Mean-Field Theory of Critical Phenomenon for Mutually Repelling Particles in Complex Plasmas

K. Avinash
Department of Physics and Astrophysics, University of Delhi, Delhi-7, India
(Received 26 March 2006; published 28 February 2007)

A mean-field theory of criticality for charged particles in complex plasmas is proposed. It is shown that the existence of the critical point and the liquid-vapor coexistence is fully consistent with a purely repulsive potential between particles; the cohesive field due to the plasma background drives these. The critical exponents, calculated by expanding the free energy near the critical point, are found to be classical. The phase coexistence curve, obtained by minimizing Gibbs potential, is similar to that of other mean-field models, e.g., van der Waals fluids, ionic fluids, etc. These results lend support to the concept of ''universality'' in widely different systems.

DOI: 10.1103/PhysRevLett.98.095003 PACS numbers: 52.27.Lw, 05.70.Jk

Complex plasma consists of electrons, ions, and submicron or micron-sized particles that usually carry a large negative charge ($\sim 10^2$ to 10^3 times the electronic charge). Because of the large mass, the size, and the charge of the particles in such systems, there is usually an intermediate length and time scale where particles can be regarded as discrete, while the background electrons and ions are statistically averaged. On this scale, particles in the plasma can exist in a strongly correlated lattice or in a liquid state. Recently 1D and 2D [1–6] triangular lattices as well as liquid states of these particles have been formed and a number of issues related to solid-liquid phase transition have been studied [7–10].

In complex plasmas, the existence of the liquid-vapor phase transition has been postulated [11–13]. According to the standard liquid state theory, the liquid-vapor coexistence is driven by the presence of a long-range, pairwise attractive force between particles. In complex plasmas, particles being negatively charged normally repel each other via the Yukawa potential. Hence, additional mechanisms for a long-range attraction between particles have been proposed [14–16]. One of these is related to the effect of the positive sheath on the electrostatic interaction between two negatively charged particles. The other mechanism, very frequently mentioned in the literature, is called the ''shadow force''. It is related to the anisotropic absorption of ions or neutral gas molecules on the surface of a pair of interacting particles. The trouble with these mechanisms is that (a) in the context of colloidal suspensions (which are very similar to complex plasmas) it has been shown that within the Poisson-Boltzmann system of equations, the electrostatic interaction between two like-charged particles, in an unbounded dielectric as well as in the presence of a nearby wall, is purely repulsive [17]. (b) Shadow forces are pairwise attractive only when the particle density is sufficiently small and hence it is inapplicable to high particle densities encountered in the liquid-vapor coexistence.

In this Letter, we propose a theory for the liquid-vapor coexistence in complex plasmas with mutually repelling particles. In our theory, we do not invoke any hypothesis of a pairwise attraction between particles. Instead, we show that the liquid-vapor coexistence and the existence of a critical point are fully consistent with a purely repulsive potential between particles. Thus, the presence of an attractive force in the Hamiltonian is a sufficient but not a necessary condition for the liquid-vapor coexistence. Phase coexistence can be driven by other factors. In the case of complex plasmas, the cohesive field due to the plasma background drives it.

Our results of this Letter are also relevant to the ongoing debate about the presence of the long-range attraction between particles in colloidal suspensions [18,19]. In these systems, there is evidence of voids in homogeneous deionized suspension [20]. To explain these observations, attractive forces, at the cost of the purely repulsive Derjaguin-Landau-Verwey-Overbeek interaction potential (DLVO) potential, have been proposed. Our results in this Letter show that it is not necessary to modify the experimentally well-established DLVO potential as it is compatible with the liquid-vapor coexistence. Roij and Hansen [21] have also shown that the volume dependent cohesive field due to the background may drive phase coexistence between mutually repelling particles in colloidal suspensions.

In this Letter, we propose a mean-field theory, which invariably is the first approach in predicting the phase diagram and critical exponents of new models. In this theory, the system has only a long-range mean order. Short-range order related to thermodynamic fluctuations is ignored and the order parameter is taken to be spatially uniform. Following Landau, we expand the free energy in terms of the order parameter, which is small near the second order critical point, to calculate the critical exponents and the phase coexistence curve.

We begin by considering N dust particles, each carrying charge $Q = Zq$ (q is the electronic charge) confined electrostatically in a volume V within a large plasma background [5,6]. The negatively charged particles repel each other via the Yukawa potential. $\varphi = -(Q/4\pi\varepsilon_0 r)e^{-r/\lambda_D}$, where λ_D is the Debye length given by $\lambda_D^{-2} = (q^2 n_p/\varepsilon_0)(1/T_e + 1/T_i)$, n_p is the plasma density away from V where there are no particles, while T_i

and T_e are the ion and electron temperatures. The system is overall quasineutral hence, $N_i q = N_e q + NQ$, where N_e and N_i are the number of electrons and ions in V. Further, we define a particle temperature T associated with the mean stochastic motion of N dust particles in equilibrium. It is determined by a balance of heating due to the Brownian motion of particles and cooling due to the neutral drag [22] and has been measured in a number of experiments [7,23–25]. The Helmhotz's free energy F will have contributions from the thermal energy of dust particles and the electrostatic energy of particle-particle and particle-plasma background interactions. The expression of F which has all these contributions is given by

$$F = \frac{1}{2}\sum_i \sum_{j\neq i} \frac{Q^2}{4\pi\varepsilon_0 r_{ij}} e^{-r_{ij}/\lambda_D} - \frac{nNQ^2\lambda_D^2}{2\varepsilon_0}\left(1 + \frac{q^2}{8\pi\varepsilon_0\lambda_D N}(N_i/T_i + N_e/T_e)\right) + NT\ln n, \quad (1)$$

where $n = N/V$ is the average particle number density.

The explanation of various terms in (1) is as follows. The first term is the sum of the Yukawa pair potential and represents the energy due to the particle-particle interaction. The second term, which is cohesive, represents the energy due to the interaction of particles with the plasma background. It is calculated as follows. The energy required to remove an ion located at $r = r_j$ from the field of a particle at $r = 0$, is $W_i = -(qQ/4\pi\varepsilon_0 r_j)\times \exp(-r_j/\lambda_D)$. The conditional probability that the ion is at r_j, given the particle at $r = 0$, is $P\langle r_j|0\rangle = 1/V[1 + (qQ/4\pi\varepsilon_0 T_i r_j)e^{-r_j/\lambda_D}]$ [26]. The average energy required to remove the ion, located anywhere, from the field of the particle is then given by $\bar{W}_i = \int P\langle r_j|0\rangle W dr_j = -qQ/\varepsilon_0 V(\lambda_d^2 + qQ\lambda_D/8\pi\varepsilon_0 T_i)$. A similar expression can be obtained for electrons. The total energy required to remove N_i ions and N_e electrons from the field of N particles is given by $W_B = (N_i\bar{W}_i - N_e\bar{W}_e)N/2$. Eliminating average energies, after performing the integration, we obtain

$$W_B = -(nNQ^2\lambda_D^2/2\varepsilon_0) \times[1+(q^2/8\pi\varepsilon_0\lambda_D N)(N_i/T_i + N_e/T_e)]. \quad (2)$$

It should be noted that if we smear out particles as well, then the first term will cancel with $-(N^2Q^2\lambda_D^2/2\varepsilon_0 V)$ in (1), leaving behind the usual electrostatic contribution due to the Debye sheath in the expression for the free energy of the plasma [26]. Finally, the last term is the thermal energy contribution. To this expression, we may also add a term corresponding to the external confining potential $mN(\omega r)^2/2$. However, since it is volume independent, it does not contribute to the pressure and hence is omitted from (1).

Next, we make the fundamental assumption that the system has only a long-range, mean order. Any short-range order related to thermodynamic fluctuations is neglected. In this case, the mean-field approximation can be invoked where the pair potential term is approximated by replacing r_{ij} by a, where a is the mean particle distance given by $a = (3/4\pi n)^{1/3}$. In the summation, we consider only the near-neighbor interactions. Thus, the energy due to the particle-particle interaction is given by $(NhQ^2/8\pi\varepsilon_0 a)\times \exp(-a/\lambda_D)$, where h is the number of near neighbors interacting with the particle. Since the Yukawa potential is shielded beyond distances greater than λ_D, we take $h = 4\pi n\lambda_D^3/3$. This approximation is somewhat similar to the Bragg-William mean-field approximation used in Ising models [27]. The error involved in it is small as it is not valid when n is small and T is large. However, in this regime F is dominated by the second and the third term in (1). With these approximations, the normalized expression of the free energy $\bar{F}(\bar{n},\bar{T})$ is given by $\bar{F} = \bar{n}^{4/3}\exp(-1/\bar{n}^{1/3}) - 1.5\bar{n}\theta - \bar{T}\ln\bar{n}$, where we have used following normalizations: $\bar{n} = (4\pi/3)n\lambda_D^3$, $\bar{T} = 4\pi\varepsilon_0\lambda_D T/Q^2$, $F = \bar{F}(NQ^2/4\pi\varepsilon_0\lambda_D)$ and θ represents the term in the parenthesis of the second term in (1). It is independent of n and T. The critical point is given by conditions:

$$\frac{\partial^2\bar{F}}{\partial(\bar{n}^{-1})^2} = 0, \qquad \frac{\partial^3\bar{F}}{\partial(\bar{n}^{-1})^3} = 0, \qquad \frac{\partial^4\bar{F}}{\partial(\bar{n}^{-1})^4} \succ 0. \quad (3)$$

The first derivative usually gives the equation of state $P(n,T)$, where P is the particle pressure calculated from the first derivative of $\bar{F}$ with $(\bar{n})^{-1}$. Eliminating $\bar{F}$ in (3) we obtain the critical point as $\bar{n}_c = 6.67$, $\bar{T}_c = 6.23$, and $\bar{P}_c = 12$, The values of Γ and κ, the two parameters used in strongly coupled plasmas, corresponding to the critical point are, $\kappa_c = a/\lambda_D = (\bar{n}_c)^{-1/3} = 0.53$ and $\Gamma_c = Q^2/4\pi\varepsilon_0 a T_c = (\bar{T}_c\kappa_c)^{-1} \cong 0.5$.

The critical exponents of this model are calculated by expanding $\bar{F}$ in terms of the order parameter in the vicinity of the critical point. For ease of calculations, we take $\bar{V} = (\bar{n})^{-1}$ as variable and define $v = \bar{V} - \bar{V}_c$, $t = \bar{T} - \bar{T}_c$, $p = \bar{P} - \bar{P}_c$. We take v to be the order parameter. Within the mean-field approximation, it is taken to be spatially uniform with a mean value. Near the critical point, where there is a continuous second order phase transition, it is guaranteed to be small. Hence, close to the critical point, $\bar{F}$ can be expanded in powers of v as $\bar{F} = h(t)v + rtv^2 + uv^4 + \ldots$, where we have kept only the leading order terms and $h(t)$ is a function of t. In the expansion, the term linear in v is retained as the first derivative of $\bar{F}$, with respect to v defines the pressure. Terms proportional to v^2 and v^3 (without t) are absent because the second and the third derivatives of $\bar{F}$ with v are zero. In order to be consistent with the condition $d^4\bar{F}/dv^4|_T > 0$, the last term with $u > 0$ is retained. Moreover, for thermodynamic stability of states with $t > 0$, we must have $d^2\bar{F}/dv^2|_T > 0$ close to the critical point, which requires $r > 0$. Using this expansion of $\bar{F}$, we calculate the critical exponents α, β, γ, and δ, which are defined as follows [27]: $\chi_T \approx |t|^{-\gamma}$, $v \approx |t|^{\beta}$, $C \approx |t|^{-\alpha}$, $v \approx |p|^{1/\delta}$, where $\chi_T = -(V\partial^2\bar{F}/\partial v^2)^{-1}$ is the isothermal compressibility and C is the specific heat. Substituting for $\bar{F}$, we have $\chi_T = 1/vrt$, which gives $\gamma = 1$. Since $d^2\bar{F}/dv^2$ is zero at the critical point, we have $v \approx |t|^{1/2}$, which gives $\beta = 1/2$. Further, $d\bar{F}/dv|_T = -\bar{P}$ hence $h(t=0) = \bar{P}_c$ and $\bar{P}_c - \bar{P}_c = p = 4uv^3$, which gives $\delta = 3$.

As is well known, not all the critical exponents are independent. In fact only two of these are independent. The rest can be determined via the scaling relations. These relations are consequences of the homogeneity of correlation function and other thermodynamic variables close to the critical point [28]. For instance β, δ, and γ satisfy the relation $\gamma = \beta(\delta - 1)$, which is known as Widom's scaling. Since β, δ, and γ calculated above do satisfy the Widom's scaling, it is reasonable to assume that other scaling relations may also hold in the case of complex plasmas. For instance, the exponent α can be calculated using Rushbrooke's scaling $\alpha + 2\beta + \gamma = 2$, which gives $\alpha = 0$. Close to the critical point, the correlation length ξ diverges as $\xi \approx |t|^{-\mu}$. The exponent μ can be calculated by including a space dependent term $\propto \nabla n$ in $\bar{F}$ [27]. In the present problem, however, we calculate it using the Josephson's hyperscaling $\mu d = (2 - \alpha)$ where d is dimensionality of the space [28]. Since $d = 3$ and $\alpha = 0$, we obtain $\mu = 2/3$ (strictly speaking Josephson's scaling is valid for the upper critical dimension $d_c = 4$, in which case $\mu = 1/2$). Hence, in the vicinity of the critical point, the correlation length diverges as $\xi \approx |t|^{-2/3}$.

The values of the critical exponents of our model are $\alpha = 0$, $\beta = 1/2$, $\gamma = 1$, $\delta = 3$, $\mu = 1/2$ to $2/3$. These values are close to the "classical" exponents obtained from other mean-field models, e.g., neutral fluids, ionic fluids, etc. Our results thus underscore and extend the concept of "universality" to include the case of complex plasmas. It is well known that systems in the same universality class show little variation in the values of critical exponents even though the critical temperature and the nature of microscopic interaction may be widely different among them [27]. Complex plasmas are very different from neutral fluids, both in terms of critical temperature and the nature of interaction between particles, yet the values of the critical exponents in the two cases are similar.

In the vicinity of the critical point, the fluctuations in the order parameter around the mean value become important, particularly in low-dimensional systems ($d < 4$). In such cases, our assumption regarding the presence of only long-range order breaks down and the mean-field approximation becomes invalid. For this reason, the values of critical exponents, calculated from low-dimensional mean-field theories, are generally at variance with the experimental values, e.g., experimentally $\mu = 1/3$ instead of $1/2$ [27]. Since in the present model $d = 3$, the values of the critical exponents calculated above may only be approximately correct. Better values of exponents may have to be obtained from the field theoretical calculations or the renormalization group analysis [27,29].

Next, we calculate the phase coexistence curve. Phase coexistence is defined as the simultaneous existence of distinct phases in an inhomogeneous equilibrium. In the present problem, it is driven by the cohesive field due to the plasma background. The phase coexistence curve is calculated from the principle that systems at constant pressure and temperature minimize the Gibbs potential, i.e., $G = \bar{F} + \bar{P}/n \leq 0$ [28]. Since the liquid and the vapor phases both coexist in the equilibrium, G has two minima of equal depth, one at vapor density n_v and another at liquid density n_l. Carrying out the minimization of G following this procedure, we obtain n_l and n_v as functions of T. In Fig. 1 we plot the coexistence curve in terms of reduced variables $\bar{T}/\bar{T}_c$ and $\bar{n}/\bar{n}_c$. The curve has characteristic features which are that (a) there are liquid and vapor branches which come together at the critical point on top of the curve; (b) it follows the law of "rectilinear diameter" [27] which implies that the curve is asymmetric around n_c, i.e., $(\bar{n}_l + \bar{n}_v)/2 = [\bar{n}_c + (\bar{T} - \bar{T}_c)]$. The similarity of this curve with the coexistence curves of van der Waals fluids and other similar systems again emphasizes the underlying universality in widely different systems.

Finally, we discuss the feasibility of conditions required for the observation of the critical point. The critical temperature and the density given earlier may be obtained in a dusty plasma with following parameters which are fairly typical of present day experiments: $n_p \approx 10^8$ cm^{-3}, $n \approx 10^4$ cm^{-3}, $d = 10^{-5}$ cm, $T_e \approx 1$ eV, $T_i \approx T \approx 0.3$ eV, and an ion streaming energy $(1/2)m_i v_i^2 \sim T_i$ [30]. The dust charge is obtained by setting $I_i + I_e = 0$ and using

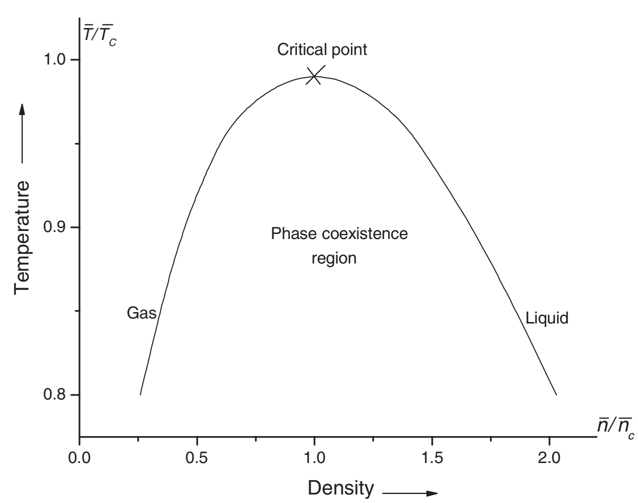

FIG. 1. The phase coexistence curve for particles in complex plasmas in terms of reduced variables $\bar{T}/\bar{T}_c$ and $\bar{n}/\bar{n}_c$.

$n_i \approx n_e$ (as $Qn/qn_i \ll 1$) where $I_i = q\pi d^2 n_i v_s(1 - 2q\psi/m_i v_s^2)$, $v_s = (8T_i/\pi m_i + v_i^2)^{1/2}$ is the mean ion speed in the presence of the streaming velocity v_i, and $I_e = -q\pi d^2 n_e (8T_e/\pi m_e)^{1/2} e^{q\psi/T_e}$. For these parameters we obtain $Q \approx 200q$, $\Gamma \approx 0.68$, and $\kappa \approx 0.7$, which are in the same range as Γ_c and κ_c.

Kharpak *et al.* [13] have recently given a set of conditions for the observation of the critical point in complex plasmas under microgravity conditions. These are related to the existence of the attractive potential between particles, maintenance of isotropic 3D conditions with void closure, and $T_c > T_n$ as the neutral temperature T_n, due to Brownian motion, is the lower limit for the particle temperature. Since here we have shown the existence of the critical point under very general conditions without the attractive force, the restrictions related to the existence of attractive force do not apply to our case. The closure of the void is expected to occur because we are using smaller particles in the submicron range, and for particles of this size and other parameters our calculations yield $T_c \sim 0.5$ eV. This is greater than T_n which, in microgravity experiments, typically, is $\sim$0.01–0.05 eV [23]. We thus concur with Khrapak *et al.* that the microgravity environment provides the most suitable conditions for phase coexistence, albeit under much less stringent conditions. The presence of the critical point may be detected by scattered radiation from large fluctuations near the critical point.

It should be noted that our theory does not imply that an attractive force between particles is absent; in fact there is some recent evidence for it [31]; however, its presence cannot be inferred by the observation of phase coexistence.

The author is grateful to R. L. Merlino and N. D'Angelo for discussions.

[1] J. H. Chu and Lin I, Phys. Rev. Lett. **72**, 4009 (1994).
[2] H. Thomas *et al.*, Phys. Rev. Lett. **73**, 652 (1994).
[3] Y. Hayashi and K. Tachibana, Jpn. J. Appl. Phys. **33**, L804 (1994).
[4] A. Melzer, T. Trottenberg, and A. Piel, Phys. Lett. A **191**, 301 (1994).
[5] J. Pramnik *et al.*, Phys. Rev. Lett. **88**, 175001 (2002).
[6] B. Liu, K. Avinash, and J. Goree, Phys. Rev. Lett. **91**, 255003 (2003).
[7] H. Thomas and G. Morfill, Nature (London) **379**, 806 (1996).
[8] D. Samsnov *et al.*, Phys. Rev. Lett. **92**, 255004 (2004).
[9] S. Hamaguchi and R. T. Farouki, J. Chem. Phys. **101**, 9876 (1994).
[10] G. Joyce, M. Lampe, and G. Ganguli, Phys. Rev. Lett. **88**, 095006 (2002).
[11] K. Avinash and P. K. Shukla, Phys. Lett. A **255**, 82 (1999).
[12] K. Avinash, Phys. Plasmas **8**, 2601 (2001).
[13] S. A. Khrapak *et al.*, Phys. Rev. Lett. **96**, 015001 (2006).
[14] D. P. Resendes, J. T. Mendonca, and P. K. Shukla, Phys. Lett. A **239**, 181 (1998).
[15] V. N. Tsytovich, Phys. Usp. **40**, 53 (1997).
[16] S. A. Khrapak, A. V. Ivlev, and G. Morfill, Phys. Rev. E **64**, 046403 (2001).
[17] J. C. Neu, Phys. Rev. Lett. **82**, 1072 (1999).
[18] A. M. Larsen and D. G. Grier, Nature (London) **385**, 230 (1997).
[19] W. R. Bowen and A. O. Sharif, Nature (London) **393**, 663 (1998).
[20] K. Ito, H. Hiroshi, and N. Ise, Science **263**, 66 (1994).
[21] René van Roij and J. P. Hansen, Phys. Rev. Lett. **79**, 3082 (1997).
[22] X. H. Zheng and J. C. Earnshaw, Phys. Rev. Lett. **75**, 4214 (1995).
[23] G. E. Morfill *et al.*, Phys. Rev. Lett. **83**, 1598 (1999).
[24] J. B. Pieper and J. Goree, Phys. Rev. Lett. **77**, 3137 (1996).
[25] V. E. Fortov *et al.*, Phys. Lett. A **229**, 317 (1997).
[26] N. A. Krall and A. W. Trivelpiece, *Principle of Plasma Physics* (San Francisco Press, San Francisco, 1986).
[27] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, England, 1998).
[28] S. K. Ma, *Modern Theory of Critical Phenomenon* (Benjamin, Reading, MA, 1976).
[29] K. G. Wilson and J. B. Kogut, Phys. Rep. **12**, 75 (1974).
[30] R. L. Merlino (private communication).
[31] T. Antonova *et al.*, Phys. Rev. Lett. **96**, 115001 (2006).