Ginzburg Criterion for Coulombic Criticality

Michael E. Fisher and Benjamin P. Lee
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742
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To understand the range of close-to-classical critical behavior seen in various electrolytes, generalized Debye-Hückel theories (that yield density correlation functions) are applied to the restricted primitive model of equisized hard spheres. The results yield a Landau-Ginzburg free-energy functional for which the Ginzburg criterion can be explicitly evaluated. The predicted scale of crossover from classical to Ising character is found to be similar in magnitude to that derived for simple fluids in comparable fashion. The consequences in relation to experiments are discussed briefly. [S0031-9007(96)01424-X]

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How can one understand the fact that some electrolyte solutions display classical (or van der Waals) critical behavior down to deviations from criticality of $|t| = |T - T_c|/T_c \sim 10^{-4}$ or less [1], while others exhibit purely Ising-type criticality [2] or, in some cases, *crossover* to Ising character at scales $t_\times \sim 10^{-1.5}-10^{-2.5}$ [3,4]? The system triethylhexylammonium triethyhexylboride ($N_{2226}B_{2226}$) in diphenyl ether [1] so far reveals no hint of Ising character and is also the one that appears to approximate most closely the simplest sensible theoretical model of an ionic system, namely, the restricted primitive model (RPM), corresponding of $N = N_+ + N_-$ hard spheres of diameter a with N_+ carrying charges $+q$ and $N_-(=N_+)$ charges $-q$, in a medium of dielectric constant D. Real solutions and molten salts deviate from the RPM in *many* ways: soft cores, differently sized ions, nonadditive ionic diameters, long-range van der Waals interactions, short-range attractions, ionic polarizability, specific ionic chemical bonding, the molecular structure of the solvent, etc. [5–7]. At least some of these features *must* be responsible for the observed *variation* of $t_\times$, from $t_\times \simeq 1$ down to, perhaps, $t_\times \sim 10^{-5}$. Nevertheless, the most appealing scenario is that the RPM itself, as an "extremal model," displays purely classical critical behavior *or*, failing that, has a very small value of $t_\times$ that is increased by more realistic interactions. (To match the results for $N_{2226}B_{2226}$ one needs $t_\times \lesssim 10^{-4}$ [5].) Here we address this scenario. Sadly, perhaps, our analysis, which encompasses all the leading physical effects [4], does *not* support this attractive picture. Instead, it provides grounds for believing that $t_\times$ for the RPM is of comparable magnitude to that for simple molecular fluids or liquid mixtures that exhibit little if any non-Ising behavior.

To introduce our approach [8], note first that all currently available theories predicting ionic criticality (for dimensionalities $d > 2$ [9]) yield classical behavior because, at heart, they are of mean-field character [5–9]. Recall also that the standard approximate integral equations such as the HNC, YBG, MSA, etc., yield *no* account of the critical region or else fail to predict divergent critical-point density fluctuations [4,5,8]. Second, direct simulations of the RPM [5,10] are far from being able to distinguish between classical and Ising criticality. In principle, a renormalization group (RG) treatment of the fluctuations could reveal the true nature of Coulombic criticality, but, in practice, that requires an appropriate LGW effective Hamiltonian which has *not* been available [5]. Furthermore, *quantitative* aspects become important if, as seems likely [5,6(a)], a scale $t_\times$ is present.

However, as emphasized previously [8], a sufficiently good mean-field free energy can provide a foundation for an LGW Hamiltonian; then one may estimate the domain of validity of classical critical behavior by using the Ginzburg criterion [11] which, indeed, is implied by RG theory [12]. If $m(\mathbf{r}) = [\rho(\mathbf{r}) - \rho_c]/\rho_c$ is the order parameter (the overall ionic density being $\rho \equiv N/V$) then, omitting the ordering field h, the expected LGW form in d spatial dimensions is

$$\mathcal{H}/k_BT = a^{-d} \int d\mathbf{r}[-\bar{f}(m) + \frac{1}{2} b_2^2(\nabla m)^2 + \ldots], \tag{1}$$

with the spatially uniform reduced free-energy density

$$-\bar{f} = \frac{1}{2} c_2 t m^2 - h_3 t m^3 + \frac{1}{4} u_4 m^4 + O(tm^4, m^5). \tag{2}$$

The further gradient terms neglected in (1) and the corrections in (2) are not needed for a leading order description of criticality: *in principle*, however, large or anomalous values of these terms could prove quantitatively significant.

To quantify the Ginzburg criterion we examine the fluctuations of the order parameter, normalized by the spontaneous order, m_0 ($t < 0$), in a d-sphere, Ξ, of radius set by the *correlation length* $\xi(T)$, that is,

$$\mathcal{G} = \int_\Xi \frac{\langle m(\mathbf{r})m(\mathbf{0})\rangle - \langle m\rangle^2}{m_0^2} \frac{d^d r}{|\Xi|_d} = \frac{\int_\Xi d\mathbf{r} G_{\rho\rho}(\mathbf{r})}{\rho_c^2 m_0^2 |\Xi|_d}, \tag{3}$$

where $G_{\rho\rho}(\mathbf{r}) = \langle \rho(\mathbf{r})\rho(\mathbf{0})\rangle - \langle \rho \rangle^2$ is the density-density correlation function, while $|\Xi|_{d=3} = \frac{4}{3}\pi\xi^3$. Since $G_{\rho\rho}(\mathbf{r})$ decays fast on the scale ξ, it is convenient to extend the integral to ∞ and accept (for $d = 3$)

$$\mathcal{G}(T) = 3\chi(T)/4\pi\rho_c m_0^2(T)\xi^3(T) \qquad (t < 0), \quad (4)$$

where $\chi = \int d\mathbf{r} G_{\rho\rho}(\mathbf{r})/\rho$ is the reduced susceptibility. Treating (1) and (2) simply as a mean-field free-energy functional, $F[\rho, T]$, yields the asymptotic relations

$$\chi \approx \frac{a^3\rho_c}{2c_2|t|}, \quad m_0^2 \approx \frac{c_2|t|}{u_4}, \quad \xi^2 \approx \frac{b_2^2}{2c_2|t|}, \quad (5)$$

for $t \to 0-$ at $\rho = \rho_c$. We may now set $\mathcal{G} = 1$ to obtain an explicit estimate for the crossover scale $t_\times$, namely

$$t_G = (9u_4^2/8\pi^2c_2)(a/b_2)^6, \qquad \text{for } d = 3, \quad (6)$$

below which fluctuations dominate and the mean-field theory loses validity: Ising behavior should be exhibited for $|t| \ll t_G$.

Now, judging by concordance with the simulation estimates of T_c and ρ_c [8(b),10], the most successful available theory for the RPM critical region [8] is based on the Debye-Hückel (DH) analysis [13], supplemented by (i) Bjerrum $(+,-)$ ion pairing (Bj), (ii) solvation of the dipolar pairs in the fluid of free ions (DI), and (iii) hard core (HC) repulsions [4,14]. From the free energy $F(\rho, T)$ of this DHBjDIHC theory {which is subject to minor numerical variants [4,8(b)]} one can, by careful numerics [15], extract, in addition to ρ_c and T_c, c_2 and u_4 in (2); note that h_3 plays no role in (6).

But the Ginzburg analysis demands also the coefficient b_2^2 of the gradient-squared term in (1) that sets the amplitude of the correlation length [see (5)]. Indeed, b_2 corresponds to the *range* of the *effective* density-density attractions in the RPM: these are embodied in the density correlations functions and, more explicitly, in the wave-vector dependent susceptibility

$$\chi(\mathbf{k}) = \frac{\chi(T)}{1 + \xi^2k^2 + \dots} \approx \frac{\rho_c a^d}{c_2 t + b_2^2 k^2 + \dots}. \quad (7)$$

The last relation (for $t \to 0+, \rho = \rho_c$) follows by identifying, as before, the free energy for a *nonuniform* system with $\mathcal{H}$ [4]. In the past, DH theory has been regarded as throwing light only on the *charge* correlation function, G_{qq}, while remaining silent on $G_{\rho\rho}$. However, in [4] we have shown how DH theory and its necessary DHBjDIHC extensions [8] can be *generalized* in a rather straightforward way to yield a classical functional of $\rho(\mathbf{r})$ and thence an explicit mean-field expression for $\chi(\mathbf{k})$. Furthermore, the unexpected divergence of $\xi(\rho, T)$ predicted when $\rho \to 0$ turns out to be universal and *exact*. By this route, therefore, the critical coefficient b_2 is revealed and the crossover scale t_G can be explicitly calculated [15].

Before describing our results for t_G, however, we note that Leote de Carvalho and Evans [16] have recently demonstrated the strategy set out above [8] by appealing to the generalized mean-spherical approximation (GMSA). This ingenious, OZ-based [14] approximate integral equation [17] repairs the simple MSA (for which the density fluctuations remain bounded) by adding to the direct correlation functions a term with parameters which are adjusted to satisfy various desirable sum rules; thence ξ diverges at criticality and b_2 can be estimated. Unfortunately, however, the GMSA exhibits some serious defects: (a) the correlation length $\xi(\rho, T)$ varies nonuniversally and quite incorrectly when $\rho \to 0$ [4], thence casting doubt on the plausibility of the results for $\rho \simeq \rho_c$; (b) the predicted value of T_c is significantly too high [8,10]; (c) no account is taken of Bjerrum pairing; and (d) apparently as a result of this, the GMSA free energy violates Gillan's upper bound [18] throughout the critical region (while DHBjDIHC theories satisfy it). Consequently, although the GMSA values for t_G [16] provide an interesting benchmark, they are surely not adequate for the purpose at hand.

For reference we start with pure DH theory [4,8] which yields $c_2 = 1/64\pi, u_4 = 1/3072\pi$ [19] while $b_2^2/a^2 = (1 + \frac{20}{3}\ln 2 - 6\ln\frac{7}{3})/64\pi \simeq (0.052)^2$ [4]. Via (6) these yield $t_G \simeq 12.90$. This number is large and certainly not suggestive of any significant regime of classical behavior, but the derivation of (6) entailed various essentially arbitrary numerical assignments. For calibration, therefore, it is essential to calculate t_G by a comparable procedure for a simple-fluid model that one can be confident exhibits typical Ising behavior.

To that end we start with the functional generalization of the Mayer expansion for a single-component fluid with a short-range pair potential $u(r)$, namely

$$\begin{aligned} F^{SR}[\rho(\mathbf{r})]/k_BT = &-\int d\mathbf{r}\,\rho(\mathbf{r})[\ln\Lambda^3\rho(\mathbf{r}) - 1] \\ &- \frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\rho(\mathbf{r})f(u(\mathbf{r} - \mathbf{r}^1))\rho(\mathbf{r}') \\ &+ O(\rho^3), \end{aligned} \quad (8)$$

where $f(x) = \exp(-x/k_BT) - 1$ and $\Lambda = h/\sqrt{2\pi m k_B T}$ [8(b)]. This second-virial level suffices to describe the attractions driving criticality, for which we take a *square well* (SqW) of range λa and depth ε. For the repulsions we adopt *hard cores* of diameter a: to treat these we follow our RPM approach [8] and approximate the $O(\rho^3)$ terms by a *local* expression of *free-volume* (FV) or Carnahan-Starling (CS) form [4,8]. Note, however, that in treating both this SqWHC model and the RPM, the CS expression is not obviously preferable since the attractive interactions (direct or effective) necessarily enter the true higher-order virial coefficients and act to soften the hard-core effects.

In the FV approximation the critical parameters are

$$\rho_c = \frac{\rho_{\max}}{3}, \qquad \frac{\varepsilon}{k_BT_c} = \ln\left(\frac{\lambda^3 + 57B^*/16\pi}{\lambda^3 - 1}\right), \quad (9)$$

with $B^* = 1/a^3\rho_{\max}$. For the range $\lambda = 1.4-1.7$ that reasonably models real simple fluids [20], T_c depends strongly on λ. However, $k_BT_c = 1.48\varepsilon$ should describe the corresponding van der Waals/classical theory quite well [5]; thus for the assignments $B^* = \frac{2}{3}$ and $\frac{4}{9}\sqrt{3}$, which correspond to the exact hard-core second virial (2V) coefficient and bcc close packing, respectively [8], we choose $\lambda \simeq 1.65$ and 1.43. The LGW parameters in (2) are found to be $u_4 = 3/16B^*$,

$$c_2 = (57B^* + 16\pi\lambda^3)\varepsilon/108k_BT_cB^{*2}, \tag{10}$$

$$b_2^2 = \frac{2\pi a^2}{135B^{*2}}\left[\frac{(\lambda^5 - 1)(1 + 57B^*/16\pi)}{\lambda^3 - 1} - 1\right]. \tag{11}$$

Note that in the infinite range Kac-Baker limit, $\lambda \to \infty$ with T_c fixed, one has $b_2 \to \infty$ and correctly finds $t_G \to 0$.

Using the CS hard-core form one can derive a quintic equation for the critical density [21] which yields $\rho_c a^3 \simeq 0.249\,129$. Normalizing to $k_BT_c/\varepsilon = 1.48$ as above leads to $\lambda \simeq 1.55$.

The third column of Table I lists the values of t_G for the SqWHC model found using the various hard-core approximations, with λ chosen as indicated, and, for reference, with $\lambda = 1.50$. For completeness, an RPA treatment [16] is included. The crucial LGW coefficients are also given. The last column presents the correlation length amplitude, ξ_0^+, defined via $\xi(\rho_c, T) \approx \xi_0^+/t^{1/2}$ as $t \to 0+$ [22]. These estimates all lie quite close to $0.41a$. On the other hand, the values of t_G prove very sensitive to the approximations, ranging from 0.33 to 2.4 (even discounting the HC/bcc value). Since $t_G \sim b_2^6$ [see (6)], a strong dependence on λ is not surprising; but one might have hoped for better agreement among the approximate methods. Nonetheless, we may conclude that $t_G = 10^{\pm 0.5}$ will characterize fluids that display only Ising behavior (or "immediate" crossover).

We may now assess the data given in Table II for the RPM. In addition to t_G and ξ_0^+/a (in the second and last columns) it is instructive to examine the estimates for $T_c^* \equiv k_BT_cDa/q^2$ and $\rho_c^* = \rho_c a^3$: These provide a measure of the merit of the various approximations relative to the simulation data [10] which may be summarized by $10^2T_c^* = 5.2-5.6$, $10^2\rho_c^* = 2.3-3.5$ [8(b)]. Although the LGW coefficients here are factors of 3–100 smaller than for the SqWHC model, the ratio ξ_0^+/a remains of order unity [4] and is again fairly insensitive to the approximations: Those yielding (T_c^*, ρ_c^*) in the simulation range suggest $\xi_0^+ \simeq 0.80$. For reference, the table also lists the critical values of $Z \equiv p/\rho k_BT$ and the inverse Debye length $\kappa = (4\pi q^2\rho_1/Dk_BT)^{1/2}$, where $\rho_1 = \rho_+ + \rho_- = \rho - 2\rho_2$ is the density of *free ions* while ρ_2 is that for the *ion pairs* [5,8]. The ratio $(\rho_2^*/\rho^*)_c$ measures the degree of pairing in the critical region: it is quite significant [8,18].

The most striking feature of Table II, however, is the evidence that t_G for the RPM lies in the range $10^{0.3}$ to $10^{1.4}$ and so significantly *greater* than the value of t_G for the hard-core-square-well model. From this perspective, the RPM should *not* have an unduly small region of Ising-like character but rather one of the same order, or even larger, than in simple fluids, a conclusion certainly at variance with the most natural interpretation of the experimental evidence [1–3,5].

Although the DHBjDIHC theories account well for the leading physical effects near criticality and all leading terms have been included in $\mathcal{H}_{LGW}$, it is *possible* that t_G, as calculated here, is a deceptive measure of the true RPM crossover scale, $t_\times$. Perhaps the ion-dipole and dipole-dipole interactions, neglected as of order ρ^3, play a special role [7]; this is being studied within a DH-style approach [23]. In principle, strong asymmetric terms, such as h_3 and u_5 in (2), could, under the full nonlinear RG flow, invalidate the perturbative Ginzburg analysis. Higher-order gradient terms in $\mathcal{H}_{LGW}$, especially if negative as arguments of Nabutovskii *et al.* [24] suggest, might, instead, bring RPM criticality within the crossover domain of some multicritical point [5]. The fact that the crossovers seen experimentally are much sharper than standard [25] (taking place in a decade or less [3,26]) supports this view. To justify such a scenario, however, seems to demand a more sophisticated and quantitative RG analysis than normally feasible.

Conversely, if the RPM itself does exhibit *no significant crossover* from classical behavior, *as our analysis indicates*, the anomalous experimental results [1,3] must be ascribed to one or more of the features lacking in the RPM that were listed initially [5–7]. Some of these, like the presence of short-range van der Waals or solvent-mediated attractions, including the breaking of the $(+,-)$ charge symmetry, can and will be incorporated in our formalism although, in truth, it is hard to see how they will significantly alter the t_G values. Indeed, the experimental trends seem, as mentioned, to indicate that $t_\times$ always *increases*

TABLE I. Ginzburg crossover scale, t_G, and critical parameters predicted for a hard-core square-well fluid (range λa) [15]. See text for hard-core (HC) approximations and Ref. 16 for RPA.

HC	λ	t_G	k_BT_c/ε	$\rho_c a^3$	c_2	u_4	b_2/a	ξ_0^+/a
bcc	1.43_3	0.09_7	1.48	0.433_0	2.023_5	0.243_6	0.550_6	0.38_7
2V	1.65_1	1.62_1	1.48	0.159_2	0.492_6	0.089_5	0.323_4	0.46_1
	1.50	2.41_8	1.13_1	0.159_2	0.539_5	0.089_5	0.298_0	0.40_6
CS	1.55_3	0.28_4	1.48	0.249_1	0.947_8	0.113_1	0.419_1	0.43_0
	1.50	0.33_0	1.33_4	0.249_1	0.979_2	0.113_1	0.406_6	0.41_1
RPA	1.50	1.5_7	1.26_7	0.245_7	0.673_5	0.112_5	0.333_2	0.40_6

TABLE II. Ginzburg crossover scale, t_G, and critical parameters predicted for the RPM at various levels of approximation [4,15]: DH, pure Debye-Hückel [4,13]; GMSA [16]; DHBj, with naive ion pairing [5,8]; +DI with dipole-ionic fluid solvation (and $a_1 = a$, $a_2 = 1.161\,98a$ [8]); hard-core treatments /bcc/2V/CS, see text and [8]; DI′, with a new charging process [23].

Approx.	t_G	$10^2 T_c^*$	$10^2 \rho_c^*$	$\kappa_c a$	$10^2 \rho_{2c}^*$	$10 Z_c$	$10^2 c_2$	$10^3 u_4$	b_2/a	ξ_0^+/a
DH	12.9_0	6.25	0.49_7	1	0	0.90_4	0.49_7	0.10_4	0.051_7	0.73_3
GMSA	1.0_8	7.85_8	1.44_8	1.52_2	0	0.84_8	1.61_6	0.33_9	0.095_3	0.75_0
DHBj	12.9_0	6.25	4.51_7	1	2.01_0	4.54_9	41.01_4	704.6	0.469_4	0.73_3
+DI	5.3_6	5.74_0	2.77_8	1.12_3	1.10_1	2.23_6	2.29_5	1.53_0	0.113_8	0.75_1
+DI/bcc	10.6_7	5.54_2	2.59_4	1.02_9	1.06_4	2.48_4	2.22_3	2.24_9	0.115_9	0.77_7
+DI/2V	23.2_5	5.22_7	2.44_3	0.92_3	1.04_4	2.82_3	2.17_8	3.71_7	0.120_8	0.81_9
+DI/CS	21.5_2	5.24_9	2.45_4	0.93_1	1.04_6	2.79_8	2.18_5	3.54_8	0.120_4	0.81_5
+DI′	1.2_3	5.96_9	2.38_1	1.06_9	0.91_9	1.68_0	1.77_0	7.98_1	0.122_3	0.91_9
+DI′/bcc	2.2_5	5.78_4	2.14_5	0.97_8	0.85_2	1.87_4	1.65_3	10.24_9	0.121_5	0.94_5
+DI′/2V	4.3_1	5.50_6	1.91_9	0.87_7	0.79_1	2.13_7	1.54_3	14.08_0	0.122_6	0.98_7

when the Coulombic forces have to compete with solvophobic effects. Unfortunately, one must also allow that particular impurities might distort the data in unexpected ways: One can imagine selective binding leading to “big” dipoles, or long ionic “rods.” The discovery, discussed in [4], that the dimensionless correlation length parameter $\xi_0^+ \rho_c^{1/d}$ fits our calculations rather well when the *Ising*-fitted amplitudes are used may point in this direction.

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