ELSEVIER

17 August 1998

PHYSICS LETTERS A

Physics Letters A 245 (1998) 274–278

Peculiarity of the Coulombic criticality?

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Received 22 April 1998; accepted for publication 13 May 1998
Communicated by J. Flouquet

Abstract

A field-theoretical approach to the restricted primitive model of charged hard spheres is proposed. It uses a scalar field φ, similar to that of the sine-Gordon theory of Coulomb gas, but allows taking into account the hard-core interactions. We observe that near criticality the effective Landau–Ginzburg–Wilson Hamiltonian obtained has a negative φ^4 coefficient. A non-perturbative RG analysis of such a Hamiltonian shows that this may lead either to a first-order transition or to an Ising-like critical behavior, the partition being formed by the tricritical surface. This may explain the theoretical wavering encountered in the literature relative to the nature of the Coulombic criticality. © 1998 Published by Elsevier Science B.V.

PACS: 61.20.Qg; 05.40.+j; 05.70.Jk; 64.60.Fr

The 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). Although there is general agreement 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 has. 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 discussed [1,2]. 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 is known [3]. With this aim in view, we have used the Hubbard–Schofield method (previously applied to one-component fluids) [4,5] to obtain the LGW Hamiltonian for the RPM. The scalar field φ arising in this approach is conjugate to the charge-density. It corresponds to the field of the sine-Gordon (SG) theory of a Coulomb gas [6], which was used to analyze the metal–insulator transition (see, e.g., Ref. [7]), and RPM criticality [8]. While the SG theory implies point particles, the Hubbard–Schofield approach (also based on an exact mapping of Hamiltonians) allows a complete account of the hard-core contributions.

We found that near criticality the LGW Hamiltonian of the RPM expressed in terms of φ, 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. RG analysis of the LGW Hamiltonians with negative values of u_4 has been performed perturbatively for three dimensions [9], or non-perturbatively

PII S0375-9601(98)00398-3

for four dimensions [10]. In these studies was concluded that no stable fixed point exists in this case, i.e. that the Ising fixed point cannot be reached starting with $u_4 < 0$. Thus the lack of "true" criticality (with no divergency of the correlation length, as in a first-order transition) was claimed [9,10].

We perform the non-perturbative RG analysis in three dimensions (which merits per se a study for $u_4 < 0$) with the following questions in mind [1]:

(1) Does the sine-Gordon-like theory of the RPM possess a criticality?

(2) Can one refer to tricriticality within the RPM [1,11] ?.

(3) Does the charge correlation length $1/\Gamma$ diverge at the critical point [1,2]?

While the first question regards the adequacy of the SG-like theories for studying the RPM criticality (which presumably exists, see, e.g., Ref. [1]), the third one is related to the nature of the field φ. If the correlation length $1/\Gamma_\varphi$ does not diverge at the critical point, then the charge correlation length $1/\Gamma$ also does not diverge [2], in accordance with Stell's suggestion [12].

In the present Letter we report the results of our non-perturbative RG analysis: an initial Hamiltonian with $u_4 < 0$ (referred to RPM) may lead either to a first-order transition or to an Ising-like critical behavior, the partition being formed by the tri-critical surface.

Let us summarize the main lines of the calculation of the effective Hamiltonian: the details will be published elsewhere [13] (see also Ref. [5]).

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

$$H = H_{\rm id} + H_{\rm hc} + \tfrac{1}{2}\sum_{k}{}' \nu(k)(\rho_k\rho_{-k} - \rho). \qquad (1)$$

The Coulombic part (denoted below as H_c) is written in terms of *charge density* fluctuation amplitudes $\rho_k = n^a_k - n^b_k$ with $n^a_k = \Omega^{-1/2}\sum_{j=1}^{N_+}\exp(-i\boldsymbol{k}\cdot\boldsymbol{r}^a_j)$ and $n^b_k = \Omega^{-1/2}\sum_{j=1}^{N_-}\exp(-i\boldsymbol{k}\cdot\boldsymbol{r}^b_j)$ being amplitudes of *density* fluctuations of positive and negative ions respectively; $\boldsymbol{r}^{a,b}_j$ are the coordinates of the particles, $\rho = 2N_+/\Omega$ is the density, Ω is the volume of the system, the prime over the sum expresses that terms with $\boldsymbol{k} = 0$ are excluded, and $\nu(k) \equiv (4\pi e^2/k_BT)/k^2$.

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

$$\mathcal{F} = \mathcal{F}_{\rm id} + \mathcal{F}_{\rm hc} - \log\left\langle e^{H_c}\right\rangle_{\rm hc} \qquad (2)$$

of the ideal part, $\mathcal{F}_{\rm id}$, the "direct" hard-core part, $\mathcal{F}_{\rm hc}$, and the Coulombic part, with H_c depending on the amplitudes ρ_k; $\langle\cdots\rangle_{\rm hc}$ denotes the average over the reference hard-sphere system. Following the Hubbard-Schofield scheme [4], we perform the "Gaussian" transformation from variables ρ_k to variables φ_k and after some algebra we get the following result [3],

$$\mathcal{F} = -\log\left(\int \mathcal{D}\varphi(\boldsymbol{r})\, e^{-\int d\boldsymbol{r}\, H_{\rm LGW}(\varphi)}\right) + C, \qquad (3)$$

where the real field $\varphi(\boldsymbol{r})$ is the Fourier transform of φ_k, C is a field-independent constant (unimportant in the subsequent RG analysis) and $H_{\rm LGW}(\varphi)$ is an effective LGW Hamiltonian

$$H_{\rm LGW}(\varphi) = \tfrac{1}{2}(\nabla\varphi(\boldsymbol{r}))^2 + V(\varphi(\boldsymbol{r})) + f_{\rm id} + f_{\rm hc} \qquad (4)$$

with the corresponding free energy densities, $f_{\rm id} = \mathcal{F}_{\rm id}/\Omega$, $f_{\rm hc} = \mathcal{F}_{\rm hc}/\Omega$ and the "potential function" [4]

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

where $b^2 = 4\pi(3\pi)^{2/3}\rho^{*1/3}/T^*$ ($\rho^* = \rho d^3$ is the reduced density and $T^* = k_BTd^3/e^2$ is the reduced temperature). As in the case of the ordinary fluid [4,5],

[1] The nature, here *scalar*, of the order parameter determines the number and nature (stable/unstable) of the fixed points and the topology of the RG flows. The field φ considered presently, or the field of the overall-density fluctuations used in footnote 5 are both scalar.

[2] According to Ref. [8], the field $\tilde{\varphi}(\boldsymbol{r}) = -i\varphi(\boldsymbol{r})$ corresponds to the electrostatic potential at point $\boldsymbol{r}$. From the Poisson equation $k^2\nabla\tilde{\varphi}_k = -4\pi\rho_k$, it follows that the correlation length $1/\Gamma$ for $\langle\rho_k\rho_{-k}\rangle \sim k^4\langle\varphi_k\varphi_{-k}\rangle$ does not diverge if the correlation length $1/\Gamma_\varphi$ of $\langle\varphi_k\varphi_{-k}\rangle$ has no divergency. The opposite is not generally true.

[3] 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 $\{\varphi_k\} \to \varphi(\boldsymbol{r})$ are abdsorbed in constant C.

[4] In studies of Coulombic criticality (see, for example, Ref. [3,14], the high-order derivatives of the field are usually discarded from the LGW Hamiltonians.

the coefficients u_{2n} are expressed in terms of the cumulant averages, $\langle \rho_{k_1} \dots \rho_{k_n} \rangle_{\rm c,hc}$, 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 and thus play the role of *additive constants* [5].

It is straightforward to show that $u_2 = 1$ and that, neglecting in (5) all terms with $n \geqslant 2$ (i.e. in the approximation $V(\varphi) \sim \varphi^2$), one obtains the usual Debye–Hückel result for the Coulombic part of the free energy. To determine the coefficients u_{2n} for $n \geqslant 2$, longer computations are required. 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 Coulomb gas [6]. To evaluate 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 [15,16]. 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 [16] 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 $g_n(1,\dots,n)$ are the 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 [16],

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

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 [16] $\rho \tilde{h}_2(0) = \rho k_{\rm B} T \chi - 1 \equiv z_0$, and obtain coefficients for the *off-lattice* effective Hamiltonian. In particular, $u_2 = 1$, $u_4 = -(1 + 3z_0)$, $u_6 = 1 + 15(z_0^2 + z_0 z_1 + z_1)$, $\dots$ where $z_1 \equiv \rho\left(\partial z_0/\partial \rho\right), \dots$ To obtain z_0 one can use the virial expansion for the hard-sphere pressure, $P/\rho k_{\rm B} T = 1 + \sum_k B_k \rho^k$ with the coefficients $B_1, \dots B_6$ known [15] (for small densities), or the Carnahan–Starling equation of state [15,16]. Therefore, applying the above scheme, *all* the coefficients of the effective potential $V(\varphi)$ may in principle be found [5].

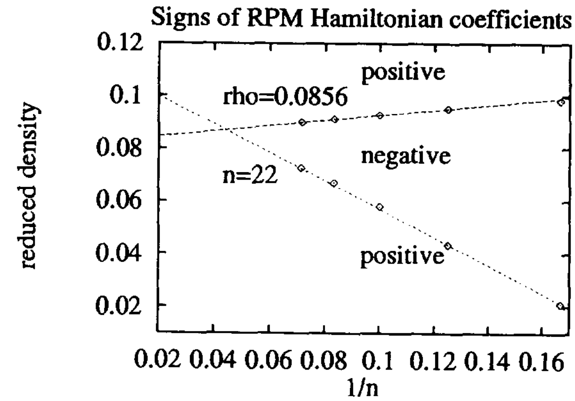

Fig. 1. Dependence of the boundaries of the density interval where the coefficients u_{2n} of the effective Hamiltonian are negative as a function of $1/n$. Extrapolation suggests that *all* the coefficients with $n > 22$ are positive. (Note that the density at which the "negative" interval shrinks to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

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 ~ 0.07–0.09 where the critical density of the RPM is expected to be [17]. 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). This assures us that the effective Hamiltonian is bounded from below, we can envisage then a RG analysis.

Certainly, our LGW Hamiltonian of RPM contains only a local potential part of its "exact" counterpart (see footnote 4). Nevertheless, the local potential approximation for the RG equations preserves all the general properties of the complete RG equations (nature and number of fixed points, nature of the RG flows) [18,19]. Using the same notations as in Ref.

[5] An attempt to derive an effective LGW Hamiltonian for the RPM has been made by Fisher and Lee
citeeeee, who used the field φ corresponding to the *overall-density* fluctuations; the coefficients at φ^n were taken from approximate theories with partial account of ion–dipole interactions and with dipole–dipole interactions neglected (see also Ref. [3]).

[6] Some (unimportant) difference of our result from the standard [6] appears since the present calculations are performed for the canonical ensemble.

[19], we write this approximate equation in three dimensions,

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

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

A detailed study of the approach to the Ising fixed point based on Eq. (7) has been reported [19]. However, all the initial Hamiltonians in Ref. [19] were taken with $u_4 > 0$. Let us analyze the solutions of Eq. (7) with initial functions involving negative values of u_4.

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 [20]),

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

$f(y,0)$ corresponds to a point with coordinates $(u_2(0), u_4(0), u_6(0), 0, 0, \ldots)$ in a space $\mathcal{S}$ of Hamiltonian coefficients (the dimension of $\mathcal{S}$ is infinite). Since we want to set $u_4(0) < 0$, at least one positive higher-order term is required to have the Hamiltonian bounded from below. We then choose $u_6(0)$ to be positive. Having chosen a (negative) value for $u_4(0)$ and a (positive) value for $u_6(0)$, we use the "shooting" method [19] to determine the critical value $u_2^c(0)$ of $u_2(0)$ which brings $f(y,0)$ on 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 for the case $u_4(0) = -6$ as an example (see Fig. 2) (Eq. (7) does not allow us to handle values of Hamiltonian coefficients as large as those calculated above.)

(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*

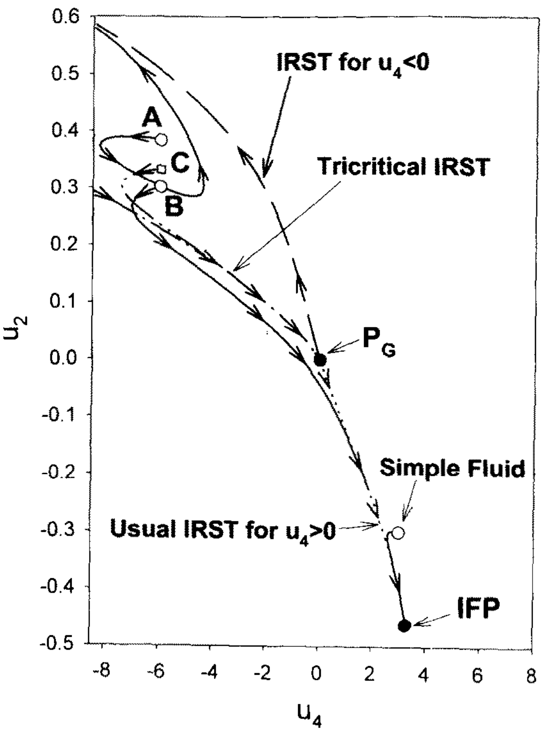

Fig. 2. Projection onto the plane $\{u_2, u_4\}$ of various RG trajectories (in the critical subspace $\mathcal{S}_c$) obtained by solving Eq. (7). Black circles represent the Gaussian (P_G) and Ising (IFP) fixed points. The arrows indicate the directions of the RG flows on the trajectories. The ideal 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). This is a source of RG trajectories flowing asymptotically toward P_G 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 accidental, due to projection of trajectories from a space of infinite dimension onto a plane shown).

$T_{u_4<0}$ means that the correlation length $1/\Gamma_\varphi$ (and thus $1/\Gamma$) remains finite at the assumed transition. This situation would confirm the suggestion by Stell [12] that the inverse correlation length Γ does not vanish

at the critical point of the RPM.

(B) If $u_6(0) = 20$, we find $0.30131 > u_2^c(0) > 0.30122$. 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 dimensions (usually called the φ_3^4 field theory). This renormalized trajectory (denoted by T_1 in Ref. [19]) 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.* This demonstrates that the SG-like theory of the RPM may possess criticality. In that case Γ_φ vanishes (however, Γ not necessarily does (see footnote 2).

(C) Between the two preceding cases, we find a trajectory (with $u_6(0) = 18.3125\ldots$ and $0.3324573 > u_2^c(0) > 0.3324549$) that directly flows towards P_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* $\mathcal{S}_t$ of $\mathcal{S}$. Any trajectory on $\mathcal{S}_t$ approaches P_G along a unique (attractive) trajectory that imposes the required very slow (logarithmic) flow in the vicinity of P_G.

So it appears that for $u_4(0) < 0$ very close Hamiltonians may lead to very different behavior. This occurs due to the vicinity of the tricritical subspace. Hence, for any SG-like theory of the RPM, which uses the field φ, conjugate to the charge density, as an order parameter, it is justified to mention a possible vicinity of a tricritical point. The possibility of an Ising behavior with a long crossover from an almost classical behavior is not excluded. The very large negative values that we have found for many coefficients of the effective LGW Hamiltonian could suggest that the transition studied with the use of φ as an order parameter corresponds rather to the case A described above with $\Gamma \neq 0$ in agreement with Ref. [12].

One of us (N.V.B.) thanks John Valleau for valuable discussions, his help and suggestions are highly appreciated; financial support of NSERC of Canada is acknowledged.

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