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Abstract

We study the Coulombic criticality of ionic fluids within the restricted primitive model (RPM). We indicate that for the RPM, analysed in terms of the field of charge density, the corresponding Landau-Ginzburg-Wilson effective Hamiltonian has a negative φ^4-coefficient. In that case, solving the "exact" renormalization group equation in the local potential approximation, we show that close initial Hamiltonians may lead either to a first order transition or to an Ising-like critical behavior, the partition being formed by the tri-critical surface. This situation apparently illustrates the theoretical wavering encountered in the literature concerning the nature of the Coulombic criticality. Nevertheless, it is most probable that, in terms of the field considered, the model does not display any criticality.

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Coulombic criticality is often studied theoretically in terms of the Restricted Primitive Model (RPM: equal number N_+ and N_- of positive and

negative hard spheres of equal diameter, d, with charges, $\pm ze$, immersed in a structureless solvent of dielectric permittivity ϵ; $z^2/\epsilon = 1$ in what follows). If one generally agrees on the existence of a liquid-gas-like transition at low concentration and low temperature in the RPM, it is still not evident what kind of critical behavior the model actually possesses. Mean-field-like or Ising-like critical behavior, crossover from mean-field to Ising behavior, tricriticality or first order transition: all these conclusions have been expressed and discussed [1]. In principle, a renormalization group (RG) treatment could yield the actual critical behavior of the model provided that an adequate Landau-Ginzburg-Wilson (LGW) effective Hamiltonian be known [2]. With this aim in view, we have used the Hubbard-Schofield method (previously applied to the liquid-gas systems) [3] to get a LGW Hamiltonian for the RPM. The field arising for the RPM in this approach is conjugate to the field of charge-density and corresponds to that of the Sine-Gordon representation of the Coulomb gas model [4]. This field was used in studies of the metal-insulator transition (see e.g. [5]) and of the RPM criticality [6]. Unfortunately, in all these studies the hard-core terms eventually disappeared, since the Sine-Gordon theory implies point particles. Irrespectively of that, there is a debate in particular to know whether or not one can refer to tricriticality within the RPM [7, 8]. In this letter we show that the LGW Hamiltonian of the RPM, expressed in terms of the above field and with all the hard-core contributions taken into account, is similar to that of the Ising-like systems but with a negative φ^4-coefficient u_4. We then emphasize, for the first time, all the possible scenari given by the RG analysis: an initial Hamiltonian with $u_4 < 0$ may lead either to a first order transition or to an Ising-like critical behavior, the partition being formed by the tri-critical surface. The large negative values found for the Hamiltonian coefficients for the RPM (expressed in terms of the field, conjugate to the charge density), suggest that the transition so described would rather be of the first order. Let us summarize the main lines of the calculation of the effective Hamiltonian: the details will be published elsewhere [9].

The Hamiltonian of the RPM (in units of k_BT) is a sum of the ideal part, $H_{\rm id}$, hard-core part, $H_{\rm hc}$, and the coulombic part, $H_{\rm c}$:

$$H = H_{\rm id} + H_{\rm hc} + \frac{1}{2}{\sum_{\mathbf{k}}}' \nu(k)\,(\rho_{\mathbf{k}}\rho_{-\mathbf{k}} - \rho) \qquad (1)$$

The coulombic part, $H_{\rm c}$, in Eq.(1) is written in terms of the *charge density* fluctuation amplitudes, $\rho_{\mathbf{k}} = n^a_{\mathbf{k}} - n^b_{\mathbf{k}}$, which are expressed in terms of the amplitudes of *density* fluctuations of positive (a), $n^a_{\mathbf{k}} = \Omega^{-\frac{1}{2}} \sum_{j=1}^{N_+} \exp\left\{-i\mathbf{k}\mathbf{r}^a_j\right\}$, and negative ($b$), $n^b_{\mathbf{k}} = \Omega^{-\frac{1}{2}} \sum_{j=1}^{N_-} \exp\left\{-i\mathbf{k}\mathbf{r}^b_j\right\}$, ions, $\mathbf{r}^{a,b}_j$ denote coordinates of the particles, $\rho = 2N_+/\Omega$ is the density, and Ω is the volume of the system. In Eq.(1) $\nu(k) \equiv (4\pi e^2/k_BT)/k^2$, and the prime over the sum denotes that terms with $\mathbf{k} = 0$ are excluded.

We write the free energy $\mathcal{F}$ of the RPM (in units of k_BT), as a sum,

$$\mathcal{F} = \mathcal{F}_{\rm id} + \mathcal{F}_{\rm hc} - \log\left\langle e^{H_{\rm c}}\right\rangle_{\rm hc} \tag{2}$$

of the ideal part, $\mathcal{F}_{\rm id}$, the "direct" hard-core part, $\mathcal{F}_{\rm hc}$, and the coulombic part, with $H_{\rm c}$ depending on the amplitudes, $\rho_{\mathbf{k}}$; $\langle\cdots\rangle_{\rm hc}$ denotes the average over the reference hard-sphere system. Following the Hubbard-Schofield scheme [3], we perform "Gaussian" transformation from variables $\rho_{\mathbf{k}}$ to variables $\varphi_{\mathbf{k}}$ and after some algebra we arrive at the following result [10]

$$\mathcal{F} = -\log\left[\int \mathcal{D}\varphi(\mathbf{r}) e^{-\int d\mathbf{r} H_{\rm LGW}(\varphi)}\right] + C \tag{3}$$

where the real field $\varphi(\mathbf{r})$ is the Fourier transform of $\varphi_{\mathbf{k}}$, C is a field independent constant (unimportant in the subsequent RG analysis) and $H_{\rm LGW}(\varphi)$ is an effective LGW Hamiltonian which, discarding the derivatives of the field (local potential approximation), may be written as

$$H_{\rm LGW}(\varphi) = \frac{1}{2}\left(\nabla\varphi(\mathbf{r})\right)^2 + V\left(\varphi(\mathbf{r})\right) + f_{\rm id} + f_{\rm hc} \tag{4}$$

with corresponding free energy densities, $f_{\rm id} = \mathcal{F}_{\rm id}/\Omega$, $f_{\rm hc} = \mathcal{F}_{\rm hc}/\Omega$ and "potential function":

$$V(\varphi) = \frac{1}{9\pi^2} \sum_{n=1}^{\infty} \frac{b^{2n}}{(2n)!} u_{2n} \varphi^{2n} \tag{5}$$

here $b^2 = 4\pi\left(3\pi\right)^{2/3} \rho^{*1/3}/T^*$ ($\rho^* = \rho d^3$ is the reduced density and $T^* = k_BTd^3/e^2$ is the reduced temperature). As for the ordinary fluid [3], the coefficients u_{2n} are expressed in terms of the cumulant averages, $\langle\rho_{\mathbf{k}_1}\ldots\rho_{\mathbf{k}_n}\rangle_{\rm c,hc}$, performed over the reference system having only hard–core interactions. Let us stress that the terms $f_{\rm id}$ and $f_{\rm hc}$ *do not depend* on the field φ, which

is conjugate to the *charge-density* fluctuations [11], and thus play a role of *additive constants*.

It is straightforward to show that $u_2 = 1$, and that neglecting in (5) all terms with $n \geq 2$, (i.e. in the approximation $V(\varphi) \sim \varphi^2$), the usual Debye-Hückel result for the coulombic part of the free energy is obtained. Longer computations are required to find u_{2n} for $n \geq 2$. First we calculate these quantities for the *lattice–gas* model and find that $u_{2n} = (-1)^{n+1}$ which, together with $f_{\rm id}$, yield the usual Sine-Gordon Hamiltonian for the RPM [12]. To perform evaluation of the *off–lattice* coefficients u_{2n} we use a symmetry of the RPM with respect to the hard-core interactions, and the definitions of the correlation functions, [13, 14]. Finally, we express these coefficients in terms of the Fourier transforms (taken at zero wave–vectors) of the "cluster" functions of the reference hard–sphere system. In obvious notations [14] these read: $h_2(1,2) \equiv g_2(1,2) - 1$, $h_3(1,2,3) \equiv g_3(1,2,3) - g_2(1,2) - g_2(1,3) - g_2(2,3) + 2$, etc., where $g_n(1,\ldots,n)$ are n-particle correlation functions. We thus conclude that the high-order terms in (5) mirror cluster-cluster (i.e. ion-dipole, dipole-dipole, etc.) interactions in the system. Using the relation between the g_{n+1} and g_n [14],

$$\chi\rho^2\frac{\partial}{\partial\rho}\rho^n g_n = \beta\rho^n\left[n\, g_n + \rho\int d\mathbf{r}_{n+1}\,(g_{n+1} - g_n)\right], \qquad (6)$$

where $\chi = \rho^{-1}\partial\rho/\partial P$ is the compressibility, we iteratively express the Fourier transforms of h_n at zero wave–vectors, $\tilde{h}_n(\mathbf{0})$, in terms of $\tilde{h}_{n-1}(\mathbf{0})$ and its density derivative, and ultimately in terms of $\tilde{h}_2(0)$ and its density derivatives. Then we use the relation [14] $\rho\tilde{h}_2(0) = \rho k_B T\chi - 1 \equiv z_0$, and obtain coefficients for the *off–lattice* effective Hamiltonian. In particular, $u_2 = 1$, $u_4 = -(1 + 3z_0)$, $u_6 = 1 + 15(z_0^2 + z_0 z_1 + z_1)$, ... where $z_1 \equiv \rho\,(\partial z_0/\partial\rho)\,,\ldots$ To obtain z_0 one can use the virial expansion for the hard-sphere pressure, $P/\rho k_B T = 1 + \sum_k B_k\rho^k$ with the coefficients $B_1,\ldots B_6$ known [13] (for small densities), or the Carnahan-Starling equation of state [13, 14]. Therefore, applying the above scheme, *all* the coefficients of the effective potential $V(\varphi)$ may in principle be found.

We have studied the density dependence of u_{2n} up to $2n = 14$ and observed that all the coefficients are *negative* in the density interval $\sim 0.07 \sim 0.09$ where the critical density of the RPM is expected to be. We have then performed an *empirical* analysis and found that the boundaries of the density interval where the coefficients u_{2n} are negative depend fairly linearly on

$1/n$ (see Fig. 1). Extrapolating this dependence we have found that all the coefficients become *positive* for $n > 22$ (see Fig. 1). Being secure in the knowledge that the effective Hamiltonian is bounded from below, we can envisage a RG analysis.

We thus consider the "exact" RG equation in the local potential approximation [15] in three dimensions which, using the same notations as in [16], reads:

$$\dot{f} = \frac{1}{4\pi^2}\frac{f''}{1+f'} - \frac{1}{2}yf' + \frac{5}{2}f \tag{7}$$

in which y stands for the dimensionless field and $f(y,l) = \partial V(y,l)/\partial y$, $f' = \partial f/\partial y$, $f'' = \partial^2 f/\partial y^2$, $\dot{f} = \partial f/\partial l$ with l the RG scale parameter (that relates two different "momentum" scales of reference such that $\Lambda_l = e^{-l}\Lambda_0$).

Ideally, the question raised may be formulated as follows: considering the effective Hamiltonian for the RPM at its assumed critical point (taken e.g. from Monte Carlo data [17, 18]) as an initial Hamiltonian ($l = 0$) for Eq. (7), will the solution of Eq. (7) flow toward the Wilson-Fisher (Ising) fixed point [the unique non-trivial fixed point of Eq.(7)] or not?

Unfortunately, considering the function $f(l = 0, y)$ which gives the initial conditions of the RPM for Eq.(7) (at $\rho_c^* = 0.0857$, $T_c^* = 0.052$ [17], or $\rho_c^* = 0.080$, $T_c^* = 0.0488$ [18]), we have observed that the denominator $1 + f'(y)$ in (7) has singularities in the interval, $0.1 < y < 0.12$. Moreover, Eq.(7) does not allow us to handle values of Hamiltonian coefficients as large as those of Eq.(5).

We have thus simply considered that the negative value of u_4 found above could be a feature of qualitative importance for (some) ionic system. Thus we turn our attention to the solutions of Eq.(7) with initial functions involving negative values of u_4.

In [16] a detailed study of the approach to the Ising fixed point using Eq. (7) has been presented. However all the initial Hamiltonians considered were taken with $u_4 > 0$. To our knowledge, the few studies based on RG techniques that have, up to now, considered negative values of u_4, either perturbatively [19] in three dimensions or, more recently, non-perturbatively [20] in four dimensions, have concluded that there is no stable fixed point (the Ising fixed point cannot be reached starting with $u_4 < 0$) and thus to the lack of "true" criticality (there would be no divergent correlation length, like in a first order transition). Let us show that these conclusions are not completely

true (in particular that the Ising fixed point can be reached starting with $u_4 < 0$).

To be short, we consider the following simple functions as initial conditions to Eq. (7) (a detailed study of the case $u_4 < 0$ will be published elsewhere [21]):

$$f(y,0) = u_2(0)y + u_4(0)y^3 + u_6(0)y^5 \tag{8}$$

corresponding to a point of coordinates $(u_2(0), u_4(0), u_6(0), 0, 0, \cdots)$ in the space $\mathcal{S}$ of Hamiltonian coefficients (the dimension of $\mathcal{S}$ is infinite). Since we want to set $u_4(0) < 0$, and at least one positive higher term is needed to make the Hamiltonian bounded from below, we choose to set $u_6(0)$ positive. Having chosen a (negative) value for $u_4(0)$ and a (positive) value for $u_6(0)$, we use the "shooting" method [16] to determine the critical value $u_2^c(0)$ of $u_2(0)$ which brings $f(y,0)$ in the critical subspace $\mathcal{S}_c$ of $\mathcal{S}$. The "shooting" method is based on the fact that, for sufficiently large values of l, the RG trajectories go away from $\mathcal{S}_c$ in two opposite directions according to the sign of $u_2(0) - u_2^c(0)$.

Let us summarize our results by considering the case $u_4(0) = -6$ as an example (see Fig. 2).

A If $u_6(0) = 16$, we find $0.3836174 > u_2^c(0) > 0.3836151$. The associated RG trajectory goes away from the Gaussian fixed point P_G and remains in the sector $u_4 < 0$ of $\mathcal{S}_c$. Hence it never reaches the Ising fixed point that lies in the sector $u_4 > 0$. Instead the trajectory is attracted to a stable submanifold of dimension one (an infra-red stable trajectory) that, apparently, emerges from P_G. Let us denote that trajectory by $T_{u_4<0}$. *The lack of any fixed point ending $T_{u_4<0}$ means that the correlation length remains finite at the assumed transition.* This situation could be compared to the fact that no heat–capacity divergency has been observed in a Monte Carlo study of the RPM [17] or to the conclusion that "*there is no criticality*" [22] for the RPM expressed in terms of the field of charge density.

B If $u_6(0) = 20$, we find $0.30131 > u_2^c(0) > 0.30122$ and the associated RG trajectory goes toward the Ising fixed point and approaches it along the usual renormalized trajectory associated with the continuum limit of the scalar field theory in three dimension usually called the φ_3^4-field

theory. This renormalized trajectory (denoted by T_1 in [16]) interpolates between the Gaussian and the Ising fixed points. Hence *there exist initial Hamiltonians with $u_4 < 0$ that, nevertheless, belong to the basin of attraction of the Ising-like fixed point.*

C Between the two preceding cases, we find a trajectory (with $u_6(0) = 18.3125\cdots$ and $0.3324573 > u_2^c(0) > 0.3324549$) that directly flows towards $P_{\rm G}$ (it is neither attracted to $T_{u_4<0}$ nor to T_1). That kind of initial Hamiltonian obtained by adjusting two coefficients ($u_2(0)$ and $u_6(0)$) lies on the *tri-critical subspace* $\mathcal{S}_{\rm t}$ of $\mathcal{S}$. Any trajectory on $\mathcal{S}_{\rm t}$ approaches $P_{\rm G}$ along a unique (attractive) trajectory that imposes the required very slow (logarithmic) flow in the vicinity of $P_{\rm G}$.

So, it appears that for $u_4(0) < 0$, very close Hamiltonians may lead to very different behaviors and this feature is due to the vicinity of the tricritical subspace. Hence, in any treatment of the RPM which uses the field conjugate to the charge density, as an order parameter, it is justified to mention a possible vicinity of a tricritical point. The eventuality of an Ising behavior with a long crossover from an almost classical behavior is not excluded. However the very large negative values that we have found for many coefficients of the effective LGW Hamiltonian suggest that the transition studied with the use of the above order parameter corresponds rather to the case A described above (no criticality) in agreement with [22].

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References

[1] For a review see: M. E. Fisher, J. Stat. Phys. **75**, 1 (1994); J. Phys.: Cond. Matt., **8**, 9103 (1996); G. Stell, J. Phys.: Cond. Matt., **8**, 9329 (1996); J.Stat.Phys., **78**, 197 (1995).

[2] Y. Levin and M. E. Fisher, Physica **A225**, 164 (1996).

[3] J. Hubbard and P. Schofield, Phys. Lett., **A40**, 245 (1972).

[4] J. Glimm and A. Jaffe, *Quantum Physics* (Springer-Verlag, New York, 1981).

[5] Y.Saito, Progr.Theor.Phys. **62**, 927 (1979).

[6] A. L. Kholodenko and A. L. Beyerlein, Phys. Rev. **A34**, 3309 (1986).

[7] M. E. Fisher, J. Stat. Phys. **75**, 1 (1994).

[8] A. L. Kholodenko and A. L. Beyerlein, Phys. Lett. **A175**, 366 (1993).

[9] N. V. Brilliantov, J. P.Valleau, in preparation.

[10] For convenience we rescale the length and the field to get a unit ultraviolet cutoff for the wave vectors and 1/2 for the coefficient at the gradient term. Coefficients appearing at this rescaling as well as coefficients from the transformation $\{\varphi_{\mathbf{k}}\} \to \varphi(\mathbf{r})$ are adsorbed in constant C.

[11] An attempt has been done by M.E.Fisher and B.P.Lee, Phys.Rev.Lett., **77**, 3561 (1996), to derive an effective LGW Hamiltonian for the RPM with the field φ corresponding to the *overall-density* fluctuations (and also with the coefficients at φ^n determined from approximate theories with the ion-dipole and dipole-dipole interactions neglected).

[12] Some (unimportant) difference of our result from the standard [4] appears since the present calculations are performed for the canonical ensemble.

[13] J. A.Barker and D. Henderson, Rev. Mod. Phys., **48**, 587 (1976).

[14] C. G.Gray and K. E.Gubbins, *Theory of molecular fluids*, Clarendon Press, Oxford, 1984.

[15] A. Hasenfratz and P. Hasenfratz, Nucl. Phys. **B270 [FS16]**, 687 (1986).

[16] C. Bagnuls and C. Bervillier, J. Phys. Stud. **1**, 366 (1997); see also Phys. Rev. **B41**, 402 (1990).

[17] J. P.Valleau and G. M.Torrie, J.Chem.Phys., submitted.

[18] J. M.Caillol, D. Levesque and J. J. Weis, J. Chem. Phys., **107**, 1565 (1997)

[19] E. K.Riedel and F. J. Wegner, Phys. Rev. Lett., **29**, 349 (1972); Phys. Rev. **B9**, 294 (1974); A. I.Sokolov, Sov. Phys. JETP, **50**, 802 (1979).

[20] K. Langfeld and H. Reinhardt, "*Asymptotic freedom in a scalar field theory on the lattice*", UNITU-THEP-18/1996 hep-ph/9702271.

[21] C. Bagnuls and C. Bervillier, in preparation.

[22] J. Stafiej and J. P. Badiali, J. Chem. Phys. **106**, 8579 (1997).

FIGURE CAPTIONS

Figure 1 Dependence of the boundaries of the density interval where the coefficients u_{2n} of the effective Hamiltonian are negative as a function of $1/n$. Extrapolation suggests that *all* the coefficients with $n > 22$ are positive. (Note that the density at which the "negative" interval shrinks to zero, $\rho = 0.0856$ is very close to the critical density from the Monte Carlo data [17, 18]).

Figure 2 Projection onto the plane $\{u_2, u_4\}$ of various RG trajectories (in the critical subspace $\mathcal{S}_c$) obtained by solving Eq. (7). Black circles represent the Gaussian (P_G) and Ising (IFP) fixed points. The arrows indicate the directions of the RG flows on the trajectories. The ideal trajectory (dot line) which interpolates between these two fixed points represents an (attractive) infra-red stable trajectory (IRST) corresponding to the so-called ϕ_3^4 renormalized field theory in three dimensions (usual IRST for $u_4 > 0$). White circles represent the projections onto the plane of initial critical Hamiltonians. For $u_4(0) > 0$, the effective Hamiltonians run toward the Ising fixed point asymptotically along the usual IRST (simple fluid). Instead, for $u_4(0) < 0$ and according to the values of Hamiltonian coefficients of higher order (u_6, u_8, etc.), the RG trajectories either (A) meet an endless IRST emerging from P_G (dashed curve) and lying entirely in the sector $u_4 < 0$ or (B) meet the usual IRST to reach the Ising fixed point. The frontier which separates these two very different cases (A and B) corresponds to initial Hamiltonians lying on the tri-critical subspace (white square C) that are source of RG trajectories flowing toward P_G asymptotically along the tricritical IRST. Notice that the coincidence of the initial point B with the RG trajectory starting at point A is not real (it is accidentally due to the projection onto a plane of the trajectories lying in a space of infinite dimension). The restricted primitive model, expressed in terms

of the field of charge density would correspond rather to the case A characterized by the lack of criticality (no fixed point may be reached).