $\langle \partial V_N / \partial Q \rangle_{Q';V}$ , the mean derivative of the total potential energy per cell with respect to the charging parameter, from  $Q' = 0$  to  $Q' = Q$ . The Madelung energy  $\Delta U_V^{\text{self}} = \xi Q^2 / (8\pi\epsilon_0 V^{1/3})$  due to the “self-interactions” [57] of the charge  $Q$  with its own images and background is included in  $\Delta F_V$ . Thus  $\Delta F_V$  differs from what Hünenberger and coworkers [58, 59] define as the *solvation* contribution to the free energy,

$$\Delta F_V^{\text{solv}} = \Delta F_V - \Delta U_V^{\text{self}},$$

from which the self-interaction term is excluded. It should be noted that the total free energy  $\Delta F_V$  is readily generalized to cases in which the test particle has internal degrees of freedom or in which the volume of the cell may fluctuate (e.g., simulations at constant pressure). Meanwhile, one cannot in general define a path-independent analog of the quantity  $\Delta F_V^{\text{solv}}$ .

where  $\bar{\kappa} = \kappa V^{1/3}$  is a reduced screening parameter. Note that  $\xi \leq \xi_{\bar{\kappa}} \leq 0$ , where  $\xi = \lim_{\bar{\kappa} \rightarrow 0} \xi_{\bar{\kappa}}$  is the usual Madelung constant (3.15). The individual terms on the right hand side of Eq. (4.40) diverge in the limit  $\kappa \rightarrow 0$ , and the sum converges slowly for  $\bar{\kappa} \lesssim 1$ . In this regime,  $\xi_{\bar{\kappa}}$  may be evaluated efficiently using the Ewald sum<sup>6</sup> given by Salin and Caillol [54].

<sup>6</sup>See Eq. (2.19) in Ref. [54]. The formula is specific to a cubic cell, but it may easily be generalized to other geometries. Note that there is a sign error in the exponential of the final term.

# 5

## Asymptotic system-size dependence

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The previous chapter dealt with approximate finite-size corrections, valid for an ionic fluid at low density. Here the focus is on the general case of finite density. The goal is to derive exact expressions for the leading-order finite-size corrections to some thermodynamic quantities of interest. One such correction, to the Coulomb energy density

$$u_V^{\text{el}} = \langle V_N^{\text{el}}/V \rangle_V, \quad (5.1)$$

was hinted at by Eq. (4.28), which suggested the limiting behavior

$$u_V^{\text{el}} \simeq u^{\text{el}} - \frac{1}{2}k_{\text{B}}T/V. \quad (5.2)$$

The reason—not yet mentioned—that the Debye–Hückel approximation might be expected to give an expression for the leading-order correction to  $u_V^{\text{el}}$  that holds in general is because it gets the charge–charge correlations right at the longest wavelengths. More formally, the Debye–Hückel expression (4.11) for the charge correlation function  $S(r)$  satisfies the Stillinger–Lovett sum rule

$$-\frac{1}{6} \int d^3\mathbf{r} r^2 S(r) = \epsilon_0 k_{\text{B}}T. \quad (2.17)$$

Chiesa et al. [26] showed clearly how a second-moment condition on  $S(r)$  may be used to derive the leading-order finite-size correction to the Coulomb energy of a charged system with periodic boundary conditions.<sup>1</sup> Their results were presented in the context of quantum Monte Carlo calculations of the ground-state energy of electronic systems, but the mathematical framework is quite general. More

<sup>1</sup>The basic idea may be traced further back to Fraser et al. [25]. Also relevant is the work of Makov and Payne [20], who considered the electrostatic energy of an isolated charged molecule (e.g., an ion or charged defect in a crystalline solid) in periodic boundary conditions. They showed that the  $1/V$  correction to the energy depends on the second radial moment of the molecular charge distribution.

systematic developments (also in the context of electronic systems) are given by Drummond et al. [27] and Holzmann et al. [28]. The application to classical ionic systems was considered in Ref. [18]. Note that the approach of Ref. [26] did not rely on the assumption that the system was translationally uniform. Here, in line with the scope of the present work, the approach is specialized to the case of uniform fluids. For continuity with the previous chapter, and in contrast to Ref. [26], most of the following relations are given in real space.

### 5.1 ENERGY AND PRESSURE

Recall from Eq. (4.18) that in the Debye–Hückel approximation, the charge–charge correlation function  $S_V(\mathbf{r})$  is related to its infinite-system counterpart by periodic summation. In the general case, the periodic boundary conditions imply only that this relationship holds in an asymptotic sense; that is,

$$S_V(\mathbf{r}) \rightarrow \sum_{\mathbf{R}} S(|\mathbf{r} - \mathbf{R}|) \quad (5.3)$$

in the bulk limit  $V \rightarrow \infty$ . Let

$$\Delta S_V(\mathbf{r}) = S_V(\mathbf{r}) - \sum_{\mathbf{R}} S(|\mathbf{r} - \mathbf{R}|) \quad (5.4)$$

be the difference of  $S_V(\mathbf{r})$  from the periodic summation of  $S(r)$ . Chiesa et al. [26] tacitly assume that to leading order,  $\Delta S_V(\mathbf{r})$  does not contribute to the finite-size correction to  $u_V^{\text{el}}$ . We shall return to the question of the validity of this assumption below. For now, following Ref. [26], it is assumed that the leading-order correction to  $u_V^{\text{el}}$  may be obtained by passing to the limit (5.3) *before* taking the thermodynamic limit. Then we have from Eq. (4.24) the relation

$$\Psi_V(\mathbf{r}) \simeq \sum_{\mathbf{R}} \Psi(|\mathbf{r} - \mathbf{R}|) - \frac{1}{V} \int d^3\mathbf{r}' \Psi(\mathbf{r}'). \quad (5.5)$$

for the  $V$  dependence of the mean fluctuation potential  $\Psi_V(\mathbf{r})$ . The correction to the Coulomb energy density is given by

$$\begin{aligned} u_V^{\text{el}} &= u^{\text{el}} + \frac{1}{2} \lim_{r \rightarrow 0} [\Psi_V(\mathbf{r}) - \Psi(r)] \\ &\simeq u^{\text{el}} - \frac{1}{2V} \int d^3\mathbf{r} \Psi(r) + \frac{1}{2} \sum_{R \neq 0} \Psi(|\mathbf{R}|). \end{aligned} \quad (5.6)$$

Noting that  $\Psi(r)$  has the Fourier transform [see Eq. (4.12)]

$$\hat{\Psi}(k) = \hat{S}(k)/\varepsilon_0 k^2, \quad (5.7)$$

we see from Eq. (2.13) that the integral in Eq. (5.6) is<sup>2</sup>

$$\int d^3\mathbf{r} \Psi(r) = \lim_{k \rightarrow 0} \hat{\Psi}(k) = k_B T. \quad (5.8)$$

Outhwaite [61] is responsible for showing that the Stillinger–Lovett condition is equivalent to a normalization condition on  $\Psi(r)$ . (Only the primitive-model electrolyte was considered in Ref. [61]. Carnie and Chan [55] generalized Outhwaite’s result to more complex models of ionic solutions, as well as to nonuniform systems.) In a classical charged fluid,  $\Psi(r)$  decays sufficiently rapidly at large  $r$  that the lattice sum in Eq. (5.6) is absolutely convergent, leaving<sup>3</sup>

$$u_V^{\text{el}} = u^{\text{el}} - \frac{1}{2} k_B T / V + o(1/V), \quad V \rightarrow \infty. \quad (5.9)$$

<sup>2</sup>For the quantum one-component plasma (uniform electron gas) at finite temperature, the long-wavelength limit of  $\hat{S}(k)$  is given by [32, 60]

$$\lim_{k \rightarrow 0} \frac{\hat{S}(k)}{\varepsilon_0 k^2} = \frac{\hbar \omega_p}{2} \coth\left(\frac{\beta \hbar \omega_p}{2}\right),$$

where  $\omega_p = (nq^2/m\varepsilon_0)^{1/2}$  is the plasma frequency, with  $q$  and  $m$  the charge and mass, respectively, of a particle. In the classical limit  $\beta \hbar \omega_p \ll 1$ , this relation reduces to the Stillinger–Lovett condition. In the zero-temperature limit  $\beta \hbar \omega_p \gg 1$ ,

$$\lim_{k \rightarrow 0} [\hat{S}(k)/\varepsilon_0 k^2] = \hat{\Psi}(0) = \frac{1}{2} \hbar \omega_p,$$

and using Eq. (5.6) one recovers the result of Chiesa et al. [26]:  $u_V^{\text{el}} \simeq u^{\text{el}} - \frac{1}{4} \hbar \omega_p / V$ .

<sup>3</sup>To revisit the comment made at the end of Chapter 3: If the self-term (3.16) were not included in the Coulomb energy, the correction  $u^{\text{el}} - u_V^{\text{el}}$  would be of order  $1/V^{1/3}$  rather than  $1/V$ .

If one defines an electrostatic contribution  $p_V^{\text{el}}$  to the pressure by Eq. (4.31), then from the comments at the end of Sec. 4.2 it is clear that the finite-size correction to  $p_V^{\text{el}}$  is just one third of the correction to  $u_V^{\text{el}}$ ; that is,  $p_V^{\text{el}} \simeq p^{\text{el}} - \frac{1}{6}k_{\text{B}}T/V$ .

The result (5.9), which agrees with Eq. (5.2), is contingent on the error  $\Delta S_V(\mathbf{r})$  in the charge–charge correlation function [see Eq. (5.4)] decaying strictly faster than  $1/V$  in the large- $V$  limit. To establish this behavior in the canonical ensemble, where the finite-size correction to the *density–density* correlation function is known to be of order  $1/V$  [62, 63], one might use the results of Gruber, Lugrin, and Martin [64] and Martin and Yalcin [65]. Note that the  $1/V$  correction to the density–density correlation function of a closed system is related to the extensivity of particle-number fluctuations—i.e., the mean-square fluctuation  $\langle N_\Lambda^2 \rangle - \langle N_\Lambda \rangle^2$  of the number of particles  $N_\Lambda$  contained in a region  $\Lambda$  of an infinite system is proportional to the volume  $V = |\Lambda|$  in the limit  $V \rightarrow \infty$ .<sup>4</sup> In contrast, the charge fluctuations are not extensive [64]; the fluctuation  $\langle Q_\Lambda^2 \rangle - \langle Q_\Lambda \rangle^2$  of the total charge  $Q_\Lambda$  in a region  $\Lambda$  scales instead as the surface area  $|\partial\Lambda| \propto V^{2/3}$  [65]. As a result of the nonextensivity of charge fluctuations, the finite-size correction to the *charge–charge* correlation function of a closed system may be expected to decay faster than  $1/V$ . I have started to pursue this line of thinking for the simple case of the one-component plasma (where the number fluctuations are proportional to the charge fluctuations). At this point, however, I cannot offer proof that  $\Delta S_V(\mathbf{r}) = o(1/V)$  as  $V \rightarrow \infty$ .

## 5.2 CHEMICAL POTENTIAL OF A CHARGED SOLUTE

This section focuses on the  $V$  dependence of the free-energy change accompanying the insertion of a charged solute particle into the system (i.e., the excess chemical potential of an ion). Intuitively, one expects the size dependence of this quantity to be connected, in large part, to the long-wavelength components of the electrostatic response of the system to the electric field of the solute. Yet isolating this contribution is complicated by the presence, in general, of short-range interactions between the solute and its environment. To focus on this part, one may imagine the solvation process described by Remsing and Weeks [66], comprising three steps: (1) introducing into the system a slowly varying (e.g., Gaussian) charge density of net charge equal to that of the solute; (2) switching on the short-range interactions

<sup>4</sup>Except in the special case of the one-component plasma [64].

of the solute particle; (3) collecting the charge from step 1 into the cavity carved out in step 2. Only the first step is formally addressed in what follows.<sup>5</sup>

Let  $\rho^{\text{ext}}(\mathbf{r})$  be a localized charge density of net charge  $Q = \int d^3\mathbf{r} \rho^{\text{ext}}(\mathbf{r})$ . In the periodic system, the charge distribution  $\rho^{\text{ext}}(\mathbf{r})$  necessarily brings along its images and background; the external charge density is thus

$$\rho_V^{\text{ext}}(\mathbf{r}) = \sum_{\mathbf{R}} \rho^{\text{ext}}(\mathbf{r} - \mathbf{R}) - Q/V. \quad (5.10)$$

It is convenient to introduce a charging parameter  $\lambda \in [0, 1]$  that linearly scales the external charge. The charge response of the system to the field produced by  $\lambda\rho_V^{\text{ext}}(\mathbf{r})$  is characterized by the mean induced charge density

$$\rho^{\text{ind}}(\mathbf{r}; \lambda) = \langle \rho(\mathbf{r}) \rangle_{\lambda; V}, \quad (5.11)$$

where  $\rho(\mathbf{r})$  is the microscopic charge density of the system, and  $\langle \cdot \cdot \cdot \rangle_{\lambda; V}$  denotes a thermal average over configurations of the periodic system in state  $\lambda$ . The electrostatic potential due to the total charge density

$$\rho_V^{\text{tot}}(\mathbf{r}; \lambda) = \rho_V^{\text{ind}}(\mathbf{r}; \lambda) + \lambda\rho_V^{\text{ext}}(\mathbf{r}) \quad (5.12)$$

is given by

$$\phi_V(\mathbf{r}; \lambda) = (4\pi\epsilon_0)^{-1} \int_{\mathcal{C}} d^3\mathbf{r}' \psi(\mathbf{r} - \mathbf{r}'; \mathcal{C}) \rho_V^{\text{tot}}(\mathbf{r}'; \lambda), \quad (5.13)$$

where  $\psi(\mathbf{r}; \mathcal{C})$  is the periodic Coulomb potential (3.10).

The free-energy change (per cell) due to the introduction of the external charge may be expressed as [cf. Eq. (4.36)]

$$\Delta F_V = \int_0^1 d\lambda \int d^3\mathbf{r} \rho^{\text{ext}}(\mathbf{r}; \lambda) [\phi_V(\mathbf{r}; \lambda) - \lambda\phi^{\text{ext}}(\mathbf{r})], \quad (5.14)$$

<sup>5</sup>One might use ideas similar to those of Siepmann, McDonald, and Frenkel [67] to derive a finite-size correction to the reversible work of step 2 (i.e., formation of the solute cavity). Note that in contrast to Ref. [67], the system considered here is not initially uniform—due to the presence of the external charge density introduced in step 1. Still one may conjecture that for a closed system, the correction to the cavity-formation work is of order  $1/V$ .

where

$$\phi^{\text{ext}}(\mathbf{r}) = \int d^3\mathbf{r}' \frac{\rho^{\text{ext}}(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|} \quad (5.15)$$

is the electrostatic potential due to the isolated charge distribution  $\rho^{\text{ext}}(\mathbf{r})$ . The charging free energy  $\Delta F_V$  is formally related to its limit  $\Delta F$  by

$$\Delta F_V = \Delta F + \int_0^1 d\lambda \int d^3\mathbf{r} \rho^{\text{ext}}(\mathbf{r}) [\phi_V(\mathbf{r}; \lambda) - \phi(\mathbf{r}; \lambda)], \quad (5.16)$$

where  $\phi(\mathbf{r}; \lambda)$  is the total electrostatic potential in the thermodynamic limit.

Similar to the assumption in the last section regarding the large- $V$  behavior of the charge correlation function  $S_V(\mathbf{r})$ , it is assumed here that the inhomogeneous charge density  $\rho_V^{\text{tot}}(\mathbf{r}; \lambda)$  is related to its bulk-system counterpart  $\rho^{\text{tot}}(\mathbf{r}; \lambda)$  by

$$\rho_V^{\text{tot}}(\mathbf{r}; \lambda) = \sum_{\mathbf{R}} \rho^{\text{tot}}(\mathbf{r}; \lambda) + o(1/V), \quad V \rightarrow \infty. \quad (5.17)$$

If the system's response is linear, this assumption reduces to the one previously employed for  $S_V(\mathbf{r})$ . Using Eq. (5.17) and following the same steps as in Eq. (4.24), the total electrostatic potential in the periodic system may be expressed as

$$\begin{aligned} \phi_V(\mathbf{r}; \lambda) &= (4\pi\epsilon_0)^{-1} \int_{\mathcal{C}} d^3\mathbf{r}' \psi(\mathbf{r} - \mathbf{r}'; \mathcal{C}) \rho_V^{\text{tot}}(\mathbf{r}'; \lambda) \\ &\simeq (4\pi\epsilon_0)^{-1} \int d^3\mathbf{r}' \psi(\mathbf{r} - \mathbf{r}'; \mathcal{C}) \rho^{\text{tot}}(\mathbf{r}'; \lambda) \\ &= \sum_{\mathbf{R}} \phi(\mathbf{r} - \mathbf{R}; \lambda) - \frac{1}{V} \int d^3\mathbf{r}' \phi(\mathbf{r}'; \lambda). \end{aligned} \quad (5.18)$$

Substitution into Eq. (5.16) yields

$$\Delta F_V \simeq \Delta F - \frac{Q}{V} \int d^3\mathbf{r} \bar{\phi}(\mathbf{r}) + \int d^3\mathbf{r} \rho^{\text{ext}}(\mathbf{r}) \sum_{\mathbf{R} \neq 0} \bar{\phi}(\mathbf{r} - \mathbf{R}), \quad (5.19)$$

where

$$\bar{\phi}(\mathbf{r}) = \int_0^1 d\lambda \phi(\mathbf{r}; \lambda). \quad (5.20)$$

Then as long as  $\bar{\phi}(\mathbf{r})$  is integrable [and Eq. (5.17) holds], the leading correction, of

order  $1/V$ , is given by

$$\Delta F_V \simeq \Delta F - \frac{Q}{V} \int d^3 \mathbf{r} \bar{\phi}(\mathbf{r}). \quad (5.21)$$

In general  $\bar{\phi}(\mathbf{r})$ , and thus the coefficient of the  $1/V$  correction, will depend on the details of the interaction between the system and the external charge. In the linear-response regime where Eq. (2.4) holds, however, it is separable into terms involving only their independent properties. Here the  $\lambda$ -dependent quantities  $f(\mathbf{r}; \lambda)$  may all be written as

$$f(\mathbf{r}; \lambda) = \lambda f(\mathbf{r}; 1) \equiv \lambda f(\mathbf{r}), \quad (5.22)$$

and we see from its definition (5.20) that

$$\bar{\phi}(\mathbf{r}) = \frac{1}{2} \phi(\mathbf{r}). \quad (5.23)$$

Going to Fourier space, Eq. (2.4) becomes

$$\hat{\rho}^{\text{ind}}(\mathbf{k}) = \hat{\chi}(k) \hat{\rho}^{\text{ext}}(\mathbf{k}). \quad (5.24)$$

Using this and  $\hat{\phi}^{\text{ext}}(\mathbf{k}) = \hat{\rho}^{\text{ext}}(\mathbf{k})/\varepsilon_0 k^2$ , we have

$$\begin{aligned} \hat{\phi}(\mathbf{k}) &= \frac{1}{\varepsilon_0 k^2} [\hat{\rho}^{\text{ind}}(\mathbf{k}) + \hat{\rho}^{\text{ext}}(\mathbf{k})] \\ &= \frac{1}{\varepsilon_0 k^2} \left[ 1 + \frac{\hat{\chi}(k)}{\varepsilon_0 k^2} \right] \hat{\rho}^{\text{ext}}(\mathbf{k}). \end{aligned} \quad (5.25)$$

The integral in Eq. (5.21) is then [noting that  $\hat{\rho}^{\text{ext}}(\mathbf{0}) = Q$ ]

$$\int d^3 \mathbf{r} \bar{\phi}(\mathbf{r}) = \frac{1}{2} \hat{\phi}(\mathbf{0}) = \frac{1}{2} Q \lim_{k \rightarrow 0} \left\{ \frac{1}{\varepsilon_0 k^2} \left[ 1 + \frac{\hat{\chi}(k)}{\varepsilon_0 k^2} \right] \right\}. \quad (5.26)$$

Since  $\chi(r)$  is both integrable and radial, its transform has a small- $k$  expansion

$$\hat{\chi}(k) \simeq \chi^{(0)} + \chi^{(2)} k^2 + \chi^{(4)} k^4 + O(k^6), \quad k \rightarrow 0, \quad (5.27)$$

with moments defined for  $n = 0, 2, \dots$  by

$$\chi^{(n)} = \frac{(-1)^{n/2}}{(n+1)!} \int d^3 \mathbf{r} r^n \chi(r). \quad (5.28)$$

The moments of  $\chi(r)$  and the charge–charge correlation function  $S(r)$  are simply related through Eq. (2.6) by  $\chi^{(n)} = -S^{(n)}/k_B T$ . Observing that the latter satisfy the neutrality constraint  $S^{(0)} = 0$  and the Stillinger–Lovett condition  $S^{(2)} = \varepsilon_0 k_B T$  [Eqs. (2.16) and (2.17)], one sees that the limit in Eq. (5.26) is

$$\lim_{k \rightarrow 0} \left\{ \frac{1}{\varepsilon_0 k^2} \left[ 1 + \frac{\hat{\chi}(k)}{\varepsilon_0 k^2} \right] \right\} = \varepsilon_0^{-2} \chi^{(4)}. \quad (5.29)$$

Substituting this expression back into Eqs. (5.26) and (5.21) gives

$$\Delta F_V \simeq \Delta F - \frac{1}{2} Q^2 \varepsilon_0^{-2} \chi^{(4)} / V. \quad (5.30)$$

The leading-order correction to  $\Delta F_V$  in the case of linear response is thus charge-symmetric (independent of the sign of  $Q$ ) and depends on the fourth moment of the charge response function.

Qualitatively, steps 2 and 3 of the solvation process discussed at the beginning of this section (i.e., formation of the solute cavity and shrinking of the charge into the cavity, respectively) involve a shorter-wavelength response of the system than does step 1, the introduction of the slowly varying charge density  $\rho^{\text{ext}}(\mathbf{r})$  (which was explicitly considered here). Thus relation (5.21) suggests that the overall finite-size correction to the excess chemical potential of an ion in the periodic system is of order  $1/V$ . From a practical standpoint, it may serve as a guide in the extrapolation of simulation results for ionic chemical potentials to the thermodynamic limit.

Meanwhile, the linear-response relation (5.30) may provide a useful estimate of the finite-size correction to the chemical potential of an ion when paired with approximate theories (e.g., the generalized Debye–Hückel theory [68] or the mean spherical approximation) that give a closed-form expression for the fourth moment  $\chi^{(4)}$  of the charge response function. Note that in the linearized Debye–Hückel theory,  $\chi^{(4)} = \varepsilon_0 / k_D^2$ , and Eq. (5.30) becomes

$$\Delta F_V \simeq \Delta F - \frac{1}{2V} \frac{Q^2}{\varepsilon_0 k_D^2}, \quad (5.31)$$

in agreement with the  $V \rightarrow \infty$  limit of Eq. (4.37).

### 5.3 ALTERNATE DERIVATION OF THE ENERGY CORRECTION

In this section, a different and perhaps somewhat illustrative method of deriving the result (5.9) is given. (This was the first way I approached the problem, before I became aware of Ref. [26].)

It is assumed that the unit cell is cubic, in which case the periodic Coulomb potential may be expressed as [42]

$$\psi(\mathbf{r}; \mathcal{C}) = \frac{\xi}{L} + \frac{1}{r} + \frac{2\pi r^2}{3V} + O(r^4/L^5), \quad \mathbf{r} \in \mathcal{C}_0, \quad (5.32)$$

where  $L = V^{1/3}$ , and  $\mathcal{C}_0$  is the cell centered at the origin. The  $r^2$  term in Eq. (5.32) is due to the neutralizing background in the source term of the Poisson equation (3.6) satisfied by  $\psi(\mathbf{r}; \mathcal{C})$  [42, 69]. Makov and Payne [20] showed how this quadratic term leads to a  $1/V$  correction to the electrostatic energy of a isolated charged molecule<sup>6</sup> in periodic boundary conditions—the correction depending on the second radial moment of the molecular charge distribution. Fraser et al. [25], who discussed the implication of the  $r^2$  term in  $1/V$  corrections to the Coulomb energy per particle in quantum Monte Carlo calculations, anticipated its similar role in classical Coulomb systems.<sup>7</sup> Here their conjecture is made more concrete.

The Coulomb energy density  $u_V^{\text{el}}$  of the periodic system may be expressed as

$$(4\pi\epsilon_0)u_V^{\text{el}} = \frac{1}{2} \int_{\mathcal{C}_0} d^3\mathbf{r} \psi(\mathbf{r}; \mathcal{C}) [S_V(\mathbf{r}) - n_0 q_0^2 \delta(\mathbf{r})] + \frac{1}{2} n_0 q_0^2 \xi / L, \quad (5.33)$$

where for convenience the integration region has been chosen as  $\mathcal{C}_0$ , and the second term in brackets along with the last term avoids divergence due to any species  $\lambda$  of point charges that may be present in the system—with  $n_0 q_0^2$  defined by

$$n_0 q_0^2 = \sum_{\lambda} n_{\lambda} q_{\lambda}^2 \quad (5.34)$$

and  $\xi$  (the Madelung constant) defined by Eq. (3.15). Using the expansion (5.32) of

<sup>6</sup>Here “charged molecule” encompasses both ions and charged defects in crystalline solids.

<sup>7</sup>From Ref. [25]: “Although our explanations have been cast in terms of QMC [quantum Monte Carlo] calculations, it is worth noting that our results are of wider relevance. ... we believe that classical simulations of Coulomb liquids should show  $1/N$  finite-size errors due to correlations in the ionic positions ...”

$\psi(\mathbf{r}; \mathcal{C})$ , Eq. (5.33) may be written as

$$(4\pi\epsilon_0)u_V^{\text{el}} = \left\{ \frac{\xi}{2L} \int_{\mathcal{C}_0} d^3\mathbf{r} [S_V(\mathbf{r}) - n_0q_0^2\delta(\mathbf{r})] + \frac{\xi}{2L}n_0q_0^2 \right\} \\ + \frac{1}{2} \int_{\mathcal{C}_0} d^3\mathbf{r} r^{-1} [S_V(\mathbf{r}) - n_0q_0^2\delta(\mathbf{r})] \\ + \frac{\pi}{3V} \int_{\mathcal{C}_0} d^3\mathbf{r} r^2 S_V(\mathbf{r}) + \dots, \quad (5.35)$$

where  $\int d^3\mathbf{r} r^2 \delta(\mathbf{r}) = 0$  was used to simplify the term on the last line, and the term in braces is identically zero due to the neutrality condition (4.20). If the volume  $V$  is taken to be macroscopic (but still finite), then it is reasonable to assume that the charge structure has converged everywhere in the cell. In that case,  $S_V(\mathbf{r})$  may be replaced with its limit  $S(r)$  in Eq. (5.35). In the limit  $\mathcal{C}_0 \rightarrow \mathbb{R}^3$ , the term on the second line of Eq. (5.35) then reduces to the bulk energy density

$$(4\pi\epsilon_0)u^{\text{el}} = \frac{1}{2} \int d^3\mathbf{r} r^{-1} [S(r) - n_0q_0^2\delta(\mathbf{r})]. \quad (5.36)$$

Using the second-moment condition (2.17), the term on the last line reduces in the same limit to

$$\frac{\pi}{3V} \int d^3\mathbf{r} r^2 S(r) = -(4\pi\epsilon_0) \frac{k_B T}{2V}. \quad (5.37)$$

The remaining terms are  $O(V^{-5/3})$  provided that  $S(r)$  decays sufficiently rapidly as  $r \rightarrow \infty$ . Combining these results, we have

$$u_V^{\text{el}} \simeq u^{\text{el}} - \frac{1}{2}k_B T/V + O(V^{-5/3}), \quad V \rightarrow \infty, \quad (5.38)$$

in agreement with Eq. (5.2). It may be possible to prove that the next-to-leading order term in Eq. (5.38) decays faster than  $V^{-5/3}$  by using the multipolar sum rules [32].<sup>8</sup> With these additional sum rules, the approach outlined in this section might also be extended to non-cubic cells.<sup>9</sup>

<sup>8</sup>Note that the  $O(r^4/L^5)$  term in Eq. (5.32) satisfies Laplace's equation and may be expanded in spherical harmonics. See for example Ref. [42].

<sup>9</sup>In general, the  $O(r^2/V)$  term in the expansion (5.32) depends on the lattice geometry [27, 42].

# 6

## Comparison with simulations

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### 6.1 ONE-COMPONENT PLASMA

It is illustrative to look back and interpret some results from the study of Brush, Sahlin, and Teller [1], who considered the classical one-component plasma (OCP). This model consists of identical point ions of charge  $q$  immersed in a uniform neutralizing background of fixed charge density  $-nq$ . The potential energy of  $N = nV$  ions in a cell of volume  $V$  with periodic boundary conditions is given by Eq. (3.14):

$$V_N = \frac{q^2}{8\pi\epsilon_0} \sum_{i=1}^N \sum_{j \neq i}^N \psi(\mathbf{r}_i - \mathbf{r}_j; \mathcal{C}) + \frac{Nq^2}{8\pi\epsilon_0} \lim_{r \rightarrow 0} [\psi(\mathbf{r}; \mathcal{C}) - 1/r], \quad (6.1)$$

where  $\psi(\mathbf{r}; \mathcal{C})$  is the periodic Coulomb potential (3.10). Note that since there are no short-range interactions, the excess internal energy  $\langle V_N \rangle$  and the mean Coulomb energy  $\langle V_N^{\text{el}} \rangle$  may be spoken of interchangeably. Moreover, the absence of a second length scale associated with short-range forces implies that the excess thermodynamic properties of the OCP are characterized by a single intensive parameter, conventionally defined by

$$\Gamma = \frac{\beta e^2}{4\pi\epsilon_0 a}, \quad (6.2)$$

where  $a = (3/4\pi n)^{1/3}$  is the Wigner–Seitz radius.

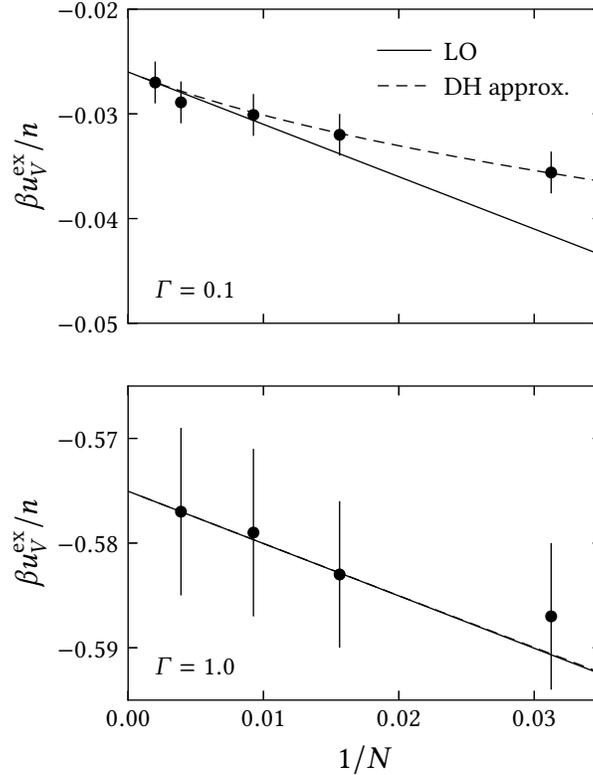
Figure 6.1 shows the excess internal energy per particle

$$u_V^{\text{ex}}/n = \langle V_N/N \rangle_V \quad (6.3)$$

of systems of varying  $N$  at coupling  $\Gamma = 0.1$  and  $1.0$ , as calculated in Ref. [1]. Shown for comparison is the leading-order correction given by

$$u_V^{\text{ex}}/n \simeq u^{\text{ex}}/n - \frac{1}{2}k_B T/N, \quad (6.4)$$

along with the system-size dependence predicted by the Debye–Hückel approximation (4.26). As  $1/N \rightarrow 0$ , the data converge to the exact limiting slope given by Eq. (6.4). Meanwhile, the Debye–Hückel approximation provides an essentially quantitative description of the  $N$  dependence at the low coupling value  $\Gamma = 0.1$ .



**Figure 6.1.** Excess internal energy per particle  $\beta u_V^{\text{ex}}/n$  of the oCP as a function of  $1/N$  at  $\Gamma = 0.1$  and  $1.0$  (upper and lower panels, respectively). Symbols are the Monte Carlo results of Brush, Sahlin, and Teller [1]. The dashed curve is the Debye–Hückel approximation (4.26) for the system-size dependence, and the solid line is the leading-order correction given by Eq. (5.9). In fitting the curves, the leading-order correction  $\beta u^{\text{ex}}/n \approx \beta u_V^{\text{ex}}/n + (2N)^{-1}$  is assumed to hold exactly for the largest simulated system (leftmost data point).

## 6.2 SYMMETRIC PRIMITIVE-MODEL ELECTROLYTE

The model considered in this section, which Remsing [70, 71] termed the symmetric primitive-model (SPM) electrolyte,<sup>1</sup> is an equimolar mixture of ions of species +

<sup>1</sup>The acronym SPM risks some confusion, as its association with the *solvent* primitive model [72] is fairly well-established.

and  $-(N_+ = N_- = N/2)$  interacting via pair potentials  $v_{\alpha\gamma}(r)$  of the form

$$\beta v_{+\pm}(r) = \beta v_{-\mp}(r) = \beta v^{\text{sr}}(r) \pm l_{\text{B}}/r. \quad (6.5)$$

Here  $l_{\text{B}} = \beta e^2/4\pi\epsilon_0\epsilon_{\text{r}}$  is the Bjerrum length (with  $\epsilon_{\text{r}}$  the relative permittivity), and

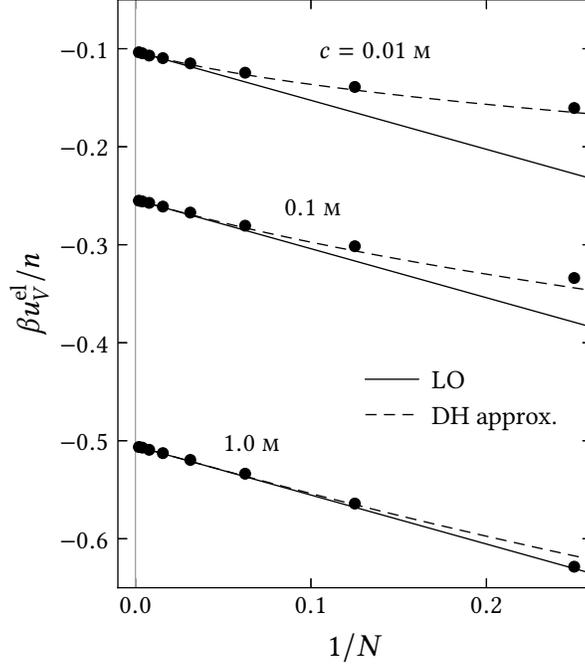
$$\beta v^{\text{sr}}(r) = \begin{cases} 4[(\sigma/r)^{12} - (\sigma/r)^6] + 1 & \text{if } r < 2^{1/6}\sigma \\ 0 & \text{if } r \geq 2^{1/6}\sigma \end{cases} \quad (6.6)$$

is a repulsive Weeks–Chandler–Andersen [73] potential—derived from a Lennard–Jones potential with diameter  $\sigma$  and well depth  $\epsilon = k_{\text{B}}T$ . The SPM is of course just a restricted primitive model (RPM) with the hard-core interactions replaced by a steep but continuous potential, making the SPM more amenable to molecular dynamics simulations.

To render the model somewhat representative of a 1:1 aqueous electrolyte solution at ambient conditions, the relative permittivity was chosen to be  $\epsilon_{\text{r}} = 78.5$ . Note that in the language of earlier chapters, the ionic charges are given by  $q_+ = -q_- = \epsilon_{\text{r}}^{-1/2}e$ . The Lennard–Jones diameter was  $\sigma = 0.5$  nm. Simulations at  $T = 298$  K were performed in the canonical ( $NVT$ ) ensemble; details of the simulation methods are given in Sec. 6.3. Cubic cells containing  $N = 2^\nu$  ( $\nu = 2, 3, \dots, 9$ ) particles were considered.<sup>2</sup> The salt concentration  $c = n/(2N_{\text{A}})$ , with  $n = N/V$  the total ion density and  $N_{\text{A}}$  the Avogadro constant, took the values 0.01, 0.1, and 1.0 M (1 M = 1 mol dm<sup>-3</sup>).

Simulation results for the system-size dependence of the Coulomb energy per particle are shown in Fig. 6.2. Unsurprisingly, the data follow the Debye–Hückel approximation (4.26) closely at low concentration ( $c = 0.01$  M). At higher concentrations (0.1 and 1.0 M), this approximation still provides a reasonable estimate of the size dependence for all but the smallest system sizes. Note that for  $c = 1.0$  M, the agreement should not be attributed to the quantitative reliability of the Debye–Hückel theory, but rather to the consistency of the approximation (4.26) with the exact leading-order correction  $u^{\text{el}} - u_{\text{V}}^{\text{el}} \simeq \frac{1}{2}k_{\text{B}}T/V$ .

<sup>2</sup>The motivation for studying such small values of  $N$  is that systems of  $\lesssim 10$  ions per cell are not at all uncommon in simulations of explicit-solvent models of electrolyte solutions, where feasible system sizes are typically limited by the number of solvent molecules.



**Figure 6.2.** Coulomb energy per particle  $\beta u_V^{el}/n$  of the SPM (with  $\sigma = 0.5$  nm and  $\epsilon_r = 78.5$ ) as a function of  $1/N$  at temperature  $T = 298$  K and various salt concentrations  $c = n/(2N_A)$ . Note that  $1 \text{ M} = 1 \text{ mol dm}^{-3}$ . Symbols are simulation results, the dashed line is the Debye-Hückel approximation (4.26), and the solid line shows the leading-order correction  $\beta u_V^{el}/n \approx \beta u_V^{el}/n - (2N)^{-1}$ . Curves are fit by assuming that the leading-order correction holds exactly for  $N = 512$ . Statistical uncertainties are smaller than the symbol size.

### 6.3 SIMULATION DETAILS

Langevin dynamics simulations of the SPM were performed using the LAMMPS software package [74]. The mass  $m$  of the particles was chosen so that  $\tau \equiv \sigma(\beta m)^{1/2} = 1.5$  ps. Simulations employed the Grønbech-Jensen-Farago [75] time discretization of the Langevin model, a damping parameter (inverse friction coefficient) of  $\gamma^{-1} = 2\tau/3$ , and a time step of  $\tau/300$ . Standard Ewald summation was used to compute the Coulomb energy for systems of  $N \leq 128$  particles per cell; for  $N = 256$  and  $512$ , a heuristic scheme was used to determine on-the-fly whether to use the conventional Ewald method or the particle-particle particle-mesh [76] method. In all cases, the long-range solver parameters were adjusted to maintain an estimated relative root-mean-square error in per-atom forces of  $\delta f/f_0 \approx 10^{-9}$ , where  $\delta f$  is the absolute error and  $f_0 = e^2/4\pi\epsilon_0 r_0^2$  is the reference force (with  $r_0 = 0.1$  nm).

Simulations were run for  $2 \times 10^7$  time steps. The first  $10^6$  steps of each simulation discarded from the analysis. Uncorrelated samples  $V_{N,i}^{\text{el}}$  ( $i = 1, \dots, M$ ) of the Coulomb energy were extracted from the simulation output using the ‘timeseries’ module of the pymbar software package [77, 78], which implements the autocorrelation analysis methods described in Refs. [78, 79]. The reported uncertainty in the average energy

$$\langle V_N^{\text{el}} \rangle_V \approx \frac{1}{M} \sum_{i=1}^M V_{N,i}^{\text{el}} \quad (6.7)$$

is the standard error of the mean.

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