Understanding the thermodynamic and correlation properties of ionic fluids has challenged both theory and experiment \[1, 2\]. Typical electrolytes exhibit phase separation that is analogous to the gas-liquid transition in simple fluids, albeit at rather low temperatures when appropriately normalized. However, the long range of the Coulomb interactions has hampered understanding especially near criticality \[2\]. One crucial aspect is Debye-Hückel screening. For a \(d\)-dimensional classical fluid system with short-range ion-ion potentials beyond the Coulomb coupling \(z_\sigma z_\sigma q^2/r^{d-2}\) (where \(z_\sigma\) is the valence of ions of species \(\sigma\) and mole fraction \(x_\sigma\) while \(q\) is an elementary charge), the charge-charge correlation function, \(G_{ZZ}(r; T, \rho)\), decays as \(\exp[-|r|/\xi_{Z,Z}(T, \rho)]\) (see, e.g., \[2, 3\]): the asymptotic screening length, \(\xi_{Z,Z}(T, \rho)\), approaches the Debye length \(\xi_D = (k_BT/4\pi\epsilon_0^2\rho)^{1/2}\) when the overall ion density \(\rho\) approaches zero (with \(\epsilon_0 = \epsilon_c + \epsilon_\xi\)).

By contrast, at a critical point of fluid phase separation, the density-density (or composition) correlation length, \(\xi_{N,\infty}(T, \rho)\), diverges, as do all the moments of \(G_{NN}(r; T, \rho)\). What then happens to charge screening near criticality? This question was first posed over a decade ago \[4\] and has been addressed recently via the exact solution of \((d > 2)\)-dimensional ionic spherical models \[5, 6\]. As anticipated \[4(b)\], the issue of \(\pm\) ion symmetry proves central. However, spherical models for fluids display several artificial features (e.g., infinite compressibilities on the phase boundary below \(T_c\); parabolic coexistence curves, \(\beta \equiv \frac{1}{d}; \text{ etc.}\)). Accordingly, understanding screening near criticality for more realistic models remains a significant task.

To that end we report here on a Monte Carlo study of the restricted primitive model (RPM), namely, hard spheres of diameter \(a\) carrying charges \(q_{\pm} = \pm q\) (so that \(z_+ = -z_- = 1, x_+ = x_- = \frac{1}{2}\)). Grand canonical simulations have been used and, to accelerate the computations, a finely discretized (\(\zeta = 5\) level) lattice version of the RPM has been adopted \[7\]. For this system the critical behavior is well established as of Ising-type with \(T_c = k_BT_c/a/q^2 \approx 0.05069\) and \(\rho_c^* \equiv \rho_c/a^3 \approx 0.079\). Furthermore, it has been demonstrated that for \(\zeta \gtrsim 3\) the fine-lattice discretization does not qualitatively affect thermodynamic or finite-size properties \[7\].

Ideally one would like to calculate \(\xi_{N,\infty}(T, \rho)\) and \(\xi_{Z,Z}(T, \rho)\) near criticality; but even in nonionic model fluids, obtaining \(\xi_{N,\infty}\) via simulations is hardly feasible. Nevertheless, the low-order moments \(M_{N,k}(T, \rho)\) are seen to fail badly when \(\zeta \approx 3\), \(k \gg 1\); \(\xi_{N,k} \equiv (M_{N,k}/M_{N,0})^{1/k}\) for \(k > 0\) diverge like \(\xi_{N,\infty}\). However, for charges the Stillinger-Lovett sum rules \[2, 3\] dictate \(M_{Z,0} = 0\) so that \(G_{ZZ}(r)\) is not of uniform sign while the second moment satisfies \(M_{Z,2} = 2\tilde{z}_2^2q^2\rho\xi_B^2\) which is fully analytic through \((T_c, \rho_c)\). On the other hand, the first moment of \(G_{ZZ}(r)\) is known \[8\] to be intimately related to charge screening via the so-called “area law” of charge fluctuations.

To explain this, consider a regular subdomain \(\Lambda\) with surface area \(A_\Lambda\) and volume \(|\Lambda|\), embedded in a larger domain, specifically say, the cubical \(L^d\) simulation box. If \(Q_1\) is the total fluctuating charge in \(\Lambda\), electroneutrality implies \((Q_1^2) = 0\); but the mean square fluctuation, \((Q_1^2)\), will grow when \(|\Lambda|\) increases. In the absence of screening one expects \((Q_1^2) \sim |\Lambda|\); however, in a fully screened, \((L \to \infty)\) conducting fluid \((Q_1^2)\) is asymptotically proportional to the surface area \(\tilde{\rho}\). This was first observed by van Beijeren and Felderhof and later proven rigorously by Martin and Yalcaín \[8\]. Following Lebowitz \[8\] one may then define a screening distance proportional to \(M_{Z,1}(T, \rho)\), which we call the **Lebowitz length**, \(\xi_L(T, \rho)\) via

\[
(Q_1^2)/A_\Lambda \approx c_d\rho\tilde{z}_2^2q^2\xi_L(T, \rho) \quad \text{as} \quad |\Lambda| \to \infty, \quad (1)
\]

where \(c_d\) is a numerical constant with \(c_0 = \frac{1}{2}\). Note that, since \(G_{ZZ}(r)\) is not necessarily of uniform sign, \(\xi_L(T, \rho) \propto M_{Z,1}(T, \rho)\) might diverge at \(T_c\) even though the second moment \(M_{Z,2} \propto \xi_B^2\) remains finite!

Clearly, by simulating \((Q_1^2)\) in various subdomains one may, as we show here, hope to calculate the Lebowitz length. To our knowledge no numerical results have been
reported previously for $d = 3$ although Levesque et al. presented a study (above criticality) for $d = 2$. An exact low density expansion proves that $\xi_L(\rho) \to \infty$ when $\rho \to 0$ and corrections of order $\rho^{1/2}$, $\rho \ln \rho$ and $\rho$ have been evaluated. This analysis also served to validate the generalized Debye-Hückel (GDH) theory for the correlations for small $\rho$.

The GDH theory, however, did not generate a $\rho \ln \rho$ term: nevertheless, as we find here, the exact expansion fails at very low densities — around $\rho_c/10$ even for $T \approx 10T_c$ — while GDH theory provides a reasonable estimate of $\xi_L(T, \rho)$ at higher densities; see Fig. below. Furthermore, our calculations show that $\xi_L$ remains finite at criticality, exceeding $\xi_0^\ast$ by only 33%. Nonetheless, the Lebowitz length does exhibit weak singular behavior that, in accord with general theory, matches that of the entropy.

The first serious computational task is to understand the finite-size effects resulting from the $L \times L \times L$ simulation box with periodic boundary conditions. Each simulation at a given $(T^*, \rho^*)$ yields a histogram of the total fluctuating charge $Q_\Lambda$ for 24 different subdomains $\Lambda$. We have used: six small cubes of edges $\lambda L$ with $\lambda = 0.3, 0.4, \cdots, 0.8$; seven ‘rods’ of dimensions $\lambda L \times \lambda L \times L$ with $\lambda = 0.2, \cdots, 0.8$, four ‘slabs’ of dimensions $\lambda L \times L \times \lambda L$ with $\lambda = 0.2, \cdots, 0.5$; and seven spheres of radius $R = \lambda L$ with $\lambda = 0.15-0.45$ in increments $\Delta \lambda = 0.05$. To minimize correlations between these various subdomains, they have been located as far apart as feasible.

While the area law for the charge fluctuation, $(Q^2_\Lambda)$, is rigorously true for $L \to \infty$ followed by $\Lambda \to \infty$, it is by no means clear how it will be distorted for a finite subdomain $\Lambda$ embedded in a finite system. To understand this Fig. presents $(Q^2_\Lambda)$, normalized by $q^2$, for the six cubic subdomains as a function of the reduced area $A_\Lambda/L^2$ at selected temperatures and densities for box sizes $L^* \equiv L/a = 6$ and 12. Surprisingly, at high temperature and moderate density $(T^* = 0.5 \approx 10T_c, \rho^* = 0.08 \approx \rho_c)$, the area law is well satisfied for $\lambda \lesssim 0.7$ even for small systems. For $L^* = 6$ the data point for $\lambda = 0.8$ deviates strongly from the linear fit (dashed line) owing to finite-size effects: indeed, electroneutrality dictates that $(Q^2_\Lambda)$ should vanish when $\lambda \to 1$, corresponding to $A_\Lambda/L^2 = 6$. At low densities around $\frac{1}{2} \rho_c$, the Debye length $\xi_D \propto \sqrt{T/\rho}$ becomes large but nevertheless we see that the area law is still well satisfied. Furthermore, the area law is found to hold even near criticality: see the lowest plot. Note, however, that the linear fits to the data do not pass through the origin. This reflects finite-size effects which are discussed further below.

Combining the observations illustrated in Fig. and the conclusions of the previous section, we conclude that charge fluctuations in the cubic subdomains are well described by

$$
(Q^2_\Lambda(T, \rho; L)) = A_0(T, \rho; L) + \frac{1}{2} pq^2 \xi_L(T, \rho; L)A_\Lambda,
$$

where the intercept $A_0(T, \rho; L)$ need not vanish. The (fitted) linear slope serves to define the finite-size Lebowitz length, $\xi_L(T, \rho; L)$, which should approach the bulk value, $\xi_L(T, \rho)$. But by what route?

To answer this question consider Fig. which displays $\xi_L(T, \rho; L)$ vs. $1/L^*$ for $T^* = 0.5$ at various densities. It is rather clear that $\xi_L(T, \rho; L)$ approaches its bulk limit as $1/L$. This can be understood by recalling the Lebowitz picture in which the uncompensated charge fluctuations in a subdomain arise only from shells of area $A_\Lambda$ and thickness of order $\xi_0$. By invoking the screening of $G_{2ZZ}(r)$ one can see that $\Delta \xi_L \equiv \xi_L(L) - \xi_L(\infty)$ for smooth subdomains decays as $1/L^2$. Indeed, by this route van Beijeren and Felderhof showed explicitly that fluctu-
atations in a sphere of radius $R$ (in an infinite system) approach their limiting behavior as $1/R^2$. For spheres in finite systems, we observe similarly that $\xi_L(L)$ approaches the bulk value as $1/L^2$. However, for cubes—which have edges and corners—and rods with edges, $\xi_L(L)$ gains a lower order, $1/L$ term as seen in Fig. 2. (The intercept $A_0(L)$ in 2 is, correspondingly, found to vary as $L$.) On the other hand, for slabs, lacking edges and corners, we find that $\xi_L(L)$ obtained via 1 approaches the limit exponentially fast.

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On general grounds weak, entropy-like behavior is predicted. Thus temperature derivatives at $\rho = \rho_c$ should diverge like the specific heat, namely as

$$\rho C_V/k_B \approx A^+/(\alpha + A^0),$$

where $\alpha = 0.109$ and $A^+a^3 = 0.50 \pm 0.07$ with, via a rough fit, $A^0a^3 \approx -0.37$. A direct comparison for finite $L$ of $\partial(\xi_L/\xi_D)/\partial T$ with the specific heat is shown in Fig. 5. Bearing in mind the lack of $\xi_L$ data near $T_c$ and its imprecision, the resemblance of the two plots is striking: we accept it as confirmation of the anticipated singularity.

Complementary nonanalytic behavior should arise on the critical isotherm as the reduced chemical potential $\mu^* = (\mu - \mu_0(T))/k_BT$ varies. This is borne out by the plots in Fig. 6 of $\partial(\xi_L/\xi_D)/\partial\rho^*$ and $\partial(\rho^*U^*)/\partial\rho^*$ with $k = 0$, where $U^*(T, \rho)$ is the configurational energy per particle; the power $\rho^k$ represents a convenient "k-locus factor". In the bulk limit both functions should, by scaling, diverge as $1/[\mu - \mu_c(\psi)]$ with $\psi = (1 - \beta)/(\beta + \gamma) \approx 0.43$.

Returning to the isochore $\rho = \rho_c$, theory indicates

$$\xi_L(T) = \xi_L^c \left[ 1 + e_{\alpha}(1-a) + e_{\delta}t + e_{\theta}1-a+\delta + e_{2}t^2 + \ldots \right],$$

where $\theta \approx 0.52$ is the leading correction exponent. By making allowance for the $L$-dependence and fitting over

![FIG. 3: Density variation of the bulk Lebowitz length extrapolated from various subdomains at $T^* = 0.5$. The dashed, solid and dotted plots represent GDH theory 10, and approximants exact at low density: see text.](image)

![FIG. 4: Lebowitz length for $L^* = 8$ and 12 on the critical isochore compared with the Debye length](image)
the exact low-density expansions \( \frac{\alpha}{T} \) are effective only for \( \rho \lesssim \frac{1}{4} \rho_c \) whereas GDH theory \( \frac{\alpha}{T} \) reproduces well the general trends. Finally, \( \xi_1 \) remains finite at criticality but exhibits weak, entropy-like singularities on approaching \( (T_c, \rho_c) \). This is the first time that charge-charge correlations and a strongly state-dependent screening length have been studied by simulations close to criticality.

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