When Is a Conductor Not Perfect? Sum Rules Fail Under Critical Fluctuations

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Perfect screening of all charges characterizes a conductor, a fact embodied in the Stillinger-Lovett sum rule: namely, the charge-charge correlation or structure factor, $S_{ZZ}(k)$, varies with momentum transfer $k \to 0$ as $\xi_D^2 k^2$ where the Debye length ξ_D is a universal function, $\sqrt{k_B T/\rho q_D^2}$, of T and the ion density ρ, with a scaled charge q_D. For a charge-symmetric hard-sphere electrolyte our grand canonical simulations, with a new finite-size scaling device, confirm the Stillinger-Lovett rule except, contrary to current theory, for its failure at criticality. Furthermore, the k^4 term in the $S_{ZZ}(k)$ expansion is found to diverge like the compressibility when $T \to T_c$ at ρ_c.

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A basic feature of an electrical conductor is its ability to screen perfectly all charges, externally imposed or otherwise. This basic fact, implicit in the work of Debye and Hückel [1], is crucial to the structure and thermodynamics of plasmas and ionic fluids [2,3]. While progress has been made in understanding phase separation and criticality in systems dominated by Coulombic interactions [4], significant questions remain open. Thus long-range ionic interactions are screened exponentially in a conducting classical fluid [5] on a scale set, at low densities, by the Debye length ξ_D. Explicitly, if $\rho_\sigma = x_\sigma \rho$ is the density of ions of charge $q_\sigma = z_\sigma q$ ($z_\sigma = 0, \pm 1, \pm 2, \ldots$), overall density ρ, at temperature T, one has [1–3]

$$\xi_D^2 = k_B T/\rho q_D^2, \qquad q_D^2 = 4\pi \bar{z}_2^2 q^2, \qquad \bar{z}_2^2 = \sum_\sigma x_\sigma z_\sigma^2. \quad (1)$$

Now one may ask: Do the diverging density fluctuations that characterize criticality destroy perfect screening near or at (T_c, ρ_c)? This issue leads directly to the remarkable Stillinger-Lovett (SL) sum rule [2(a),6] which encapsulates perfect screening in the nature of the ionic pair correlation functions $G_{\sigma\tau}(\boldsymbol{r}; T, \rho)$ and derived structure functions, $S_{ZZ}(\boldsymbol{k})$, $S_{NN}(\boldsymbol{k})$, etc. [2(a),7]. Specifically, the charge structure factor may be written

$$S_{ZZ}(\boldsymbol{k})/\bar{z}_2^2 = 0 + S_2 k^2 - S_4 k^4 + \ldots, \qquad k = |\boldsymbol{k}|. \quad (2)$$

The zero term reflects internal screening (or bulk electroneutrality) while the second charge-correlation moment S_2 obeys the unexpectedly simple *universal* SL rule

$$S_2(T, \rho) = \xi_D^2(T, \rho) \propto T/\rho, \quad (3)$$

implying a dielectric function $\varepsilon(k) \approx \xi_D^2/S_4 k^2$ [2(a)].

Here, we study the validity of this sum rule near criticality for *charge-symmetric* systems, especially the 1:1 equisized hard-sphere ionic fluid or so-called "restricted primitive model" (RPM) [2–4]. Previous analytical studies [3(b),7,8] concluded that the SL sum rule still holds *at criticality*. Similarly, the fourth charge-correlation moment $S_4(T, \rho)$ is expected to remain bounded through the critical region. Put briefly, symmetry dictates that long-range charge coupling and diverging density fluctuations do not mix. This conclusion seems of broad theoretical relevance for complex systems like liquid crystals, quark-gluon plasmas, etc. [9], with competing sources of potentially slow correlation decay or massless excitations.

Nevertheless, we provide below convincing proof via extensive computer simulations, entailing crucial finite-size analyses, that the SL sum rule is, in fact, *violated* at criticality for the RPM. We find indeed that S_2^c exceeds $\xi_D^2(T_c, \rho_c)$ by about 16% [10]. Furthermore, our data reveal that $S_4(T, \rho)$ diverges at criticality in a manner closely mirroring the compressibility [11]. These findings are in evident disagreement with available theory for charge-symmetric models and, although our results are *qualitatively* similar to behavior expected for charge-*asymmetric* systems [3(b),7,8], even a *semi*quantitative understanding has eluded us.

A technical point of broader interest (illustrated in Fig. 2 below) concerns extrapolation of data, say $g(x; L)$, for systems of dimensions L when the limit $g_\infty(x)$ is continuous except at $x = x_c$ where the jump $[g_\infty^c - \lim g_\infty(x \to x_c)]$ is desired. We find that evaluations at $x - x_c \approx y_j/L^{1/\nu}$ for sets $\{y_j \to 0\}$ with allowance for leading "corrections to scaling" [12] in L prove effective.

Our specific grand canonical Monte Carlo simulations are for a finely discretized RPM with hard-sphere diameters $a_\pm = a$ at the $\zeta = a/a_0 = 5$ level [4,13], where a_0 is the underlying lattice spacing, so $\zeta \to \infty$ describes the continuum. For $N = N_+ + N_-$ hard-sphere ions convenient reduced variables are

$$T^* = k_B T D a/q^2, \qquad \rho^* = N a^3/V, \quad (4)$$

where periodic boundary conditions are imposed on a cubical box of volume $V = L^3$ and reduced edge length $L^* = L/a = 8, \ldots, 18$ [12]. The $\zeta = 5$ critical point is $(T_c^*, \rho_c^*) \simeq (0.050\,69, 0.079)$ [4] slightly higher than the continuum result (0.0493, 0.075) [13]. As already stressed, in all cited studies [4,13] thorough examination of finite-size effects and the employment of verified scaling and extrapolation techniques has proved essential.

The charge structure factor $S_{ZZ}(\boldsymbol{k})$ was evaluated at each selected state point for seven values $\boldsymbol{k} = (\epsilon_\alpha k_{\min}) \neq 0$ with $k_{\min} = 2\pi/L^*$ while $\epsilon_\alpha = 0, 1$ $(\alpha = 1, 2, 3)$. Values for $|\boldsymbol{k}| = (1, \sqrt{2}, \sqrt{3})k_{\min}$ were then obtained by averaging. Histogram reweighting [14] was important for studying general state points. For $L/\xi_D \gtrsim 10$ the data were readily fitted to (2) using only two terms. At low densities, however, the divergence of ξ_D implies strong finite-size effects. Accordingly, we defined finite-size second and fourth charge-correlation moments via [15]

$$S_2(L; T, \rho) \equiv S_{ZZ}(k_{\min})/4\sin^2(k_{\min}/2), \tag{5}$$

$$S_4(L; T, \rho) \equiv \frac{S_2(L)}{k_{\min}^2}\left[1 - \frac{S_{ZZ}(\sqrt{2}k_{\min})}{2S_{ZZ}(k_{\min})}\right]. \tag{6}$$

When $L \to \infty$ (so $k_{\min} \to 0$) these approach the desired thermodynamic limits, $S_2(T, \rho)$ and $S_4(T, \rho)$, respectively [12].

Well above criticality ($T \gg T_c$), the simulation data support the validity of the SL sum rule. Nevertheless, at low densities where $\xi_D/L > 0.1$, the convergence of $S_2(L; T, \rho)$ to $\xi_D^2(T, \rho)$ is slow and a careful finite-size analysis is needed to convincingly verify the SL rule as, in fact, we have done [16].

Closer to T_c, the plots in Fig. 1 of the second-moment charge-correlation length $\xi_{Z,1}(L) := \sqrt{S_2(L)}$ on the critical isochore $\rho = \rho_c$ for $L^* = 10, \cdots, 18$, suggest a further possibility. For T greater than, say, $1.05T_c$ the approach of $\xi_{Z,1}(L)$ to ξ_D as L increases is rapid and, as expected, fully in accord with SL. But nearer T_c the convergence slows markedly and, by contrast, *at* $T^* = T_c^*$, the data suggest that $\xi_{Z,1}(L \to \infty; T_c, \rho_c)$ might well *differ* from the critical Debye length, $\xi_D^c = \xi_D(T_c, \rho_c)$.

To support such a surmise, however, a closer look is imperative. Indeed, a plot of the numerical parameter

$$X(L; T) := (\xi_{Z,1}/\xi_D)^2 = S_2(L; T, \rho_c)/\xi_D^2(T, \rho_c), \tag{7}$$

at the critical point T_c proves nonmonotonic as L increases; see the open circles in Fig. 2. *A priori*, one cannot, therefore, escape the possibility that $X(L; T_c) \to X_\infty^c = 1$, in accordance with the SL rule. Conversely, if, as we will conclude, $X_\infty^c \neq 1$, one needs a more transparent grasp of the behavior of the data in Fig. 1 for large L.

To that end we recall [4] that two-phase coexistence in a canonical system of finite size displays an effective critical temperature, $T_c^{\text{can}}(L)$, at which two distinct peaks of the density distribution merge; this lies above the thermodynamic T_c. In accord with finite-size scaling theory [12], one expects, and checks [4], that the difference, $\Delta T_c^{\text{can}}(L) = T_c^{\text{can}}(L) - T_c$, vanishes as $L^{-1/\nu}$ with $\nu \simeq 0.63$, where the *density* correlation length, $\xi_N(T, \rho_c)$, diverges as $t^{-\nu}$ when $t \equiv (T - T_c)/T_c \to 0$. By the same token, we anticipate that the plots in Fig. 1 will, for large L, approach ξ_D, the dotted locus, except for a peak of narrowing width, $\sim \Delta T_c^{\text{can}}(L)$, around T_c.

To study this peak and, crucially, to estimate its asymptotic height, we have plotted in Fig. 2, $X(L; T)$ evaluated not only at $T = T_c$ but also at other temperatures, $T_f(L)$ above but close to T_c on the scale $1/L^{1/\nu}$; specifically we take $t_f T_c = T_f(L) - T_c =: \Delta T_f(L) = f \Delta T_c^{\text{can}}(L) \to 0$ as $L \to \infty$. An examination of Fig. 2 provides, we believe, strong support for the natural scaling hypothesis

$$X[L; T_f(L)] \approx W(x; t_f^\theta), \qquad x = L/\xi_N(T), \tag{8}$$

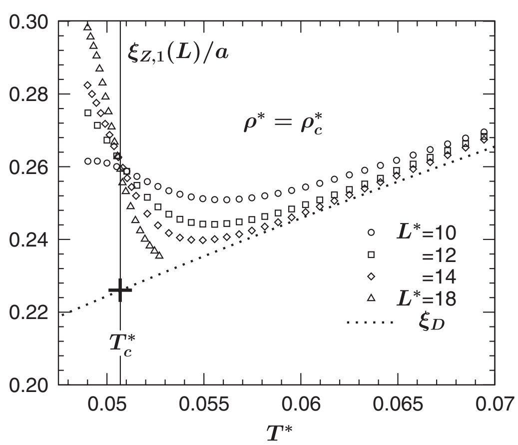

FIG. 1. Plots of $\xi_{Z,1}(L) = \sqrt{S_2(L)}$ vs T^* on the critical isochore. The almost linear dotted curve depicts the SL prediction, $\xi_D(T, \rho_c)$, while the vertical line marks criticality.

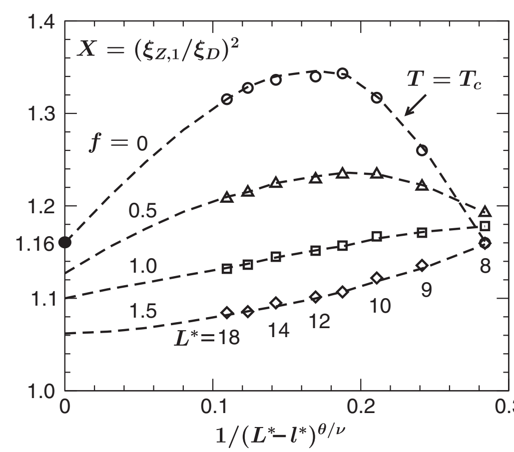

FIG. 2. Plots of $X(L; T_f) = S_2(L)/\xi_D^2$ vs $(L^* - l^*)^{-\theta/\nu}$ (with $\theta/\nu \simeq 0.823$ and $l^* = 3.4$) for loci $\Delta T_f(L)/\Delta T_c^{\text{can}}(L) = f$. The dashed lines are guides to the eye.

where, as a refinement, we have introduced the exponent $\theta \simeq 0.52$ that describes the leading correction to thermodynamic scaling [12]. This exponent is also reflected in the abscissa in Fig. 2 along with the useful but asymptotically negligible "shift" l^* that allows for higher-order corrections; the value adopted is based on a close analysis of $\Delta T_c^{\mathrm{can}}(L)$. Extrapolation on L then yields our conclusion, namely, $X_\infty^c \equiv W(0;0) = S_2^c/\xi_D^2 = 1.16 \pm 0.05$. This implies, unequivocally, a failure of SL *at* and, for finite L, *near* criticality.

To further test current theories, note that the fourth charge moment $S_4(T,\rho) =: \xi_{Z,2}^4$ is known analytically to approach $\xi_D^4(T,\rho)$ when $\rho \to 0$ [3(c)]. At first sight the high-temperature data ($T/T_c \simeq 10, 20$) in Fig. 3 say otherwise; but this merely reflects the overwhelming finite-size effects when $\xi_D \propto \sqrt{T/\rho} = O(L)$. For intermediate densities one may call on generalized Debye-Hückel (GDH) theory [17] which predicts that $S_4(T,\rho)$ changes sign while decreasing approximately linearly with ρ; see the solid plots in Fig. 3. The simulations indeed confirm this prediction although the densities at which S_4 vanishes for high T are some 30%–50% greater: see Fig. 3.

At lower temperatures, $T/T_c \simeq 2$ to 6, on the critical isochore the simulations again mirror GDH results [16,17]. However, as evident from the inset in Fig. 4, the point $T_0/T_c \simeq 4.0$ at which S_4 vanishes before reaching a surprising but predicted *minimum*, is about 40% lower than anticipated. However, a striking unpredicted feature of Fig. 4 is the seemingly strong divergence of S_4 near T_c as L^* increases from 8 to 18. Qualitatively, the behavior resembles that seen previously [4,11] for the *compressibility* $\chi(T,\rho) \propto S_{NN}(\boldsymbol{k}=\mathbf{0})$ which for $\rho = \rho_c$ diverges as $t^{-\gamma}$ with $\gamma \simeq 1.239$ [7,18]; but quantitatively further analysis is called for.

As noted above, violation of the SL sum rule at criticality and a divergence of S_4 contradict previous conclusions for charge-symmetric models [3(b),7,8]. In these treatments symmetry prevents charge and density fluctuations from mixing; consequently the diverging *density* correlation length, $\xi_{N,1}$, has no effect on the *charge* correlations. On the other hand, in *asymmetric* models the fluctuations do couple resulting in diverging fourth-moment charge-correlation lengths, as well as violations of the SL rule at (T_c, ρ_c). Might density and charge fluctuations mix even for the symmetric RPM?

To examine this possibility it is useful to look at special models [7] in which density and charge fluctuations can couple. The charge structure factor, S_{ZZ}, then relates to the density factor, S_{NN}, via [7,16]

$$S_{ZZ}(k) \approx S_{ZZ}^0(k) + \delta_\varphi^2(k_\mathrm{B}T/\rho)k^4a^2S_{NN}(k), \qquad (9)$$

where the regular "background" term satisfies

$$S_{ZZ}^0(k) = \xi_D^2k^2 - S_4^0k^4 + \cdots, \qquad (10)$$

with $S_4^{0c} < \infty$, while δ_φ is a "charge asymmetry" [7,16] or, for present purposes, a *de facto* mixing parameter. Of course, $\delta_\varphi = 0$ implies the SL rule at $T = T_c$ and the finiteness of S_4 when $T \to T_c$. If one now invokes the Ornstein-Zernike approximation at criticality, namely [18], $S_{NN}^c(k) \approx C_c/k^2$ as $k \to 0$, one obtains

$$S_2^c/\xi_D^2 = (\xi_{Z,1}^c/\xi_D^c)^2 = 1 + \delta_\varphi^2C_c(k_\mathrm{B}T_ca^2/\xi_D^{c2}\rho_c) \geq 1.$$

Thus, the SL rule is violated whenever $\delta_\varphi \neq 0$.

On the other hand, for small k on the critical isochore above T_c, $S_{NN}(k;T,\rho_c)$ approaches the diverging compressibility, $\chi(T) \approx C^+/t^\gamma$ [18]. Via (9) this yields $-S_4 \sim \delta_\varphi^2C^+/t^\gamma$. The suggested *divergence* of S_4 accords with the data of Fig. 4, but the sense is opposite to that observed for the RPM. Neglecting this feature of the models [7], we propose the finite-size *trial form*

$$\frac{S_4}{\xi_D^2a^2} \equiv Y(T,\rho;L) = Y^0(T,\rho;L) + \Delta Y(T,\rho;L), \quad (11)$$

where the background, $Y^0 = S_4^0/\xi_D^2a^2$, remains bounded while $\Delta Y(T,\rho;L\to\infty)$ diverges as $t^{-\gamma}$. Finally, at

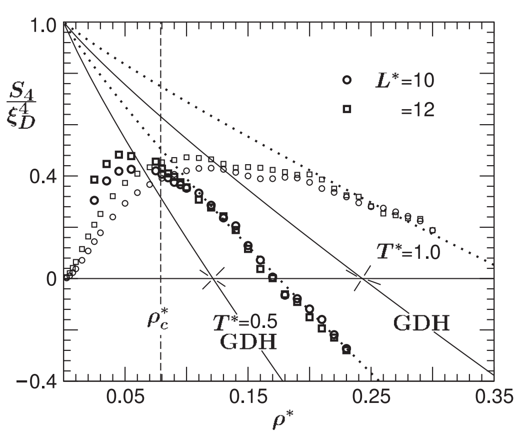

FIG. 3. Plots of $S_4/\xi_D^4 \equiv \xi_{Z,2}^4(L)/\xi_D^4$ vs ρ^* for isotherms, $T^* = 0.5$ and 1.0. The solid curves represent GDH predictions, while the dotted curves are versions rescaled to fit [16].

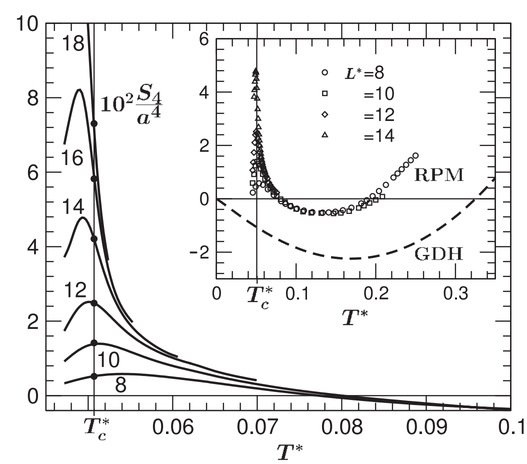

FIG. 4. Variation of $S_4/a^4 = (\xi_{Z,2}/a)^4$ with T on the critical isochore for increasing L^*. In the inset, note the GDH prediction (dashed) and the zero crossings and minima.

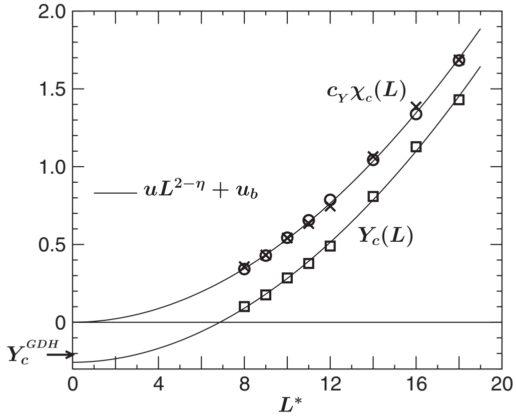

FIG. 5. Critical-point plots vs L^* of $Y_c(L) = S_4^c(L)/(a\xi_D^c)^2$ and the rescaled compressibility $\chi_c(L)$. The solid curves are fits to $uL^{2-\eta} + u_b$. The arrow marks the GDH value of $Y_c(\infty)$.

criticality in a finite system, when $\xi_{N,1}(T_c, \rho_c; L) = O(L)$, standard scaling theory [12] yields the expectation

$$Y_c(L) \equiv Y(T_c, \rho_c; L) \approx Y_0 + A_Y L^{2-\eta}, \qquad (12)$$

where $\eta \simeq 0.036$ is the anomalous critical-point decay exponent [18] while A_Y is a critical amplitude.

Figure 5 presents a test of this proposal: specifically, $Y_c(L)$ is compared with the compressibility $\chi_c(L)$ at criticality which obeys a similar form. Evidently, the fits for both quantities are quite satisfactory and yield a background Y_0 close to the (L-independent) value derived from GDH theory. In short, the data indicate a mixing of charge and density fluctuations. Thus, the critical-point decay of the density fluctuations [11,18] as $1/r^{1+\eta}$ ($\eta < 1$) accords with a theorem [19] linking the failure of the SL rule to the presence of particle correlation decays slower than $1/r^5$ and, via (9), implies that the *charge* correlations at criticality decay more rapidly as $1/r^{5+\eta}$.

In summary, we have asked if a charge-symmetric ionic conductor will, even at criticality, still screen charges perfectly in accordance with the Stillinger-Lovett sum rule Eq. (3). Our answer, based on grand canonical Monte Carlo simulations of the hard-sphere 1:1 or RPM electrolyte, is "No." Away from criticality the sum rule for the second moment S_2 is confirmed, but a special finite-size scaling analysis reveals a 16% violation at criticality with $S_2/\xi_D^2 > 1$.

On the other hand, the fourth charge moment $S_4 \equiv \xi_{Z,2}^4$ displays changes of sign and minima as predicted by GDH theory [17] but, unexpectedly, diverges at criticality in a fashion matching the compressibility. Our findings contradict all present theoretical treatments although the observed behavior somewhat resembles expectations for charge-*asymmetric* systems. Thus despite the symmetry, charge and density fluctuations become coupled even for the simplest model, resulting effectively in a diverging *charge-correlation length* near criticality. We believe that such failures of symmetry restrictions might well feature in other complex systems with competing interactions. Be that as it may, previous theoretical analyses need to be revised or augmented to successfully describe the breakdown of perfect screening in charge-symmetric—and, by extension, in near-symmetric—ionic fluids.

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