Phase Coexistence and a Critical Point in Ultracold Neutral Plasmas

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We show the existence of the liquid-vapor phase coexistence and a critical point for strongly coupled ions in ultracold neutral (UCN) plasmas. Expressions for the free energy of UCN plasmas and an equation of state for the ions are obtained in the mean field approximation. A van der Waals-like isotherm shows the existence of a critical point in UCN plasmas. Depending on the ion temperature, the ions are shown to exist in a mixed vapor-liquid phase for a range of the ion Coulomb coupling parameter Γ_i (defined by the ratio between the ion interaction and the ion kinetic energies), and in a strongly coupled liquid state for values of Γ_i above this range. The estimates of critical constants show that it may be possible to observe these phenomena in the present day UCN plasmas.

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Phase transitions or phase separations [1], which depend on critical points and critical exponents controlled by temperature, pressure, and the thermodynamic free energy of a system, are unique phenomena that occur in a variety of chemical and physical systems. The latter include the early evolution of the Universe as the temperature cooled, the core of Jupiter, a number of condensed matters, as well as colloidal suspensions and many strongly coupled systems (e.g., dusty and ultracooled neutral plasmas). In fact, the two emerging fields of the modern plasma physics, namely, the dusty [2,3] and ultracold neutral (UCN) [4] plasmas, are at the heart of physical sciences exploring the new knowledge that holds the promise of industrial and astrophysical applications. Recently, there has been a surge in investigating numerous collective processes [5–8] in UCN plasmas, which are created by the photoionization of laser cooled atoms near the ionization threshold [9–11]. The electron temperature T_e in most of the experiments may be set anywhere from a few to a few tens of Kelvins by suitably tuning the laser frequency just above the ionization threshold, while the ion component, which receives only a small momentum during this process may have the temperature T_i in the range of milli-Kelvins. With these initial temperatures and typical plasma number densities of 10^9–10^{10} cm^{-3}, the Coulomb coupling parameters (CCPs) for the electrons and ions lie in the range $\Gamma_e \approx 5$–10 and $\Gamma_i \geq 100$, respectively. Hence, one of the early motivations for UCN plasma experiments was to explore the possibility of strongly coupled regimes at ultralow temperatures in plasmas. However, UCN plasmas are created in a disordered state that is far from thermal equilibrium. The concomitant disorder induced heating [12–15] causes a rapid rise of the electron and ion temperatures (typically on the time scale of the ion plasma period $\sim$ few μs), thereby limiting the strength of correlations in a state where the electrons are weakly (or mildly) coupled with $\Gamma_e \leq 0.1$, and the ions are in a strongly coupled liquid phase with $\Gamma_i \approx 2$ [4]. Several methods have been proposed to alleviate this disorder induced heating and to take the electrons and ions deep into the strongly coupled regime, such as by ionizing and heating ultracold atoms with preset correlations on a lattice [16].

However, even in the present moderately coupled states [4], there are several interesting manifestations and challenges of strong coupling effects, which make them worthy of investigation as a fundamental issue in UCN plasmas. One of these is the oscillations in an initial relaxation of the average ion temperature, which has fundamental implications for relaxation processes in a kinetic theory [17]. Furthermore, the propagation of ion-acoustic (IA) waves in UCN plasmas has also been investigated both experimentally [6] and theoretically [8]. Finally, collective interactions in UCN plasmas should have potential applications [4] for ion sources (e.g., ion milling), ion microscopy, and seeding free-electron lasers [18].

In this Letter, we show the existence of a novel phenomenon of a critical point (CP) and liquid-vapor phase coexistence in UCN plasmas, which are of significant interest for computer simulations (e.g., Refs. [11,12]) and also for future laboratory experiments that are challenging. Specifically, we will analytically demonstrate the existence of a critical point and liquid-vapor coexistence in a strongly coupled ion component in the quasiequilibrium or near equilibrium phase of UCN plasmas. Earlier, a number of authors carried studies of phase separations or critical points for the Yukawa system [19–22]. Specifically, in a series of papers, Hamaguchi *et al.* [23–25] formulated the thermodynamics of the Yukawa system, and performed molecular dynamics (MD) simulations to find phase separations or critical points for solid-solid and liquid-liquid transitions. In this Letter we study the liquid-vapor transitions in UCN systems.

The existence of phase separations and CPs has also been postulated in other nonequilibrium systems (e.g., dilute colloidal suspensions and ionic fluids [26–29], as well as in complex (dusty) plasmas composed of highly charged dust particles [30–33]).

According to the standard liquid state theory, the liquid-vapor phase coexistence is driven by the presence of a pairwise long-range attraction between particles (i.e., Lennard-Jones potential). Therefore, the existence of a CP in systems with purely repelling particles, like negatively charged microspheres in dusty plasmas and colloidal suspensions and positively charged ions in UCN plasmas, may appear somewhat surprising. However, it has been shown [27,31,33] recently that the volume dependent cohesive fields due to the neutralizing plasma background or the Debye sheath can drive phase coexistence in colloidal suspensions [27] and in dusty plasmas [31,33]. Hence, the presence of pairwise attraction between particles is only a sufficient (and not necessary) condition for the liquid-vapor phase coexistence. It may be driven by other factors as well. In the case of UCN plasmas, we show here that cohesive fields due to the weakly coupled electron background drives liquid-vapor phase coexistence in the strongly coupled ion component.

In the following, we propose a mean field theory which invariably is the first approach in calculating the critical constants and exponents especially in new models, which have not yet been probed by more rigorous methods. In our theory, the system has only a long-range mean order. Short-range order usually related to thermodynamic fluctuations is ignored and the N body interactions are approximated by one body interaction with an average mean field generated by neighboring particles [1,34]. Admittedly, in some cases, this approximation may not give very accurate estimates of critical constants especially in low-dimensional models where fluctuations near critical points become significant [35] However, it does serve a useful purpose as it shows the existence of a critical point and phase coexistence in UCN plasmas. Once this is confirmed, then more rigorous and complex approaches based on field theoretic calculations and renormalization group analysis [35,36] can be undertaken to obtain better estimates of critical constants.

It should be noted that UCN plasmas continuously expand and hence are not quite in equilibrium state at all times. In fact, in the later stages of evolution when the correlation time becomes smaller than the hydrodynamic expansion time, the correlations freeze out leaving the system in a nonequilibrium state [37]. However, numerical simulations [9,37] show that the system does relax to local thermal equilibrium on the time scale of few tens of $\omega_{\mathrm{pi}}^{-1}$, where ω_{pi} is the ion plasma frequency.

To calculate the equation of state for ions, we consider a system of N_i discrete ions (strongly coupled) immersed in a neutralizing weakly coupled background of N_e electrons, such that the system is overall quasineutral, i.e., $N_i = N_e$ in volume V. The ion charge is shielded by the electrons. The shielded potential is given by the Yukawa potential

$$\Psi = \frac{q_i^2}{4\pi\varepsilon_0 r}\exp\left(-\frac{r}{\lambda_d}\right) \tag{1}$$

where q_i is the ion charge, ε_0 the permittivity of free space, $\lambda_d = (\varepsilon_0 \kappa_B T_e / n_e e^2)$ the electron Debye radius, κ_B the Boltzmann constant, and e the magnitude of the electron charge. It should be noted that the Yukawa potential is strictly valid [38] in the limit $\lambda_d \gg a$, where a is the mean distance between the particles. However, experiments in UCN plasmas [10] and MD simulations in dusty plasmas [23–25] have indicated that the Yukawa potential gives a good description of the system even when $\lambda_d \approx a$. The Helmholtz free energy F of the electrons and ions will typically consist of an ideal gaslike contribution due to the thermal energy. Additionally, there will be a "Coulomb energy excess," which is the energy in excess of the thermal energy due to the Coulomb interactions in such systems.

We now proceed to obtain the free energy F for our UCN plasmas, which is given by $F = U - \sum_{\alpha=e,i} T_\alpha S_\alpha$ where U is the internal energy while T and S are the temperature and entropy. The total internal energy of the system is [23]

$$U = \frac{3}{2}\kappa_B(N_i T_i + N_e T_e) + \frac{1}{2}\int \rho\psi\, d\tau - \frac{q_i^2}{8\pi\varepsilon_0}\sum_{j=1}^{N_j}\int \frac{\delta(r - r_j)}{|r - r_j|}d\tau, \tag{2}$$

where ρ is the total charge density and ψ the electrostatic (ES) potential and $d\tau$ is the volume element. In the right-hand side of (2), the first term gives the usual thermal contributions, the second term gives the ES contributions, while the third term subtracts the infinite self-energy of discrete ions which is formally contained in the second term. The charge density ρ and ψ satisfy Poisson's equation

$$-\varepsilon_0 \nabla^2 \psi = \rho = q_i \sum_{j=1}^{N_p} \delta(r - r_j) - q n_e. \tag{3}$$

Since the electrons are weakly correlated, their number density is given by the Boltzmann distribution. Following Hamaguchi and Farouki [23], we consider the electron density to be linear in ψ, viz. $n_e = \bar{n}_e(1 + q\varphi/T)$, where $\varphi = \psi - \bar{\psi}$, $\bar{\psi}$ is the spatially averaged ES potential and $\bar{n}_e = N_e/V$ is the average electron number density. The solution of Eq. (3) is

$$\psi = (q_i/4\pi\varepsilon_0)\sum_j \frac{\exp(-\kappa_d|r - r_j|)}{|r - r_j|}, \tag{4}$$

where $\kappa_d = 1/\lambda_d$. We now use ρ and ψ from Eqs. (3) and (4) in the second term in Eq. (2) and perform the integration with the delta function (after subtracting the singular term) to obtain

$$U = \frac{3}{2}\kappa_B(N_eT_e + N_iT_i) + \frac{q_i^2}{8\pi\varepsilon_0}\sum_i\sum_{j\neq i}\frac{\exp(-\kappa_d|r_i - r_j|)}{|r_i - r_j|} - \frac{q_i^2N_i\bar{n}_i}{2\varepsilon_0\kappa_d^2} - \frac{q_i^2N_i\kappa_d}{8\pi\varepsilon_0} - \frac{\varepsilon_0\kappa_d^2}{2}\int\varphi^2 d\tau, \quad (5)$$

where $\bar{n}_i$ is the average ion number density. In the right-hand side of Eq. (5) the second term is the ion-ion interaction energy, while the third term represents the energy due to the uniform electron background. The fourth term gives the energy due to the ion charge interacting with its own Debye sheath, while the fifth term is due to the ion charge interacting with the sheath of other ions. This expression, which is valid only in the linear response approximation [23], clearly shows that the ion interaction energy makes contributions to the internal energy U. The entropic part of F is again the sum of the electron and ion contributions including the contributions due to the ES interactions. It is given by [23]

$$T_iS_i + T_eS_e = -\sum_{\alpha=e,i}N_\alpha\kappa_BT_\alpha(\ln\bar{n}_\alpha\Lambda_\alpha^3 - 1) + \frac{3}{2}\sum_{\alpha=e,i}N_\alpha\kappa_BT_\alpha - \frac{\varepsilon_0\kappa_d^2}{2}\int\varphi^2 d\tau, \quad (6)$$

where $\Lambda_\alpha = (\hbar^2/2\pi m_\alpha\kappa_BT_\alpha)^{1/2}$ and the last term in the right-hand side of [6] is the contribution due to the ES interactions. The expression for F is the sum of the expressions in Eq. (5) and (6), and is given by

$$F = \sum_{\alpha=e,i}N_\alpha\kappa_BT_\alpha(\ln\bar{n}_\alpha\Lambda_\alpha^3 - 1) - \frac{q_i^2N_i^2}{2\varepsilon_0\kappa_d^2V} + \frac{q_i^2}{8\pi\varepsilon_0}\sum_i\sum_{j\neq i}\frac{\exp(-\kappa_d(r_i - r_j))}{|r_i - r_j|} - \frac{q_i^2N_i\kappa_d}{8\pi\varepsilon_0}. \quad (7)$$

It is instructive to compare this expression with the free energy F_V of the van der Waals gas given by (in the low density limit)

$$F_V = N\kappa_BT(\ln n\Lambda^3 - 1) - \frac{aN^2}{V} + \frac{b\kappa_BTN^2}{V}, \quad (8)$$

where $\Lambda = (\hbar^2/2\pi\kappa_BmT)^{1/2}$. The first term on the right-hand side of (8) is the thermal contribution, the second term is the cohesive field, which is inversely proportional to the volume and makes the system unstable as the volume is lowered (spinodal instability). The third term in the right-hand side of (8) is the effective repulsion between particles due to the finite size which stabilizes the system in the high-density limit. Our expression for F in Eq. (7) is similar to F for the van der Waals gas given in Eq. (8). There is a cohesive part proportional to $1/V$ in both expressions, while the effective repulsion due to finite particle size in real gases is replaced by the Yukawa repulsion between charged particles in UCN plasmas. If this interparticles repulsion in Eq. (7) can be shown to stabilize the instability of the system driven by the second term at high densities, then the system will exhibit first order liquid-vapor phase transition and a critical point [the last term in Eq. (7), being independent of V does not contribute]. The ion pressure is given by the relation

$$P_i = \frac{n_i}{V}\frac{\partial F}{n_i}\bigg|_{T_i} = \frac{q_i^2n_i}{8\pi\varepsilon_0}\frac{\partial}{\partial n_i}\sum_i\sum_{j\neq i}\frac{\exp(-\kappa_d|r_i - r_j|)}{|r_i - r_j|} - \frac{q_i^2n_i^2}{2\varepsilon_0\kappa_d^2} + \frac{N_ik_BT_i}{V}, \quad (9)$$

where n_i (or V) dependence of the first term in the right-hand side of (9) is implicit in the double summation. A critical point is given by the condition [35]

$$\frac{dP_i}{d(1/n_i)}\bigg|_{T_i} = 0, \qquad \frac{d^2P_i}{d(1/n_i)^2}\bigg|_{T_i} = 0, \qquad \frac{d^3P_i}{d(1/n_i)^3}\bigg|_{T_i} < 0. \quad (10)$$

The free energy F, the ion pressure P_i, and a CP can be calculated by evaluating the double summation in Eqs. (7) and (9) by MD simulations of the motion of N_i ions interacting via the Yukawa potential. In the following, we present a mean field theory of phase transitions and phase coexistence.

Mean field theory.— This theory is based on the fundamental assumption that the system has only a mean long-range order. Any short-range order related to thermodynamic fluctuations is neglected. In this case, the mean field approximation can be invoked where the double summation is replaced by N_ih, where h is the number of nearest neighbors and $|r_i - r_j|$ is approximated by a, where $a = (3/4\pi n_i)^{1/3}$ is the average interparticle distance. This approximation is similar to the Bragg-William mean field approximation commonly used in Ising models [34]. Since the Yukawa potential is shielded beyond λ_d, we take $h = 4\pi n_i\lambda_d^3/3$. Thus, the energy due to the Yukawa repulsion between the ions is $\approx N_i(4\pi n_i\lambda_d^3/3a)\exp(-\kappa_da)$.

Since the latter scales as $n_i^{4/3}$ in Eq. (7), it will be able to stabilize the low temperature phase (of the ions) at high densities. We use the following normalization for the density and the temperature: $n = 4\pi n_i\lambda_{\mathrm{de}}^3/3$, $T = T_i\lambda_{\mathrm{de}}/q_i^2$. With these normalizations, the equation of state for the ions is

$$P = \frac{n^{7/3}}{6}(4 + n^{-1/3})\exp(-n^{-1/3}) - \frac{3}{2}n^2 + nT. \quad (11)$$

From the condition given in Eq. (10), the critical constants, in normalized variables are $T_C = 6.65$, $n_C = 6.66$. The CCPs are usually defined as $\Gamma_i = q_i^2/4\pi\varepsilon_0\kappa_BT_i$, $\kappa = a/\lambda_d$. In terms of the CCPs, the critical constants are given by $\Gamma_C = 0.3$, $\kappa_C = 0.53$.

For temperatures $T > T_C$, the ions are supercritical while for $T < T_C$ they are subcritical. In Fig. 1, we display the critical isotherm ($T_C = 6.65$), a supercritical isotherm

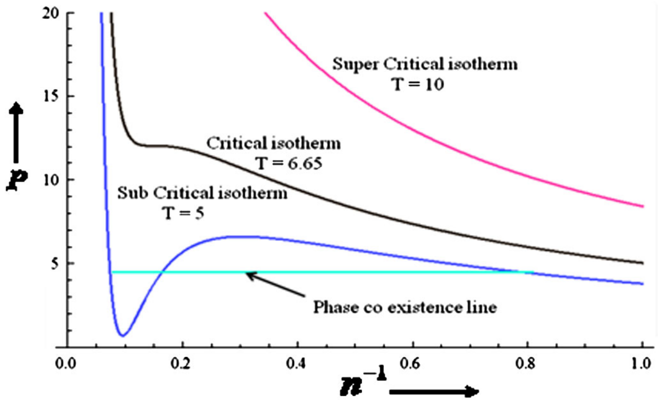

FIG. 1 (color online). The variation of P against $1/n$ for different ion temperatures in UCN plasmas. The critical isotherm for $T_C = 6.65$, the supercritical isotherm for $T = 10$, and the subcritical isotherm for $T = 5$ are shown. In the subcritical isotherm, the phase coexistence line drawn by minimizing the Gibb's potential is also shown.

($T = 10$) and a subcritical isotherm ($T = 5$). The liquid phase and the phase coexistence of the ion component occurs for subcritical temperatures in the range $T < T_C$ and for inverse normalized ion densities in the interval $0.1 < 1/n < 1$. For typical UCN plasma parameters $n_e \approx 5 \times 10^9\ \mathrm{cm}^{-3}$, $T_e \approx 40$ K [10], the liquid phase and phase coexistence will occur for $T_i < T_{iC} \approx 15$ K, and ion number densities in the interval $10^9 \leq n_i \leq 10^{10}\ \mathrm{cm}^{-3}$. Since these are in the range of typical ion densities and temperature that are experimentally available [10,11], it is possible to observe liquid-vapor phase coexistence and a critical point in the present day UCN plasmas. The ions will be in the liquid state or in the mixed phase $T_i < 15$ K. Along the isotherm for $T = 5$ (or $T_i = 12$ K) we have also shown the phase coexistence line which is drawn by minimizing the Gibbs potential $G = F + P_i/n_i$ [34]. The ions will undergo a first order phase transition and exist in vapor and liquid phases along this line. Thus, in Fig. 1, for $T_i = 12$ K, the ions will be in a mixed phase of vapor and liquid for $0.5 > \Gamma > 0.2$, while they will be in a strongly coupled liquid phase for $\Gamma > 0.5$. This is consistent with the results of numerical simulations, which show the ions to be in a strongly coupled liquid state with $\Gamma \approx 2$ [11,12,37]. For a certain range of parameters, especially for very low ion temperatures, Eq. (11) predicts a negative ion pressure. These may be attained only during phase transitions and is unstable. However, as is well known, the van der Waals equation also predicts negative pressure of real gases, which is unstable but exists in nature and is important for some biotic mechanisms. Furthermore, negative pressures have also been encountered in numerical studies of strongly coupled pure ion plasmas [39], indicating the possibility of liquid-vapor transitions in such systems.

The mean field theory presented here thus indeed shows the existence of a critical point and liquid-vapor phase coexistence in UCN plasmas. The values of critical constants calculated from low-dimensional mean field theories are generally at variance with experimental values [35]. Since UCN plasmas are three dimensional, the critical constants calculated here by using the mean field theory may only be approximately correct. Better estimates may be obtained from MD simulations, field theoretic calculations or renormalization group analysis [35,36]. The use of the Yukawa potential, which is strictly valid for $\kappa \ll 1$, for values of κ in the range $\kappa \leq 1$ may be another source of error in values of critical constants, and a better nonlinear model for the interparticle potential is needed. However, as stated before, experiments and simulations have shown that the Yukawa potential gives a good description of UCN plasmas for a wide range of κ values, viz. $0 \leq \kappa \leq 5$ [25].

To summarize, we have demonstrated that for typical parameters of UCN plasmas, the ions will exist either in a mixed (liquid-vapor) or in a strongly coupled liquid phase. The expressions for the Helmholtz energy and the ion pressure are obtained by using the mean field approximation. The isotherm of the ion pressure shows the existence of a critical point and liquid-vapor phase coexistence. The first order phase transition is driven by the cohesive fields in the background of weakly coupled electrons. Depending on the ion temperature (below a critical point), the mixed phase occurs for a range of Γ values. For values of Γ above this range, the ions are in a strongly coupled liquid state. In the present day UCN plasmas with $T_i = 12$ K, the strongly coupled liquid state occurs for $\Gamma > 0.5$. This is consistent with the results of numerical simulations [11,12,37], which show the ions to be in a strongly coupled liquid state with $\Gamma \approx 2$.

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