Liquid-Gas Phase Transition and Instabilities in Asymmetric Two Component Systems

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The liquid-gas phase transition and associated instability in two component systems are investigated using a mean field theory. The importance of the role of both the Coulomb force and symmetry energy terms are studied. The addition of the Coulomb terms bring asymmetry into a mean field and thus result in important differences with previous approaches which did not include such terms. The Coulomb effects modify the chemical instability and mechanical instability domains shifting many features away from proton fraction point \( y = 1/2 \) to a value closer to the valley of \( \beta \) stability. These features are discussed in detail.

Thermodynamic properties of two and, more generally, multi-component systems are of interest in many areas of physics. For example, binary systems of two components are encountered in nuclei where the two components are neutrons and protons. While light nuclei have \( N = Z \), heavy nuclei have \( N > Z \) and systems with large neutron excess such as neutron stars exist in astrophysics. In condensed matter physics two component systems appear in liquid \(^3\)He where the two components are spin-up and spin-down fluids. Such systems contain a more complex phase structure than one component systems. This letter is an extension of previous work concerning the nuclear case which was discussed from both the fragmentation point of view and from a mean field picture. In the mean field picture we studied the phase surface associated with the liquid-gas phase transition incorporating the role of surface and Coulomb effects. Previous mean studies of two component systems were investigations of the role of the symmetry energy on the phase structure of the liquid-gas phase transition. While the symmetry energy plays an important role in governing the proton/neutron ratios in the liquid and gas phases, favoring more symmetric systems in the liquid phase than the gas phase, the effects of both the Coulomb interaction and surface energy were also shown to be important. This was first discussed in Ref. and more recently in Ref. Here we will focus on the stability, metastability and instability of asymmetric systems of protons and neutrons. Such systems are of interest for radioactive beams studies which can be used to explore nuclei at the limits of isospin asymmetry. In a recent article, V. Baran et al have pointed out some new effects associated with two component systems where a new kind of liquid-gas phase transition associated with chemical instability may appear. This new type of transition may manifest itself as an isospin distillation or fractionization as reported in Ref. where the gas phase is enriched in neutrons relative to the liquid phase. Such observations suggest that neutron diffusion occurs at the same rate or is more rapid than fragment production. These observations are based solely on symmetry energy effects, which make the liquid phase more symmetric, with the role of the Coulomb interaction not included. The importance of Coulomb effects driven by \( Z^2 \) terms versus symmetry energy effects arising from \((N-Z)^2\) terms can be seen by just looking at the most stable nucleus for a given \( A \). Using a liquid drop model, the \( Z \) with the smallest mass or greatest binding energy is given by \( Z = (A/2)/(1 + B_c A^{2/3}/B_s) \) where \( B_c \) is the Coulomb coefficient \( B_c Z^2/A^{1/3} \) and \( B_s \) is the symmetry energy coefficient \( B_s (N-Z)^2/A \). When the Coulomb interaction is turned off \( Z \) is simply \( A/2 \). Moreover, the Coulomb interaction was shown to have a very dramatic effect on the specific heat associated with a first order liquid-gas phase transition, substantially reducing the peak previously reported in Ref. where surface energy effects associated with one component systems played the dominant role. Moreover, the Coulomb force introduced another pair of coexistence densities having larger proton concentration in gas phase than in liquid phase due to its asymmetry in the mean field.

In symmetric systems, mechanical instability from \( dP/d\rho < 0 \) and chemical instability from \( d\mu/d\rho < 0 \) at fixed \( T \) are simply related since

\[
Nd\mu = -SdT + VdP
\]

where \( \mu \) is the chemical potential, \( S \) the entropy, \( P \) the pressure, \( N \) the number of particles and \( T \) the temperature. Thus \( \rho d\mu/d\rho = dP/d\rho \) at fixed \( T \) and the boundaries of both instabilities are common with \( d\mu/d\rho = dP/d\rho = 0 \). The coexistence curve of the Maxwell pressure \( P \) versus density \( \rho \) or volume \( V \) is determined by the equality of the pressure and chemical potentials between the liquid and gas phase at the same \( T \). In the region between the spinoidal...
curve determined by the instability line and the coexistence line are metastable regions of supercooled liquid and superheated gas where nucleation processes can occur. These processes for one component systems were studied in Ref. [11], where nucleation processes gave a dynamical picture of the liquid-gas phase separation. Specifically, classical nucleation theory [11] looks at the change in the Gibbs free energy with and without a liquid drop made of $A$ particles. This change is written as $\Delta G = (\mu_l - \mu_p)A + 4\pi R^2\sigma$ where $\mu_l$ is the liquid chemical potential of the drop, $\mu_p$ is the gas chemical potential from which the drop is formed, $R$ the radius of the drop and $\sigma$ is the surface tension. A superheated gas has $\mu_g > \mu_l$, while equilibrium states have $\mu_g = \mu_l$. This change in Gibbs free energy has a maxima at a critical size drop whose radius is given by $R_c = 2\sigma / (\mu_g - \mu_l)\rho_l$, where $\rho_l$ is the liquid drop density. The $A = \rho_l V$ with $V$ the volume of the drop. Drops with smaller $R$ evaporate particles thereby lower their free energy, while drops with bigger $R$ grow by accumulating particles and also lowering their free energy. Such processes in two component systems of neutrons and protons with additional Coulomb and symmetry energy effects have also been partly explored. Some preliminary studies of Coulomb effects in nucleation were done in Ref. [12].

For a two component drop, the $\Delta G$ is

$$\Delta G = (\mu_{lp} - \mu_{gp})Z + (\mu_{ln} - \mu_{gn})N + 4\pi R^2\sigma + \delta E_C + \delta E_{sym}$$

The $\delta E_C$ is the change in Coulomb energy with and without the drop and $\delta E_{sym}$ is the change in symmetry energy.

In two component systems the coexistence line of a one component system now becomes a surface in $(P, y, T)$, with $y$ the proton fraction. This surface has several new elements associated with it that are not present in one component systems. For example, the isolated critical point of a one component system now becomes a line of critical points with $y = 1/2$ the critical point of a one component system. Associated with this surface is also a line of maximal asymmetry in the proton/neutron ratio and a line of equal concentration in liquid and gas phase [13]. The intersection of this $(P, y, T)$ with a plane at fixed $T$ leads to loops of $P$ versus $y$ as shown in Fig. 4 of Ref. [4]. The chemical potentials $\mu_n$ and $\mu_p$ versus $y$ at fixed $T$, $P$ also have interesting behavior as shown in Fig. 3 of Ref. [4]. For two component system, Eq.(3) is replaced by

$$y(d\mu_p/d\rho) + (1 - y)(d\mu_n/d\rho) = (1/\rho)(dP/d\rho)$$

$$y(d\mu_p/dy) + (1 - y)(d\mu_n/dy) = (1/\rho)(dP/dy)$$

In the first equation, $y$ and $T$ are held fixed, and in the second equation $\rho$ and $T$ are held fixed. We will use these figures to study the spinoidal instability region and its associated surface in $(P, y, T)$.

Some properties of the instability region can best be analyzed using some thermodynamic identities. We first note that the pressure and the chemical potentials are usually written as functions of $\rho, y$ and $T$; $P(\rho, y, T)$ and $\mu_q(\rho, y, T)$. One important identity arises from the equation of state $P = P(\rho, y, T)$ which gives

$$\left(\frac{dy}{d\rho}\right)_{P,T} = - \left(\frac{dP}{dy}\right)_{y,T} \left(\frac{dP}{\rho}\right)_{y,T}$$

for the relation of $y$ and $\rho$ at fixed $P$ and $T$. Since $P, T, y$ and $\rho$ are connected by an equation of state $P(\rho, y, T)$, we can write

$$\left(\frac{d\mu_q}{dy}\right)_{P,T} = \left(\frac{d\mu_q}{\rho}\right)_{y,T} + \left(\frac{d\mu_q}{d\mu_p}\right)_{y,T} \left(\frac{d\mu_p}{dy}\right)_{P,T}$$

Combining Eqs.(2) and (3), we can write $(dP/d\rho)_y,T$ as

$$\left(\frac{dP}{\rho}\right)_{y,T} = \left(\frac{(d\mu_p/d\rho)_{y,T}}{(d\mu_p/d\rho)_{P,T}}\right)$$

Since $(d\mu_p/d\rho)_{P,T}$ is finite, singularities in $(d\mu_p/d\rho)_{y,T}$ (chemical instability) give rise to zeroes in $(dP/d\rho)_{y,T}$. The zeroes of $(dP/d\rho)_{y,T}$ form the spinodal surface, boundary for mechanical instability region. In two component systems, mechanical and chemical instability regions are separated for asymmetric cases. Using Eq.(2), the chemical instability boundary $((d\mu_q/d\rho)_{P,T} = 0)$, determined by setting Eq.(3) equal to 0, is obtained from

$$\left(\frac{dP}{d\rho}\right)_{y,T} = \left(\frac{dP}{\rho}\right)_{y,T} \left(\frac{d\mu_q/d\rho}{d\mu_q/d\rho}_{y,T} \right)$$

The following features should be noted. First, mechanical equilibrium $(dP/d\rho)_{y,T} = 0$ is determined by the condition that the left hand side of this equation is 0. Thus the mechanical and chemical instability boundaries are the same.
when \((dP/dy)_{\rho,T} = 0\) since \((d\mu_q/dy)_{\rho,T} \neq 0\) here. Due to Eq.(2), \((d\rho/dy)_{P,T} = 0\) too when \((dP/dy)_{\rho,T} = 0\) except on the mechanical instability boundary. This condition is also related to the equal concentration \(y_E\) of liquid and gas phase on the coexistence surface \(\tilde{\mathcal{E}}\). For systems without Coulomb terms this occurs at \(y = 1/2\). Secondly, for chemical equilibrium the right hand side can be obtained from the equation of state \(P = P(\rho, y, T)\) and the behavior of the proton or neutron chemical potentials \(\mu_q = \mu_q(\rho, y, T)\). The \(q\) will distinguish neutron results from proton results. We will use Eq.(5) to explore the boundary of chemical equilibrium.

We begin our study by first considering a simpler system where Coulomb and surface effects are turned off. Using Eq.(54) of Ref. \cite{4} with \(C_s = 0\) (surface term), \(C = 0\) (Coulomb term), \(x_3 = -1/2\) and \(\alpha = 1\), then \((dP/d\rho)_{y,T}\) is quadratic in \(\rho\) and is given by

\[
\left(\frac{dP}{d\rho}\right)_{y,T} = T + \left(\frac{3}{4}\right) t_0 \rho + \left(\frac{3}{8}\right) t_3 \rho^2 + T \left(\frac{1}{4\sqrt{2}}\right) \frac{\lambda^3}{\gamma} \rho
\]

\[
- \left[ t_0 (1/2 + x_0) - T \left(\frac{1}{2\sqrt{2}}\right) \left(\frac{\lambda^3}{\gamma}\right) \left(\frac{\rho}{2}\right) (2y - 1)^2 \right]
\]

The last term involving \((2y - 1)^2\) does not contribute for symmetric systems. The terms involving \(\lambda^3\) arise from degeneracy corrections. The mechanical instability points can easily be obtained by solving the quadratic equation \((dP/d\rho)_{y,T} = 0\) to obtain the two densities that define the instability region for each \(T\) and \(y\). These two roots become a single solution at a specific \(T_c(y)\) at each \(y\). This occurs when \((d^2P/d\rho^2)_{y,T} = 0\). In one component systems and in symmetric systems with \(y = 1/2\), this is the critical point \(T_c\).

\[\text{FIG. 1. Chemical (thick solid curve) and mechanical (thin solid curve) instability curves at temperature } T = 10 \text{ MeV with (upper boxes) and without (lower boxes) Coulomb effect of } R = 8 \text{ fm uniform sphere. The dashed curves are the coexistence curve at } T = 10 \text{ MeV. The dotted curves are for } (d\mu_p/d\rho)_{y,T} = 0 \text{ and the dash-dotted curves are for } (d\mu_n/d\rho)_{y,T} = 0. \text{ The equal concentration } y_E = 0.4256 \text{ at } T = 10 \text{ MeV. The curves are the constant } T \text{ plane cuts of the corresponding surfaces in } (\rho, y, T) \text{ space (left column), in } (\rho, P, T) \text{ space (center column), and in } (P, y, T) \text{ space (right column).}\]

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FIG. 2. The temperature dependence of the chemical and mechanical instability curves at fixed proton concentration $y$. The curves here are the constant $y$ plane cuts of the corresponding surfaces in $(\rho, y, T)$ space. The curves are the same as in Fig. 1 except the dashed curves. With the temperature dependent equal concentration $y_E(T)$, all the curves coincide as shown by dashed line here (notice here that $y_E(T) = 1/2$ without Coulomb force).

The calculations using Eqs.(53) and (54) of Ref. 4 with degeneracy correction are shown in Fig. 1 and Fig. 2. The mean field force parameters are the same as used in Ref. 4 except for using a larger radius $R = 8$ fm of a uniform sphere for a larger Coulomb force. These figures show that the mechanical instability boundary (thin solid line) is inside of the chemical instability region (thick solid line) and these coincide at the proton concentration of $y_E = 0.4256$ at $T = 10$ MeV (Fig.1 and upper middle box of Fig.2). The curves of $(d\mu_q/\rho)_y,T = 0$ also coincide with the instability boundary at $y_E$. The coexistence boundary coincides with the chemical instability boundary at the line of critical points (peaks in Fig.1 for a $T = 10$ MeV plane cut) but not with the mechanical instability boundary. We can see from Fig.2 that the chemical and mechanical instability boundaries coincide at the proton concentration $y_E(T)$ which is on the line of equal concentration on the coexistence surface. While all the curves coincide at $y = 1/2$ (without Coulomb) as shown in the lower left box of Fig.2, the top middle box of Fig.2 with Coulomb exhibit a separation between these curves due to the temperature dependence of $y_E(T)$. All curves in the upper middle box of Fig. 2 coincide at $T = 10$ MeV since $y_E = 0.4256$ at this temperature. From Fig.2 and the left column of Fig.1 we can see that all the four surfaces in $(\rho, y, T)$ space coincide at the line of temperature dependent $y_E(T)$ and that the mechanical instability surface is inside of the chemical instability surface. Upper Fig. 2 and upper left box of Fig.2 also shows that the role of $(d\mu_q/\rho)_y,T = 0$ and $(d\mu_\nu/\rho)_y,T = 0$ are exchanged when $y$ crosses $y_E$.

To keep equations simple in the discussions of various new features in two component system with Coulomb force, we will drop the degeneracy corrections. However, they are included in the actual calculations done and in the figures (Figs. 1 and 2) presented here. In this limit $P = \rho T - a_0(y)^2 + 2a_3y^3$ where we have followed the notation of Ref. 10 with $P$ now generalized to the case of asymmetric systems. The generalization changes $a_0$ to $a_0(y) = a_0[1 - (3/6)(1/2 + x_0)(2y - 1)^2]$ with $a_0 = -(3/8)t_0$ and $a_3 = t_3/16$. Then $dP/\rho \neq 0$ at

$$\rho = \left(a_0(y) \pm \sqrt{a_0^2(y) - 6a_3T}\right)/\left(6a_3\right)$$

(7)

The two roots are equal at $T_c(y) = a_0^2(y)/(6a_3)$ and are $\rho_c(y) = \rho_- = \rho_+ = a_0(y)/(6a_3)$. At this point the pressure is $P_c(y) = a_0^2(y)/(108a_3^2)$. Under the same limits the chemical potentials are given by

$$\mu_q = T \ln[(\lambda^2/\gamma)(\rho/2 \pm (2y - 1)\rho/2)] - 2a_0\rho \pm (4/3)(1/2 \pm x_0)a_0(2y - 1) - 3a_3\rho^2$$

(8)

with the upper sign for protons and the lower sign for neutrons and $\gamma = 2$ for the spin up and down degeneracy. This equation for $\mu_q = \mu_q(\rho, y, T)$ when combined with the equation of state $P(\rho, y, T)$ can be used to calculate the chemical potentials as a function $\mu_q = \mu_q(P, y, T)$. Boundaries of the chemical instability region can also be determined using the condition $d\mu_q/\rho = 0$ at constant $T, P$. Substituting the simplified equation of state and expression for the chemical potential into Eq. (2) leads to a cubic equation $c_2\rho^3 + c_2\rho^2 + c_1\rho + c_0 = 0$ with $c_2 = 32(1/2 + x_0)C_3a_3(1 - y)y$, $c_1 = -(4/3)(1 - x_0)a_3T$, $c_0 = T^2$. Chemical instability occurs when three real roots exist, two of which will be positive, one negative. One negative root is present because $c_0/c_3$ is positive. At $y = 1/2$, the two positive solutions are the same as that for mechanical instability. When $y$ is no longer $1/2$, the mechanical instability and chemical instability regions are no longer the same. This result is shown in the lower part of Fig.2 for various choices of $y$ with the degeneracy correction of Ref. 4. It should also be noted that the coefficients of the cubic equation have a certain symmetry arising from the form in which $y = (y - 1)$, i.e., interchanging $y$ (protons) and $1 - y$ (neutrons) leaves the solution invariant (see curves for $(d\mu_q/\rho)_y,T = 0$ in Figs. 1 and 2). This result is no longer true when Coulomb interactions are included. We now turn our attention to the simple EOS and $\mu_q$, but now with Coulomb effects included in a simplified form which will illustrate its qualitative effects.

When Coulomb effects are included in the approximation of a uniformly charged sphere of fixed radius $R$, the pressure equation contains an additional term $Cy^2\rho^2$ and the proton chemical potential contains an extra term $2Cy\rho$. The $C$, which depends on $R$, is taken to be constant. For this choice, we can consider $R$ as an effective range of the Coulomb force which is now independent of the density. This simplification reduces the complexity of many results. To make the Coulomb effects more visible in our figures (Figs. 1 and 2), we use a large value of $C = 231$ MeV$^2$/fm$^3$ which is appropriate for systems near $U$. These additions to $P$ and $\mu_p$ change the equation for chemical and mechanical instability. Specifically the coefficients of the cubic equation for chemical instability for both protons and neutrons are now $c_3 = [32(1/2 + x_0)a_0 + 12C]a_3(1 - y)y$, $c_2 = 6a_3T - [(32/3)(1/2 + x_0)a_0^2 + (8/3)(1 - x_0)a_0C]y(1 - y)$, $c_1 = -(4/3)(1 - x_0)a_0 + 2CyT$, $c_0 = T^2$.

Some qualitative features of the effects of such a Coulomb behavior are the following (see Fig. 1 and Fig. 2 also).

1) The mechanical and chemical instability curves are the same when $(dP/dy)_{y,T} = 0$ which occurs at $y_E = 0.5/(1 +
C/[(8/3)(1/2 + x_0)a_0]) and thus no longer at y_E = 0.5 when C \neq 0. This equation for y has a similar structure to the equation that gives the Z which has the maximum binding energy at fixed A (valley of \beta stability) obtained from the liquid drop mass formulae or from Eq.(55) of Ref. [1]. With higher order T dependence coming from degeneracy corrections, y_E depends on T and y_E = 0.4256 for x_0 = 1/2 at T = 10 MeV. Explicitly, with first order degeneracy corrections, y_E = 0.5/(1 + C/[(8/3)(1/2 + x_0)a_0 + T\lambda^3/(2\sqrt{2}gamma)]). 2) For both larger and smaller values of y from y_E, the chemical instability curve is outside the mechanical instability curve as shown in Fig.1 and 2. The mechanical instability has its peak in T versus \rho at T_c(y) = [a_0 - (2/3)(1/2 + x_0)a_0(2y - 1)^2 - Cy^2]^2/(6a_3) which is maximum at y = y_E and coincide with chemical instability at y_E. 3) The maximum critical T obtained from the peak in the chemical equilibrium surface of T versus \rho, occurs at y \neq 0.5, but is now shifted to y = y_E(T). At y = y_E(T), the equilibrium curve or binodal curve of P versus y obtained by cutting the binodal surface at a given T meets at a point, i.e., the liquid and gas phase have the same proton concentration (see Fig.4 of Ref. [1]). For y > y_E the gas phase is proton richer than the liquid phase when compared to a situation without Coulomb effects [4]. When Coulomb effects are turned off the binodal section meets at y = 1/2. At y = y_E \neq 1/2 with Coulomb effects included a two component system will behave as a one component system, keeping the proton/neutron ratio the same in both liquid and gas phases.

In summary, we have presented calculations based on a mean field theory with asymmetry which include the role of Coulomb force on the liquid-gas phase instability regions for both the mechanical (spinodal) surface and the chemical (diffusive) surface. The Coulomb force modifies these surfaces so that their peaks are no longer at proton fraction y = 1/2 but shifted to a smaller value called y_E which is close to the proton fraction in the valley of \beta-stability. The mechanical instability surface is always inside the chemical instability surface and the two surfaces are the same at the equal concentration y_E (allowing for T dependence in y_E). At y_E, the peak in the chemical instability surface and binodal equilibrium surface also coincide. For systems with y \neq y_E, the peak in the T versus \rho curve for chemical instability and chemical equilibrium – binodal or coexistence curve – coincide, but the peak for mechanical or spinodal instability is below that of the other two. At y = y_E, a phase transition in a two component system behaves the same as a one-component system, keeping the proton fraction at y_E in both phases during the entire transformation.

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[1] S.J. Lee and A.Z. Mekjian, Phys. Rev. C56, 2621 (1997); C47, 2266 (1993); C45, 1284 (1992); K.C. Chase and A.Z. Mekjian, Phys. Rev. C49, 2164 (1994); C50, 2078 (1994).
[2] P. Bhattacharyya, S. Das Gupta, and A.Z. Mekjian, Phys. Rev. C57, 1361 (1998).
[3] S. Das Gupta and A.Z. Mekjian, Phys. Rev. C60, 054616 (1999).
[4] S.J. Lee and A.Z. Mekjian, Phys. Rev. C63, 044605 (2001).
[5] H. Müller and B.D. Serot, Phys. Rev. C52, 2072 (1995).
[6] P. Pawlowski, Phys. Rev. C65, 044615 (2002).
[7] V. Baran, M. Colonna, M. Di Toro, and V. Greco, Phys. Rev. Lett. 86, 4492 (2001).
[8] S. Das Gupta, A.Z., Mekjian, and M.B. Tsang, Advances in Nuclear Physics V26, 81 (J.M. Negele and E. Vogt ed., Kluwer Academic/Plenum Pub. 2001).
[9] H.S. Xu etal, Phys. Rev. Lett. 85, 716 (2000).
[10] A.L. Goodman, J.I. Kapusta and A.Z. Mekjian, Phys. Rev. C30, 851 (1984).
[11] C. Kittel and J.I. Kroemer, Thermal Physics (2nd Ed. W. Freeman and Company, N.J. 1980).
[12] A.R. DeAngelis and A.Z. Mekjian, Relativistic Heavy Ion Collisions in the International Review of Nuclear Science V.6 (L.P. Csernai and P.D. Strottman Eds, 1991, World Science) 343-424.