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Phase separation for a dense fluid mixture of nuclei*

E. L. Pollock and B. J. Alder
University of California, Lawrence Livermore Laboratory, Livermore, California 94550
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It is shown by Monte Carlo calculations that fluid mixtures of classical point ions in an uniform electron-gas background separate into two phases primarily from potential-energy considerations. For protons and α particles the critical temperature over an enormous pressure range is found to be near 1 eV, and only at extremely high pressures ($\sim 10^8$ Mbar) does the mixture become stable. Phase separation at lower pressures, as in the interior of Jupiter ($\sim$40 Mbar, 1 eV), is shown to be unlikely on the basis of more realistic models which modify, however crudely, the uniform electron approximation.

I. INTRODUCTION

It has been suggested[1,2] that under the pressure and temperature conditions in the interior of giant planets, such as Jupiter, helium may not be completely soluble in hydrogen. A more recent detailed calculation[3] predicts phase separation for such a mixture at sufficiently low temperature. In order to help understand the physical basis of such a possible phase separation a simple model, rigorously valid at sufficiently high pressure and low temperature, has been worked out.

In that model helium and hydrogen are assumed to be completely pressure ionized so that the electrons can be considered to form a uniform background. This is an extension of the so-called one-component plasma (OCP) considered earlier[4,5] to mixtures of nuclei. Applicability of that model depends on the pressure not being so high that the nuclei have to be treated quantum mechanically nor so low that the clustering of electrons around the nuclei (screening) is important, that is the pressure is high enough so that the zero point or Fermi energy of the electrons exceeds their Coulomb attraction to the bare nuclei. Under these circumstances the problem reduces to the evaluation of classical statistical mechanical averages for the ions which can be done rigorously, with only insignificant caveats, by either the Monte Carlo or molecular dynamics numerical computational technique. In fact some such results are already available[6] and have been exploited for present purposes.

The above model is, however, not a very accurate description of the state of matter at the center of Jupiter where the pressure is estimated to be about 40 Mbar and the temperature about 1 eV. At that pressure hydrogen is certainly metallic[7] and the zero point energy of the electron comparable to the binding energy, so that the uniform electron approximation is reasonable. However, helium is not expected to become even metallic until about 100 Mbar[8] so that the uniform electron approximation is hardly justified below about 200 Mbar.[9] Hence, under Jovian conditions it is necessary to take screening into account and this can be done by several approaches. The earlier calculation[3] allowed the electrons to respond to the ionic potential by treating the electron-ion interaction as a perturbation which was carried out to third order. Such a perturbation treatment is expected to be valid only when the screening effects are small, hardly the situation in Jupiter. Furthermore, this earlier calculation approximated even the OCP by equivalent hard sphere properties.

Alternatively an effective screened potential between the ions, through the assumption of a dielectric function obtained from the linear response of the electron gas to the ionic potential and hence valid to first order in the screening, can be introduced in the Monte Carlo calculations. Although considerable calculations of this type have been carried out for the one-component case,[10] only preliminary calculations for mixtures are available,[6] and they have not been utilized here, awaiting more extensive results. Instead it was thought most realistic to work out a simple model where helium is completely screened or neutral and acts merely to exclude electrons and protons of the one component hydrogen plasma from its neighborhood. An intermediate case of screening in which the helium atom is singly ionized can also be easily treated if the atom is approximated by a hard sphere of the same charge as the surrounding one-component hydrogen plasma. However, the singly ionized state of helium is not likely to be a realistic representation over a wide region of pressure in as much as once helium becomes metallic the band structure is such that it would allow both electrons to become delocalized.

II. MONTE CARLO RESULTS

In the case of the completely degenerate electron gas that forms a uniform background, exact results can be obtained by the Monte Carlo method. The present thermodynamic considerations are based on such calculations which have been summarized by an empirical fit to the numerically generated Helmholtz free energies, F, under various conditions.[11] This free energy of N_1 ions of charge Z_1 and N_2 ions of charge Z_2 confined to a volume v in a uniform electron gas background at temperature T can be written as the sum of three contributions

$$F = F_i + F_e + F_c \,.$$

The first term is the ideal gas contribution

$$F_i/NkT = x_1[\ln(\lambda_1^3\rho) + \ln x_1] + x_2[\ln(\lambda_2^3\rho) + \ln x_2] - 1 \,,$$

where the mole fraction of species 1 is $x_1 = N_1/(N_1+N_2)$, the number density $\rho = N/v$ and λ is the de Broglie thermal wavelength of the nuclei. The middle term accounts for the background electron gas of a total of $N_1Z_1 + N_2Z_2$ electrons, whose energy per electron in rydberg's is given by

$$E_e = 2.21/r_s^2 - 0.916/r_s - 0.115 + 0.031 \ln r_s \,,$$

where r_s is the electron sphere radius in units of the Bohr radius. At finite temperatures the well-known first correction in the expansion relative to the Fermi energy has been added. Finally, the last term obtained from the Monte Carlo results has been fitted by[11]

$$F_c/NkT = 0.89461\Gamma + 3.26591\Gamma^{1/4} - 0.50123 \ln\Gamma - 2.186 \,,$$

where

$$\Gamma = (x_1Z_1^{5/3} + x_2Z_2^{5/3})(x_1Z_1 + x_2Z_2)^{1/3} e^2/kTa,$$

and where a is the ion sphere radius. This same form was found to fit both the one-component results[5] and the mixture data[11] within statistical uncertainty of the data. This form is hence well suited to get the excess properties of mixing which involves differences between thermodynamic properties. An earlier empirical free energy fit[6] based on less extensive Monte Carlo data gave qualitatively the same results but with large quantitative differences. The sensitivity of the results to F_c underscores the need for additional high-precision Monte Carlo data on the mixtures.

The excess mixing properties at constant pressure $\Delta G = G_M(x,p,T) - x_1G_1(p,T) - x_2G_2(p,T)$ require knowledge of the Gibbs free energy, evaluated by $G = F - v(\partial F/\partial v)_T$, where the subscript M signifies mixture. A typical example of ΔG at various mole fractions of protons and at a temperature below the critical temperature is given in Fig. 1. Phase separation is indicated, since $\partial^2\Delta G/\partial x^2 < 0$, and the standard double tangent construction determines the concentration of the two phases in equilibrium with each other. Such calculations permit the construction of the phase diagrams at various pressures as given in Fig. 2.

At the highest pressure of 200 Mbar shown in Fig. 2, the model ought to be a realistic representation, and hence phase separation below a critical temperature of about 1 eV should correspond to actual observations. Incidentally, mixing at constant volume, which is theoretically easier to treat, leads to virtually indistinguishable results to those at constant pressure at 200 Mbar. At lower pressure where the model cannot be taken seriously, the critical temperature does not shift much, but is observed to rise a little. This corresponds to the observation that the higher the pressure the more the electron gas pressure dominates, and hence the more ideal the mixture or the lower the critical temperature becomes. A comparison at 60 Mbar to an earlier calculation that includes the effect of screening[3] shows that, as expected, screening lowers the critical temperature since it can be looked upon as reducing the effective charge difference between the species.

At 60 Mbar the results are also compared to the predictions based on only the first term in the above expansion for F_c/NkT. As will be seen from lattice model considerations, the coefficient of that term as well as its functional form suggest that it represents the potential energy contribution to the free energy. Hence the qualitative argument can be made that phase separation is caused by the potential energy being lower in the pure phases than in the mixture because, given the constraint of a uniform charge distribution, local charge neutralization is not as easily satisfied in a mixture as in the two separated phases. This can be quantitatively seen from the following argument. For a single-component lattice of point charges in a uniform electron background at 0 °K, the potential or Madelung energy, U/N, per ion is accurately approximated by surrounding each ion by a charge neutralizing sphere of uniform density electron gas. For that model U/N is calculated to be $0.9\, Z^2e^2/a$ whereas the exact result for a bcc lattice is $-0.8959\, Z^2e^2/a$.[12] A simple extension of this model to mixtures requires that each different ion species be surrounded by a different neutralizing sphere of the same uniform density electron gas, so that

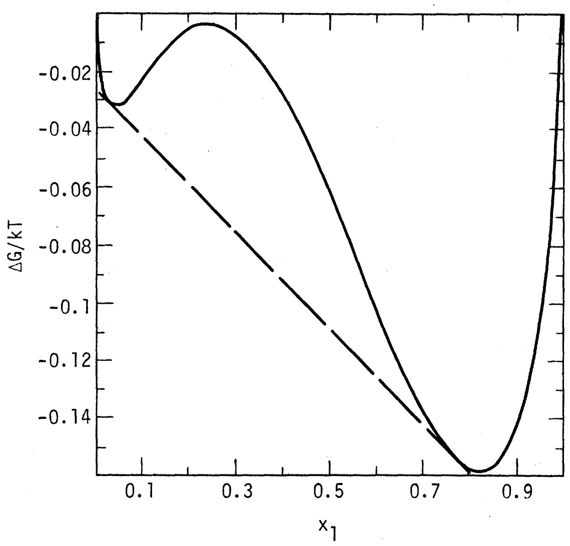

FIG. 1. Typical excess free energy of mixing as a function of mole fraction of helium at 60 Mbar below the critical temperature at $T=0.7$ eV. The dashed line indicates the double tangent construction from which the mole fraction of the two phases in equilibrium can be determined.

$$\frac{U}{N}=-0.9e^2\left[Z_1^2x_1\left(\frac{Z_1x_1+Z_2x_2}{Z_1}\right)^{1/3}+Z_2^2x_2\left(\frac{Z_1x_1+Z_2x_2}{Z_2}\right)^{1/3}\right]/a\,,$$

equivalent to the form used earlier

$$U/N=-0.9\,e^2(Z_1x_1+Z_2x_2)^{1/3}(x_1Z_1{}^{5/3}+x_2Z_2{}^{5/3})/a\,.$$

It is this result which motivated the first term in the empirical free energy fit given above for F_c/NkT and which shows that the uniform background does not allow the charge neutralization in the mixture to be as effective in lowering the potential energy as in the pure components. The 60-Mbar example illustrates that this potential term alone makes semiquantitative predictions of the phase diagram and the further terms in F_c/NkT, representing the thermal energy contribution of the ions, do not qualitatively alter the phase diagram.

It remains to demonstrate that the above approximation for the potential energy of a mixture is close to the value obtained for a lattice model of a mixture, although for mixtures the lattice of highest stability is generally not known. Hence two different lattices were considered for the

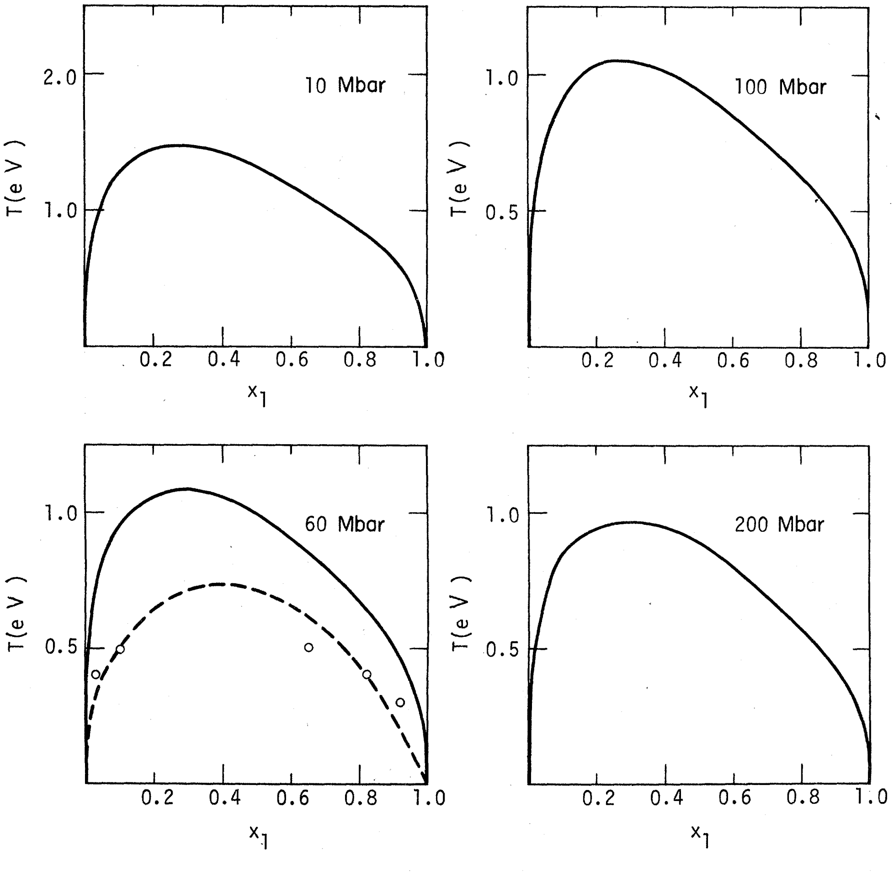

FIG. 2. Phase diagram for mixtures of hydrogen and helium at the various pressures indicated for classical point charges in a uniform electron background. At 60 Mbar the results for the lattice model are indicated by circles, and the dashed curve represents the results from an earlier model. (Ref. 3).

specific case of a 50% mixture, namely the CsCl and NaCl structure in which the two different nuclei occupy the two different ion positions. The potential energy can be evaluated by the usual Ewald technique or more readily by taking advantage of the symmetry with respect to the charges of the ions and determining the constants from the known limiting cases when $Z_1 = Z_2$ and when $Z_2 = 0$. The result for the CsCl lattice is

$$U/N = -e^2[0.349254(Z_1^2 + Z_2^2) + 0.197427\, Z_1 Z_2]/a$$

and for the NaCl lattice is

$$U/N = -e^2[0.355528(Z_1^2 + Z_2^2) + 0.169004\, Z_1 Z_2]/a\,.$$

Both of these potential energies agree with the neutralizing sphere approximation to better than 1% for the 50% proton-α-particle mixture, confirming that the first term in F_c/NkT is representative of the potential energy of the system. The fact that a lattice, that is the configuration correct in the high-density limit, can give a good first approximation to the potential energy of a fluid of ions is because in such fluids the potential energy is large relative to the kinetic energy and that the long range forces make the potential energy relatively insensitive to small displacements of the ions about their lattice positions.

If to the above potential energy, the background electron gas energy, given earlier, is added, a good approximation to the total energy or equivalently at 0 °K, the free energy can be obtained. From the dependence of these two contributions on volume, it is then evident that at sufficiently high density the electron gas term will dominate so that both the mixture and the two pure components at the same pressure will all have the same electron density or, in other words, the mixture is ideal with no phase separation possible. The pressure at which the mixture will no longer phase separate is shown for a hydrogen-helium mixture in Fig. 3. The excess free energy ΔG is seen to decrease with increasing pressure which, as pointed out earlier, corresponds to a decrease in the critical temperature and finally becomes negative indicating that at a pressure of about 10^8 Mbar the mixture is stable even at 0 °K. At that high pressure the mixture of classically behaving nuclei would certainly be crystalline and so the lattice model used should be applicable, however the density is so high that the quantum mechanical zero point energy of the nuclei cannot be neglected.[13] This nuclear zero point energy is such that melting of the ionic lattice is predicted. Nevertheless, the calculation of the pressure at which the mixture is stable is not expected to be significantly affected by the melting effect since the stability consideration involves energy differences between the mixture and the pure components, both of which undergo melting.

III. SCREENED HELIUM MODELS

A primitive model at lower pressures where the uniform electron background approximation becomes poor is to consider the helium as a hard sphere which is singly ionized and the hydrogen atom as still completely unscreened. The hard sphere diameter can be picked to correspond to the known size of the He^+ ion which is in the range of 0.5 to 1 Å. The protons and other He^+ ions are not likely to approach a He^+ ion within that distance anyway since the ions interact via the repulsive Coulomb energy. The free electrons on the other hand, are considered to be merely excluded from the volume occupied by the singly charged hard spheres.

Indeed, previous studies of the radial distribution function[4] of a one-component plasma of singly charged point ion under the conditions of a pressure of 10 Mbar and a temperature of 0.5 eV, corresponding to a value of $e^2/kTa = 50$ indicate, that two singly charged ions have a vanishing probability of approaching each other within 1 Å. Hence as far as the ions are concerned the hard sphere might as well not be there at these low pressures. Thus it is safe to assume that the main effect of the bound electrons is to exclude the free electrons from the region occupied by them. The Gibbs free energy of mixing is easily calculated from the previous OCP calculations at the appropriate electron densities. The result is given in Fig. 4 for two different charged-sphere radii at a pressure and

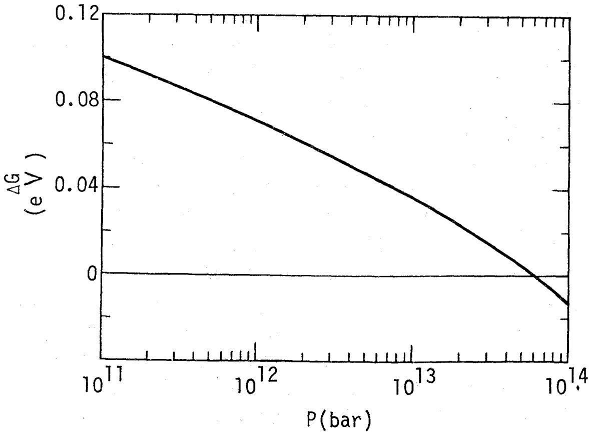

FIG. 3. The excess free energy of mixing for a 50% hydrogen-helium mixture from the bcc lattice model at 0 °K as a function of the logarithm of the pressure.

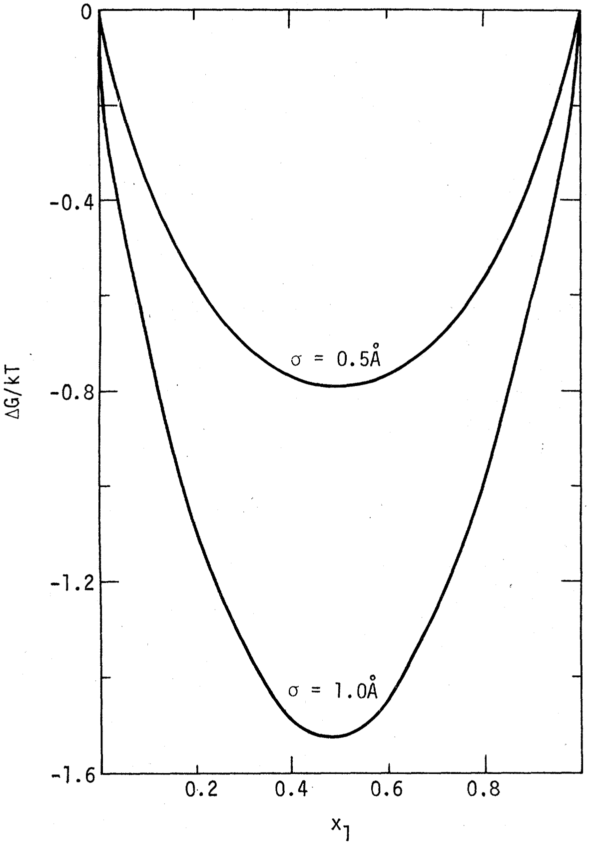

FIG. 4. The excess free energy of mixing for protons and singly charged helium ions in a uniform electron gas background at 10 Mbar and 0.5 eV at two different helium ion radii as indicated.

temperature where hydrogen is just becoming metallic in the interior of Jupiter. No phase separation is indicated where the previously completely unscreened case did show such phase separation. This result is not unexpected in view of the above observation that the two ionic species interact in a virtually identical manner.

Inclusion of any attractive interaction of the neutral helium atom with either the protons or electrons would stabilize the mixture even further. An extension of the above model that is valid when the screening of the helium in still stronger, considers the helium as neutral or a sphere with no charge. The hydrogen is still considered as a one-component plasma and the protons and electrons are again excluded from a hard sphere of size $\sigma = 1$ Å, that is, confined to a volume $v - N_1\pi\sigma^3/6$. If it is further assumed, as is rigorously valid for sufficiently long-range forces, that the properties of the OCP are independent of the configuration of the spheres, the free energy can be written as a sum

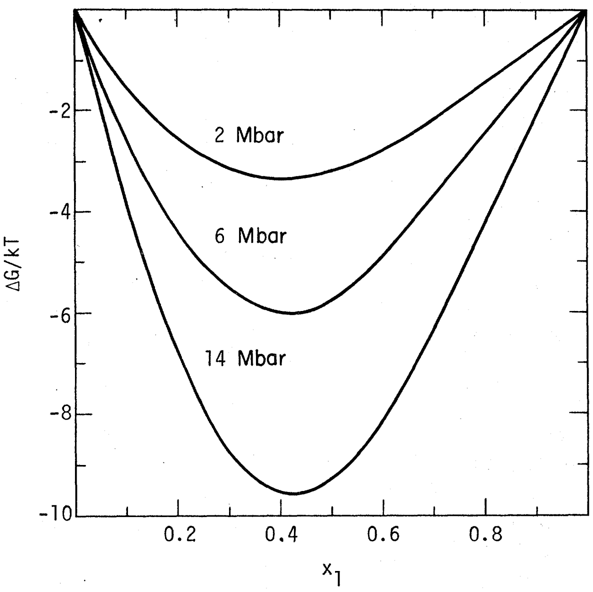

FIG. 5. The excess free energy of mixing of protons and neutral helium atoms in a uniform electron background at 0.5 eV and the various pressures indicated.

$$F_M(N_1, N_2, v, T) = F_{\mathrm{OCP}}(N_2, v - N_1\pi\sigma^3/6, T) + F_{\mathrm{He}}(N_1, v, T) .$$

To accurately evaluate the helium-helium free energy F_{He} in the mixture as well as in the pure component, a more realistic representation of the intermolecular potential, $V(r)$ than hard spheres is necessary. For that purpose atomic beam deduced intermolecular potentials[14,15] were adequately represented by Ar^{-6}, where A is taken to be 5 eV. From previous Monte Carlo calculations[16] for particles interacting by Ar^{-6}, the free energy can be obtained for that system. The resulting Gibbs free energy of mixing at a temperature of 0.5 eV and several pressures, shown in Fig. 5, indicates no phase separation.

This model ignores the energy shift of the helium bound-state level due to interaction with the surrounding plasma. Our result of no phase separation should not be affected by this since the shift will be mainly a function of the electron-gas density. For the calculations presented in Fig. 4 the electron-gas density for the pure He^+ and for the 50% mixture of (He^+, H^+) differ by less than 5%. The bound-state level shift is thus very nearly the same for the pure He^+ and for the He^+ in the mixture and, therefore, cancels in ΔG. These considerations as well as the earlier mentioned perturbation treatment show that screening lowers the critical temperature and in the case of the above two models inhibits phase separation completely. Since the above two models should be a more realistic representation of the state of matter in the interior of Jupiter, no phase separation is expected there.

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