Universality Class of Criticality in the Restricted Primitive Model Electrolyte

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(Received 12 December 2001; published 18 April 2002)

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 loci in the temperature-density or (T, ρ) plane of isothermal ρ^{2-k} vs pressure inflections, of $Q \equiv \langle m^2\rangle^2/\langle m^4\rangle$ maxima, and of canonical and C_V criticality, yield estimates of (T_c, ρ_c) to $\pm(0.04, 3)\%$. Extrapolated exponents and Q ratio are $(\gamma, \nu, Q_c) = [1.24(3), 0.63(3); 0.624(2)]$, which support Ising ($n = 1$) behavior with $(1.23_9, 0.630_3; 0.623_6)$, but exclude classical, XY ($n = 2$), self-avoiding walk ($n = 0$), and $n = 1$ criticality with potentials $\varphi(r) > \Phi/r^{4.9}$ when $r \to \infty$.

DOI: 10.1103/PhysRevLett.88.185701 PACS numbers: 64.60.Fr, 02.70.Rr, 05.70.Jk, 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]: 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 expected [1,3,4]. 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 poor [1–5]; the order parameter, namely, the ion density or concentration difference, is a scalar; so Ising-type behavior is indicated. Field-theoretic approaches support this picture [6].

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 research reported here. We have studied a finely discretized version [7] of the simplest continuum model (considered by Debye and Hückel in 1923 [1,2], 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 $r \geq a$, like (unlike) ions interact through the potential $\pm q_0^2/Dr$; thus appropriate reduced density, $\rho = N/V$ for volume V, and temperature variables are

$$\rho^* = \rho a^3, \quad T^* = k_B T D a/q_0^2, \quad t = (T - T_c)/T_c\,. \tag{1}$$

Except at low densities and high temperatures, when the inverse Debye length $\kappa_D a = (4\pi\rho^*/T^*)^{1/2}$ is small, the RPM is intractable analytically or via series expansions [1,3,8]. However, it has been much studied by Monte Carlo (MC) simulations [1,9–11], 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 employed [9,10] (which, even then, neglect potentially important, asymmetric "pressure-mixing" terms [12]). 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 conditions [13]) *cannot* exhibit a sharp critical point; a finite canonical system may become critical but can display *only classical* or vdW behavior [14].

Thus, while previous RPM simulations [9,10] demonstrate *consistency* with Ising (or $n = 1$) behavior, *no other* universality classes are ruled out: see also [11,14,15]. Putative "nearby" candidates are XY or $n = 2$ systems (with $\gamma \simeq 1.316$, $\nu \simeq 0.670$), self-avoiding walks (SAWs, $n = 0$: with $\gamma \simeq 1.159$, $\nu \simeq 0.588$) [14,16] and long-range, $1/r^{d+\sigma}$ scalar systems (with $d = 3$, $\sigma < 2 - \eta$) [15,17]. On the other hand, in a preparatory GCMC study, OFP [14(b)], 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 OFP to the RPM [11(b), (c)]; however, the extreme *asymmetry* of the critical region in the model (see Fig. 1) has demanded further developments. By extending finite-size scaling theory [18] and previous applications of the Binder parameter or fourth-moment ratio [17–19]

$$Q_L(T; \rho) \equiv \langle m^2\rangle^2/\langle m^4\rangle \quad \text{with} \qquad m = \rho - \langle\rho\rangle \tag{2}$$

[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 $\sigma \lesssim 1.9$.

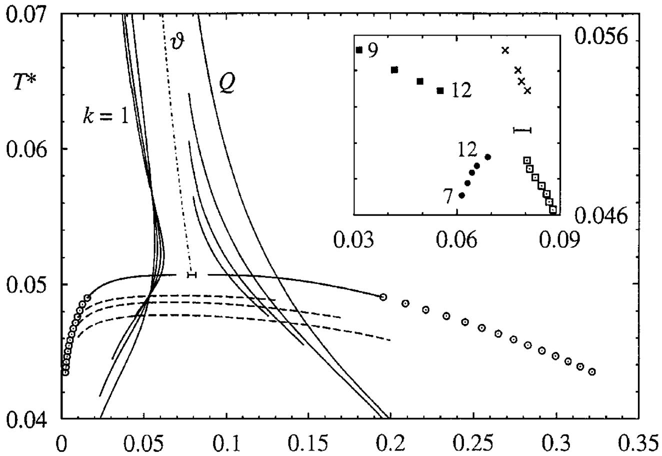

FIG. 1. Approximate coexistence curve of the RPM in the (T, ρ) plane: open circles and fitted line. The estimated critical point is shown as an uncertainty bar. The dashed curves are loci of $C_V(T)$ maxima at fixed ρ for $L^* \equiv L/a = 8$, 10, and 12. The loci labeled $k = 1$, ϑ, and Q are explained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

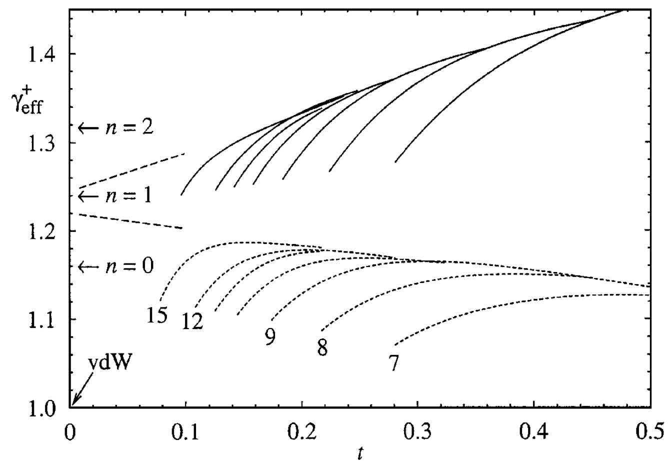

FIG. 2. Effective susceptibility exponent $\gamma^+_{\rm eff}(T)$ for $\rho = \rho_c$ (solid curves) and $\tilde{\gamma}^+_{\rm eff}(T)$ on the theta locus (dashed curves; see text), for sizes $L^* = 7-12$ and 15. Values for vdW and for $n = 0$, 1, and 2 are marked on the γ axis. By construction $\gamma_{\rm eff}$ for any finite system must approach and pass through 0 when $t \to 0$; but for clarity these smooth and featureless finite-size limited sections of the plots (for $t < 0.07$, etc.) have been omitted.

Our work [11(b)] employs multihistogram reweighting [21] and a $(\zeta = 5)$-level fine-discretization formulation (with a fine-lattice spacing a/ζ [7]). Since $\zeta < \infty$, *non*universal parameters, such as T_c^*, will deviate slightly from their continuum limit $(\zeta \to \infty)$ [7,22]; 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 [23]. The inset in Fig. 1 shows how these values are approached (i) by the canonical values $T_c^0(L)$, $\rho_c^0(L)$, and $\rho_c^\dagger(L)$ $(= \langle\rho\rangle_{T_c^0(L),\mu_c^0(L)}$ [20]) derived from the isothermal density histograms [see OFP(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. 1 and OFP Sec. III, Fig. 7], and (iii) by the $\sqrt{\rho}$ diameter, $\overline{\rho}_{1/2}(T)$, defined below.

Exponents γ and ν.—Before justifying the precision of our (T_c, ρ_c) estimates, we consider their implications. The solid curves in Fig. 2 portray the effective susceptibility exponent $\gamma^+_{\rm eff}(T;L)$ on the critical isochore above T_c, as derived from $\chi_{NN} \equiv V\langle m^2\rangle = k_B T \rho^2 K_T$: see OFP(3.7). Within statistical precision the data are independent of the (T_c, ρ_c) uncertainties.

Also presented in Fig. 2 are the modified estimators $\tilde{\gamma}^+_{\rm eff}(T)$ [defined as in OFP(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* (OFP) above T_c, derived from the behavior of the isothermal inflection loci $\rho_k(T;L)$, on which $\chi^{(k)} \equiv \chi_{NN}(T,\rho;L)/\rho^k$ is maximal [see OFP(2.26)–(2.32)]. The $k = 1$ loci are shown in Fig. 1 for $L^* \equiv L/a = 6$, 8, 10, 12; the selected value $\vartheta = 0.20$ corresponds roughly to $k \simeq 0.60$ (which may be identified with an optimal value: see OFP 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),24].

Extrapolation of the effective susceptibility exponents in Fig. 2 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 ν 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 3 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 [11(c)]], using an established approach [see OPF(7)–(13), Fig. 1; OFP(3.1) [14(a)]]. 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 (2), when $L \to \infty$. In *any single*-phase region of the (T, ρ) plane $Q_L \to \frac{1}{3}$, 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,* $\overline{\rho}(T) \equiv \frac{1}{2}(\rho_- + \rho_+)$ for $T < T_c$, while, more generally,

$$1 \geq Q_\infty(T;\rho) = 1 - 4y^2/(1 + 6y^2 + y^4) > \tfrac{1}{2}, \quad (3)$$

where $|y| = 2|\rho - \overline{\rho}(T)|/(\rho_+ - \rho_-) < 1$. Finally, *at criticality,* $Q_L(T_c;\rho_c)$ approaches a *universal value* Q_c which, for cubic boxes with periodic boundary conditions, is $Q_c = 0.4569\cdots$ for classical (vdW) [19(b)] or ∞-range

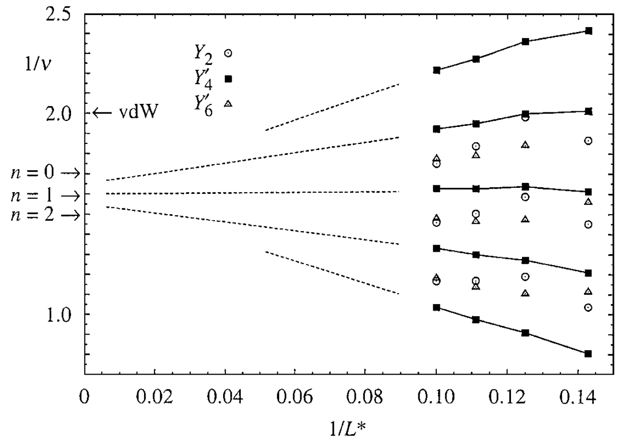

FIG. 3. Estimation of the correlation exponent ν from the deviations $T_j(L) - T_c$ for various properties $Y_j(T)$ on the critical isochore: see text and [11(c)]. Values for $n = 0$, 1, 2, i.e., SAW, Ising, and XY, and classical (vdW) criticality are indicated.

systems [19(c)] but $Q_c(n = 1) = 0.6236(2)$ for Ising [19(d),(e)] and $Q_c(n = 2) = 0.8045(1)$ for XY [19(f)] systems, while $Q_c(n = 0) = 0$ [19(b)]. For long-range, $1/r^{3+\sigma}$ systems, $Q_c(\sigma)$ and also $\gamma(\sigma)$ increase almost linearly from vdW to Ising values in the interval $\frac{3}{2} \leq \sigma \leq (\gamma/\nu)_{n=1} \simeq 1.96_6$ with $Q_c(\sigma = 1.9) \simeq 0.600$ and $\gamma(\sigma = 1.9) \simeq 1.20_5$ [17(b)].

The result (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 $\overline{\rho}(T)$ when L increases. (For $T \lesssim T_c$, 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 [19], 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 θ $(= \omega\nu)$ is the leading correction-to-scaling exponent;

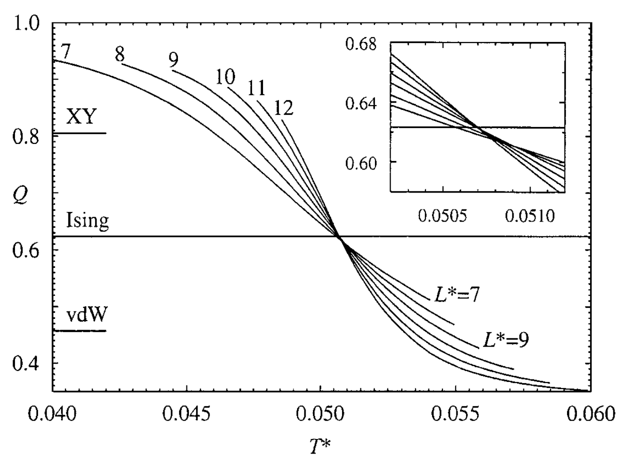

FIG. 4. Plots of $Q_L(T; \rho)$ on the Q-loci, $\rho_Q(T; L)$, providing estimates for T_c and Q_c. Classical, XY, and Ising values of Q are shown. The inset enlarges the intersection region.

for classical and Ising criticality one has $(\theta/\nu, \varphi) = (1, 3)$, $\simeq (0.82, 2.41)$, respectively [16]. With this guidance, the large-scale inset in Fig. 4 leads to our estimate $T_c^* \simeq 0.05069(2)$ but also yields $Q_c \simeq 0.624(2)$: this is surprisingly close to the Ising value [25] and far from the vdW, XY, and SAW values—an unexpected bonus. Likewise, $1/r^{3+\sigma}$ effective potentials with $\sigma \leq 1.9$ are excluded.

Estimation of ρ_c.—Finally, we examine $\rho_0^c(L)$ and $\rho_Q^c(L)$, i.e., the $(k = 0)$ and Q-loci intersections with the estimated critical isotherm, $T = T_c$. According to scaling, the deviations, $\Delta\rho_0^c$ and $\Delta\rho_Q^c$, decay as $L^{-\psi}$ with $\psi = (1 - \alpha)/\nu$ [18], so we may suppose $1.2 < \psi \leq 2$ [16]. Figure 5 displays the deviations vs $L^{-\psi}$ for $\psi = 1.2$, 1.4, 1.7, and 2 with "l_0 shifts" [OPF(19), Fig. 2; OFP(3.1)] chosen to provide linear plots. From these and further plots [11(c)] we conclude $\rho_c^* = 0.0790(25)$.

In further support of our ρ_c estimate, we mention first that when the coexistence curve, $\rho_\pm(T)$, is plotted vs $\sqrt{\rho^*}$—as is reasonable since all powers $\rho^{j/2}$ for integral j appear in virial expansions for the RPM [8]—it becomes markedly more symmetrical [resembling (ρ, T) plots for the HCSW and other simple fluids]. Then, the *corresponding* diameter, $\sqrt{[\overline{\rho}^*_{1/2}(T)]} = \frac{1}{2}(\sqrt{\rho_-^*} + \sqrt{\rho_+^*})$, is only mildly curved and naive extrapolations to T_c yield $\rho_c^* = 0.078(4)$.

In conclusion.—By implementing recently tested [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 ν and γ, and for the critical fourth-moment ratio,

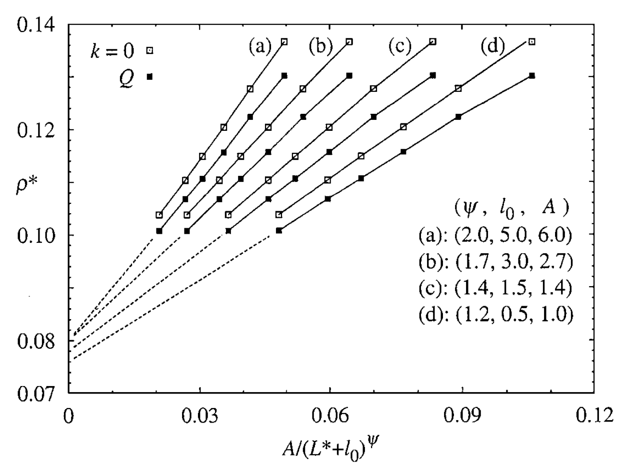

FIG. 5. Estimation of ρ_c^* from plots of $(k = 0)$ and Q-locus values at T_c (open and solid squares) vs $A/(L^* + l_0)^\psi$ for various values of ψ and optimal shifts l_0. The scale parameter A has been invoked merely for graphical clarity. Note $\psi < 1.6$ requires smaller shifts tending to exclude vdW criticality $(\psi = 2)$.

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 criticality [18], and for his discovery of effective estimators for ν. The support of the National Science Foundation (through Grant No. 99-81772, M. E. F.) and the Department of Energy, Office of Basic Energy Sciences (DE-FG02-01ER15121, A. Z. P.) is gratefully acknowledged.

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[23] For the extrapolations at the heart of our approach, precise *and* reliable simulation data are essential [11(c)]: this restricts the maximum size of the systems we can *usefully* simulate. To provide a basis for judging this matter we note (but see also [11(c)]) that for $L^* = 12$ a total of 167 state points (SPs) were used in the range $0.04 < T^* < 0.083$ with close spacing in T^* and ρ^* near criticality. A typical SP had $(2-10) \times 10^4$ *independent* samples amounting to $\sim 10^{10}$ MC steps *per* SP. For smaller L^*, the number of independent samples was larger by factors of 10–50. All simulations were analyzed for autocorrelation. Reweighted histograms were crosschecked using *nonoverlapping* SP sets.
[24] For this reason the estimates quoted in the "Note added in proof" in [11(a)] are inaccurate.
[25] A similar analysis of $Q_L^{(1,2)} \equiv \langle |m| \rangle^2 / \langle m^2 \rangle$ on the RPM Q-loci confirms T_c^* and yields $Q_c^{(1,2)} \simeq 0.807$ close to the corresponding Ising value 0.8070(9) [E. Luijten (unpublished)].