Universality Class of Criticality in the Restricted Primitive Model Electrolyte

Erik Luijten,1,‡ Michael E. Fisher,1,† and Athanassios Z. Panagiotopulos2

1Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742
2Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540
(Dated: November 2, 2018)

The 1:1 equisized hard-sphere electrolyte or restricted primitive model has been simulated via grand-canonical fine-discretization Monte Carlo. Newly devised unbiased finite-size extrapolation methods using temperature-density, \((T, \rho)\), loci of inflections, \(Q \equiv \langle m^2 \rangle \langle m^4 \rangle\) maxima, canonical and \(CV\) criticality, yield estimates of \((T_c, \rho_c)\) to \(\pm (0.04, 3\%)\). Extrapolated exponents and \(Q\)-ratio are \((\gamma, \nu, Q) = (1.24(3), 0.63(3); 0.624(2))\) which support Ising \((n = 1)\) behavior with \((1.23; 0.630; 0.623)\), but exclude classical, XY \((n = 2)\), SAW \((n = 0)\), and \(n = 1\) criticality with potentials \(\varphi(r) > |r|^{4.9}\) when \(r \to \infty\).

PACS numbers: 02.70.Rr, 05.70.Jk, 64.60.Fr, 64.70.Fx

Since the experiments of Singh and Pitzer in 1988,1,2, an outstanding experimental and theoretical question has been: What is the universality class of Coulombic criticality? Early experimental data for electrolytes exhibiting phase separation driven by long-range ionic forces suggested classical or van der Waals (vdW) critical behavior, with exponents \(\beta = \frac{1}{2}, \gamma = 1, \nu = \frac{1}{2}\), etc.1,2,4,9: But the general theoretical consensus has been that asymptotic Ising-type criticality, with \(\beta \simeq 0.326, \gamma \simeq 1.239, \nu \simeq 0.630\), etc., should be expected1,2,4: Naively, one may argue that the exponential Debye screening of the direct ionic forces results in effective short-range attractions that can cause separation into two neutral phases: ion-rich and ion-poor1,2,4,9,10: the order parameter, namely, the ion density or concentration difference, is a scalar; so Ising-type behavior is indicated. Field-theoretic approaches support this picture4,10.

However, the theoretical arguments are by no means rigorous and have not, so far, been tested by precise calculations for appropriate models. To do that is the aim of the researches reported here. We have studied a finely-discretized version10 of the simplest continuum model (considered by Debye and Hückel in 19231,2,10, three years before Ising’s work), namely, the restricted primitive model (RPM), consisting of \(N = N_+ + N_-\) equisized hard spheres of diameter \(a\), precisely half carrying a charge \(+q_0\) and half \(-q_0\), in a medium (representing a solvent) of dielectric constant \(D\). At a separation \(r > a\), like (unlike) ions interact through the potential \(\pm q_0^2 / r\); thus appropriate reduced density, \(\rho = N/V\) for volume \(V\), and temperature variables are

\[
\rho^* = \rho a^3, \quad T^* = k_B T D a / q_0^2, \quad t = (T - T_*) / T_c. \quad (1)
\]

Except at low densities and high temperatures, when the inverse Debye length \(\kappa T a = (4 \pi \rho^* / T^*)^{1/2}\) is small, the RPM is intractable analytically or via series expansions1,2,4,9. However, it has been much studied by Monte Carlo (MC) simulations1,2,4,9,21 which have recently approached the consensus \(T_c^* \simeq 0.049, \rho_c^* = 0.060–0.085\). However, these values have been derived by assuming Ising-type criticality: on that basis Bruce–Wilding extrapolation procedures have been employed1,2,4 (which, even then, neglect potentially important, asymmetric ‘pressure-mixing’ terms12,13). It must be stressed that implementing appropriate finite-size extrapolation methods constitutes the heart of the computational task since a grand-canonical (GC) system confined in a simulation ‘box’ of dimensions \(L \times L \times L\) (with, say, periodic boundary conditions14,15) cannot exhibit a sharp critical point; a finite canonical system may become critical but can display only classical or vdW behavior4,10.

Thus, while previous RPM simulations1,2,10 demonstrate consistency with Ising \((n = 1)\) behavior, no other universality classes are ruled out: see also1,4,14,15. Putative ‘nearby’ candidates are XY \((n = 2)\) systems (with \(\gamma \simeq 1.316, \nu \simeq 0.670\), self-avoiding walks (SAWs, \(n = 0\): with \(\gamma \simeq 1.159, \nu \simeq 0.588\)18,19 and long-range, \(1/|x-d|^{\sigma}\) scalar systems (with \(d = 3, \sigma < 2 - \eta\))16,17. On the other hand, in a preparatory GC simulation19 of the hard-core square-well (HCSW) fluid—for which Ising criticality has long been anticipated—new, unbiased, finite-size extrapolation techniques enabled the \(n = 2\) and 0 classes to be convincingly excluded.

Present approach.—We have now applied the methods of II to the RPM; however, the extreme asymmetry of the critical region in the model (see Fig. 1) has demanded further developments. By extending finite-size scaling theory13 and previous applications of the Binder parameter or fourth-moment ratio17,18,19

\[
Q_L(T; \rho) \equiv \langle m^2 \rangle^2 / \langle m^4 \rangle \quad \text{with} \quad m = \rho - \langle \rho \rangle, \quad (2)
\]

20 to systems lacking symmetry, we have assembled evidence, outlined below, that excludes not only classical criticality in the RPM but also the XY and SAW universality classes and \((d = 3)\) long-range Ising criticality with \(\sigma \lesssim 1.9\).

Our work employs multihistogram reweighting21 and
a ($\zeta = 5$)-level fine-discretization formulation (with a fine-lattice spacing $a(\zeta)$). Since $\zeta < \infty$, nonuniversal parameters, such as $T_c$, will deviate slightly from their continuum limit ($\zeta \to \infty$) [3,22]; but, at this level, there are no serious grounds for contemplating changes in universality class. For the critical parameters we find $T_c = 0.05069(2)$ and $\rho_c = 0.0790(25)$: the confidence limits in parentheses refer, here and below, to the last decimal place quoted. The inset in Fig. 1 shows how these values are approached (i) by the canonical values $T_c(L)$, $\rho_c(L)$ and $\rho_c(L)$ (= $\langle \rho \rangle_{T_c(L)}$, $\rho^*_{\rho}(L)$) [21]) derived from the isothermal density histograms [see II(2.18)–(2.23), Figs. 1, 3], (ii) by $T_c(L)$ and $\rho_c(L)$, from the isochoric maxima of $C_V(T; \rho; L)$ [see Fig. II and II Sec. III, Fig. 7], and (iii) by the $\sqrt{\rho}$ diameter, $\hat{\rho}_{1/2}(T)$, defined below.

**Exponents $\gamma$ and $\nu$.**—Before justifying the precision of our ($T_c$, $\rho_c$) estimates, we consider their implications. The solid curves in Fig. 1 portray the effective susceptibility exponent $\gamma_{\rho}(T; L)$ on the critical isochore above $T_c$, as derived from $\chi_{NN} \equiv V(m^2) = k_B T \rho^2 K_T$: see II(3.7). Within statistical precision the data are independent of the ($T_c$, $\rho_c$) uncertainties.

Also presented in Fig. 1 are the modified estimators $\gamma_{\rho}(T)$ [defined as in II(3.7) but with $t$ replacing $t^*$] evaluated on the ‘theta locus,’ $\rho_{\vartheta}(T) = \rho_c(\vartheta + (1 - \vartheta)T_c/T)$. This relation approximates an effective symmetry locus (II) above $T_c$, derived from the behavior of the isothermal inflection loci $\rho_6(T; L)$, on which $\chi_{NN} = \chi_{NN}(T, \rho; L) / \rho^k$ is maximal [see II(2.26)–(2.32)]. The

FIG. 1: Approximate coexistence curve of the RPM in the ($T$, $\rho$) plane: open circles and fitted line. The estimated critical point is shown as an uncertainty bar. The dashed curves are loci of $C_V(T)$ maxima at fixed $\rho$ for $L^* = L/a = 8, 10,$ and 12. The loci labeled $k = 1$, $\vartheta$, and $Q$ are explained in the text. The inset shows the canonical critical points $T_c^0(L)$, $\rho_c^0(L)$ (squares), and corresponding GC mean densities $\rho^*_0(L)$ (crosses) for $L^* = 9–12$, the $C_V(L)$ extrema $T_c(L)$, $\rho_c(L)$, for $L^* = 7–10$ and 12 (solid circles), and the $\sqrt{\rho}$ diameter, $\hat{\rho}_{1/2}(T)$, defined in the text (open squares).

FIG. 2: Effective susceptibility exponent $\gamma_{\rho}(T)$ for $\rho = \rho_c$ (solid curves) and $\gamma_{\rho}(T)$ on the theta locus (dashed; see text), for sizes $L^* = 7–12$ and 15. Values for vdW and for $n = 0, 1,$ and 2 are marked on the $\gamma$ axis.

$k = 1$ loci are shown in Fig. 1 for $L^* = L/a = 6, 8, 10, 12$; the selected value $\vartheta = 0.20$ corresponds roughly to $k \approx 0.60$ (which may be identified with an optimal value: see II and [18]). However, the variation of the $k$ loci when $L$ increases is significantly more complicated in the RPM than in the HCSW fluid [11(c), 23].

Extrapolation of the effective susceptibility exponents in Fig. 1 and those on the $k = 0$ locus, etc. (11(c)], to $t = 0$ indicates $\gamma = 1.24(3)$, upholding Ising-type behavior while both XY and SAW values are implausible.

To determine the exponent $\nu$ we have examined the peak positions, $T_j(L)$, of various properties, $Y_j(T; L)$, on the critical isochore. Finite-size scaling theory [18] yields $\Delta T_j(L) \equiv T_j(L) - T_c \sim L^{1-\nu}$; Figure 2 demonstrates the estimation of $1/\nu$ (unbiased except for the imposed $T_c$ estimate) from the ratios $\Delta T_j(L_1)/\Delta T_j(L_2)$ for various $j$ (see II(11)–(13), Figs. 1; II(3.1)). The data indicate $\nu = 0.63(3)$, excluding classical but supportive of Ising ($n = 1$) criticality, while $n = 2$ and 0 seem less probable.

**Estimation of $T_c$.**—Consider, now, $Q_L(T; \rho)$ in II, when $L \to \infty$. In any single-phase region of the ($T$, $\rho$) plane $Q_L \to \frac{1}{2}$, indicative of Gaussian fluctuations about $\langle \rho \rangle$; conversely, within a two-phase region, $\rho_-(T) < \rho < \rho_+(T)$, one finds $Q_L \to 1$ on the diameter, $\hat{\rho}(T) = \frac{1}{2}(\rho_- + \rho_+)$ for $T < T_c$; while, more generally,

$$1 \ge Q(t; \rho) = 1 - \frac{4y^2}{(1 + 6y^2 + y^4)} > \frac{1}{2}, \quad (3)$$

where $|y| = 2|\rho - \hat{\rho}(T)|/(\rho_- + \rho_+ < 1$. Finally, at criticality, $Q(t; \rho)$ approaches a universal value $Q_c$ which, for cubic boxes with periodic boundary conditions, is $Q_c = 0.4569 \cdots$ for classical (vdW) [II(b)] or $\xi$-range systems [II(c)] but $Q_c(n = 1) = 0.6236(2)$ for Ising [II(d),e) and $Q_c(n = 2) = 0.8045(1)$ for XY [II(f)]
estimates for loci are observed to approach the diameter $\bar{T} < L^* \Delta T$ increases. (For systems, while $Q_c(n = 0) = 0$ \cite{19b]. For long-range, $1/\nu^{3+\sigma}$ systems, $Q_c(\sigma)$ and also $\gamma(\sigma)$, increase almost linearly from vdW to Ising values in the interval $\frac{2}{3} \leq \sigma \leq (\gamma/\nu)_{n=1} \simeq 1.966$ with $Q_c(\sigma = 1.9) \simeq 0.600$ and $\gamma(\sigma = 1.9) \simeq 1.205$ \cite{17b}.)

The result \cite{3} leads us to propose $Q$-loci, $\rho_Q(T; L)$, on which $Q_L(T; \rho)$ is maximal at fixed $T$. For $T < T_c$, these loci are observed to approach the diameter $\bar{\rho}(T)$ when $L$ increases. (For $T \geq T_c$, but not above $T_c$, the $Q$-loci also follow the $k = 0$ loci quite closely.)

Figure 4 displays $Q_L(T; \rho)$ on the $Q$-loci $\rho_Q(T; L)$, for $L^* = 7$–12. As often seen in plots for symmetric systems \cite{14}, inflection points and successive intersections, $T_Q(L)$, almost coincide! Scaling yields $Q_L(T_c; \rho_c) \sim L^{-\theta/\nu}$ and $|T_c - T_Q(L)| \sim L^{-\varphi}$ with $\varphi = (1 + \theta)/\nu$, where $\theta = \omega_\nu$ is the leading correction-to-scaling exponent; for classical and Ising criticality one has $\theta(\nu, \varphi) = (1, 3)$, $\simeq (0.82, 2.41)$ \cite{18}. With this guidance, the large-scale inset in Fig. 4 leads to our estimate $T^* \simeq 0.05009(2)$ but also yields $Q_c \simeq 0.624(2)$: this is surprisingly close to the Ising value \cite{24} and far from the vdW, XY, and SAW values—an unexpected bonus! Likewise, $1/\nu^{3+\sigma}$ effective potentials with $\sigma \leq 1.9$ are excluded.

Estimation of $\rho_c$—Finally, we examine $\rho_0^*(L)$ and $\rho_Q^*(L)$, i.e., the $(k = 0)$ and $Q$ loci intersections with the estimated critical isotherm, $T = T_c$. According to scaling, the deviations, $\Delta \rho_0^*$ and $\Delta \rho_Q^*$, decay as $L^{-\psi}$ with $\psi = (1 - \alpha)/\nu$ \cite{18}, so we may suppose $1.2 < \psi \leq 2$ \cite{16}. Figure 5 displays the deviations vs $L^{-\psi}$ for $\psi = 1.2, 1.4, 1.7$ and 2 with ‘$t_0$ shifts’ \cite{II, 19}, Fig. 2; \cite{II, 31} chosen to provide linear plots. From these and further plots \cite{1c} we conclude $\rho_c^* \simeq 0.0790(25)$.

In further support of our $\rho_c$ estimate, we mention first that when the coexistence curve, $\rho_\pm(T)$, is plotted vs $\sqrt{\rho^2}$—as is reasonable since all powers $\rho^{j/2}$ for integral $j$ appear in virial expansions for the RPM \cite{3}—it becomes markedly more symmetrical [resembling $(\rho, T)$ plots for the HCSW and other simple fluids]. Then, the corresponding diameter, $\sqrt{[\rho_{1/2}^0(T) + \sqrt{\rho_{1/2}^0(T) \rho_c^*}]}$, is only mildly curved and naive extrapolations to $T_c$ yield $\rho_c^* = 0.078(4)$.

In conclusion.—By implementing recently tested \cite{14} and newly devised extrapolation techniques for nonsymmetric critical systems, our extensive grand-canonical Monte Carlo simulations for the RPM have provided, in toto, convincing evidence to exclude classical, XY $(n = 2)$, or SAW $(n = 0)$ critical behavior as well as long-range (effective) Ising interactions decaying more
slowly than $1/r^{4.90}$. Rather, the estimates for the exponents $\nu$ and $\gamma$, and for the critical fourth-moment ratio, $Q_c$, point to standard, short-range Ising-type criticality. Studies underway \[11(c)\] should provide further confirmation and additional quantitative results, such as the scale, $R_0$, of the equivalent single-component short-range attractions generated by the RPM near criticality.

We are indebted to Young C. Kim for extensive assistance in the numerical analysis, for his elucidation of the finite-size scaling properties of asymmetric fluid precision and additional quantitative results, such as the scale, $R_0$, of the equivalent single-component short-range attractions generated by the RPM near criticality.

\[\nu \approx 0.63 \text{ (to be published).}\]

We are indebted to Young C. Kim for extensive assistance in the numerical analysis, for his elucidation of the finite-size scaling properties of asymmetric fluid precision and additional quantitative results, such as the scale, $R_0$, of the equivalent single-component short-range attractions generated by the RPM near criticality.

We are indebted to Young C. Kim for extensive assistance in the numerical analysis, for his elucidation of the finite-size scaling properties of asymmetric fluid precision and additional quantitative results, such as the scale, $R_0$, of the equivalent single-component short-range attractions generated by the RPM near criticality.

We are indebted to Young C. Kim for extensive assistance in the numerical analysis, for his elucidation of the finite-size scaling properties of asymmetric fluid precision and additional quantitative results, such as the scale, $R_0$, of the equivalent single-component short-range attractions generated by the RPM near criticality.

We are indebted to Young C. Kim for extensive assistance in the numerical analysis, for his elucidation of the finite-size scaling properties of asymmetric fluid precision and additional quantitative results, such as the scale, $R_0$, of the equivalent single-component short-range attractions generated by the RPM near criticality.