

Thermodynamics and phase separation of dense fully ionized hydrogen-helium fluid mixtures

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The free energy of a hydrogen-helium fluid mixture is evaluated for the temperatures and densities appropriate to the deep interior of a giant planet such as Jupiter. The electrons are assumed to be fully pressure ionized and degenerate. In this regime, an appropriate first approximation to the ionic distribution functions can be found by assuming hard-sphere interactions. Corrections to this approximation are incorporated by means of the perturbation theory of Anderson and Chandler. Approximations for the three-body interactions and the nonlinear response of the electron gas to the ions are included. We predict that a hydrogen-helium mixture, containing 10% by number of helium ions, separates into hydrogen-rich and helium-rich phases below about 8000°K, at the pressures relevant to Jupiter (4–40 Mbar). We also predict that the alloy occupies less volume per ion than the separated phases. The equation of state and other thermodynamic derivatives are tabulated. The implications of these results are mentioned.

I. INTRODUCTION

The mass and radius of a giant planet such as Jupiter can only be explained by assuming that the main constituent is hydrogen.¹ This suggests that Jupiter may have solar composition such that about one atom in ten is helium. Moreover, Jupiter emits about twice as much radiation as it receives from the sun.² This indicates an internal heat source and is consistent with a temperature in the deep interior that exceeds the melting point of metallic hydrogen or of helium.¹ It has also been suggested that the helium may have only limited solubility in the hydrogen.^{3,4} Clearly, detailed models of the giant planets require an understanding of the thermodynamics and phase diagram of dense hydrogen-helium fluids. In this paper, the relevant properties of such a system are calculated. We assume that all the electrons are pressure ionized although our calculations have at least approximate validity at the lower pressure relevant to Jupiter.

The only previous relevant calculations are the incomplete Monte Carlo studies by Hubbard.^{5,6} The lengthy computational time of those calculations is avoided here by choosing an appropriate trial solution for the ionic distribution functions and then by using a perturbation theory (the optimized random-phase approximation of Anderson and Chandler⁷) to closely approximate the real ionic distribution. At the densities and temperatures of interest ($1 \lesssim \rho \lesssim 10 \text{ g/cm}^3$, $10^3 \lesssim T \lesssim 5 \times 10^4 \text{ }^\circ\text{K}$), the ion-ion interaction (in the presence of screening electrons) is characterized by a repulsive core and a weak long-range part,⁸ so the appropriate trial solutions are the distribution functions for hard spheres. At higher densities or temperatures, a different approximation scheme (or the Monte Carlo method) is more appropriate.

Our calculation contains features not present in

Hubbard's calculations. We have used a more realistic dielectric function, and corrections have been made for the quantum mechanics of the ions, the three-body interactions, the nonlinear response of the electron gas to the ions, and the finite temperature corrections to the electron gas. Some of the thermodynamic properties are significantly affected by these corrections. Nevertheless, our results are similar to those of Hubbard in most instances. We do make an important new prediction: the existence of a miscibility gap in the hydrogen-helium alloy. We also predict that there is a small but non-negligible volume nonadditivity (i. e., the alloy occupies less volume per ion than the separated phases). The detailed astrophysical implications will be discussed elsewhere; they are only briefly mentioned in the present paper.

In Sec. II, the free-energy calculation is described. In Sec. III, the thermodynamic properties are discussed. In Sec. IV, the phase separation is described and in Sec. V, the validity of our calculation is assessed.

II. FREE ENERGY

Consider a binary system in which a fraction x of the nuclei have charge $Z = 2$, and a fraction $1 - x$ have charge $Z = 1$. The compensating electron gas has an average density $Z^*N = (\frac{4}{3}\pi r_s^3 a_0^3)^{-1}$ where N is the ion number density, the effective valence is $Z^* = 1 + x$, $a_0 = 0.529 \times 10^{-8} \text{ cm}$, and r_s is the electron spacing parameter ($r_s \sim 1$ in Jupiter). The free energy is written

$$F = F_{eg} + F_{hs} + E_M + E_{BS} + \Delta F_{int} + F_Q . \quad (1)$$

We now discuss the meaning and evaluation of each term.

The free energy of a uniform electron gas F_{eg} can be expressed as the sum of a zero-temperature contribution and a small finite-temperature correction since we assume

$$T \ll \frac{6 \times 10^5}{\gamma_s^2} \text{ }^\circ\text{K} = T_F, \quad (2)$$

where T and T_F are the actual and Fermi temperatures, respectively. The zero-temperature contribution is

$$E_{eg} = (2.21/\gamma_s^2 - 0.916/\gamma_s - 0.115 + 0.031 \ln \gamma_s) Z^* \text{ Ry/ion}, \quad (3)$$

where an interpolation approximation has been used for the correlation energy.⁹ (Any small inaccuracy in the correlation energy has negligible effect on the final results.) The only finite-temperature correction that we have retained is the kinetic energy term¹⁰

$$\Delta F_{eg} = -\frac{1}{4} \left(\frac{4}{3}\pi^2\right)^{2/3} \gamma_s^2 (k_B T)^2 Z^* \text{ Ry/ion}, \quad (4)$$

where $k_B T$ is in Rydbergs ($k_B = 6.34 \times 10^{-6}$ Ry/ $^\circ\text{K}$). The other corrections can be shown to be negligible at the temperatures of interest.¹¹

As a first approximation, we assume that the ions, with their comoving screening clouds of electrons, interact like hard spheres. Consequently, we have, in addition to electrostatic energy contributions, the free energy F_{hs} of an equivalent neutral hard-sphere liquid. This has been approximately calculated by Mansoori *et al.*¹²

$$F_{hs} = F_{1g} + k_B T \left[-\frac{3}{2} (1 - y_1 + y_2 + y_3) + (3y_2 + 2y_3)/(1 - \eta) + \frac{3}{2} (1 - y_1 - y_2 - \frac{1}{3} y_3)/(1 - \eta)^2 + (y_3 - 1) \ln(1 - \eta) \right],$$

$$F_{1g} = -k_B T \left\{ 1 + x \ln \left[\frac{1}{xN} \left(\frac{M_2 k_B T}{2\pi\hbar^2} \right)^{3/2} \right] + (1 - x) \ln \left[\frac{1}{(1 - x)N} \left(\frac{M_1 k_B T}{2\pi\hbar^2} \right)^{3/2} \right] \right\}, \quad (5)$$

where

$$\begin{aligned} y_1 &= x(1-x)(1-\alpha)^2(1+\alpha)/d, \\ y_2 &= x(1-x)\alpha(1-\alpha)^2[(1-x)\alpha^2+x]/d^2, \\ y_3 &= [(1-x)\alpha^2+x]^3/d^2, \\ d &= (1-x)\alpha^3+x, \\ \eta &= \frac{\text{volume occupied by hard spheres}}{\text{total volume}}, \\ \alpha &= \frac{\text{diameter of hydrogen hard spheres}}{\text{diameter of helium hard spheres}}, \end{aligned}$$

and M_1 , M_2 are the hydrogen and helium ionic masses, respectively. F_{1g} is the free energy of an ideal gas mixture. (A hard-sphere mixture deviates from an ideal gas to the extent that η is nonzero.) For $\eta \geq 0.45$, a classical liquid is expected to solidify.¹³ The predictions of Eq. (5) are almost indistinguishable from hard-sphere Monte Carlo calculations, in contrast to the alternative formula of Lebowitz.¹⁴ The parameters η and α

are not known in advance and are to be determined variationally.

We next evaluate the Madelung energy E_M which is the electrostatic energy of point ions immersed in a *uniform* electron gas

$$E_M = \frac{e^2}{2N\Omega} \left\langle \sum_{n \neq m} \frac{Z_n Z_m}{|\vec{r}_n - \vec{r}_m|} - 2NZ^* \sum_m Z_i \int \frac{d\vec{r}'}{|\vec{r}_m - \vec{r}'|} + N^2 Z^{*2} \int \frac{d\vec{r} d\vec{r}'}{|\vec{r} - \vec{r}'|} \right\rangle, \quad (6)$$

where the integrals extend over the entire volume Ω and $\langle \dots \rangle$ denotes an ensemble average. In (6), \vec{r}_n^i refers to a nucleus of charge Z_i at position \vec{r}_n . It can then be shown that

$$E_M = \frac{1}{2\Omega} \sum_{\vec{k} \neq 0} \frac{8\pi}{k^2} \{ (1-x) Z_1^2 [S_{11}(\vec{k}) - 1] + 2Z_1 Z_2 x^{1/2} (1-x)^{1/2} S_{12}(\vec{k}) + Z_2^2 x [S_{22}(\vec{k}) - 1] \} \quad (7)$$

($Z_1 = 1$, $Z_2 = 2$ for H-He), where the partial structure factors $S_{ij}(\vec{k})$ are defined as

$$S_{ij}(\vec{k}) = \frac{1}{(N_i N_j)^{1/2} \Omega} \left\langle \sum_{n,m} e^{i\vec{k} \cdot (\vec{r}_n^i - \vec{r}_m^j)} \right\rangle - (N_i N_j)^{1/2} \Omega \delta_{\vec{k},0}, \quad (8)$$

and N_i , N_j are the partial number densities of the two ionic species. We approximate S_{ij} by the Percus-Yevick hard-sphere result found by Ashcroft and Langreth.¹⁵ Ross and Seale¹⁶ have shown that in this approximation, the summation in (7) can be evaluated exactly. We give the rather complicated result here because of an error in their paper:

$$E_M = \frac{-3\eta^{2/3}}{5[(1+x)d^2]^{1/3} \gamma_s (1+2\eta)} \left[\alpha^2 Z_1^2 (1-x)^2 G_{11} + 2 \left(\frac{1+\alpha}{2} \right)^2 Z_1 Z_2 x (1-x) G_{12} + Z_2^2 x^2 G_{22} \right] \text{ Ry/ion},$$

$$\begin{aligned} G_{11} &= [\eta_1^2 - 2\eta_1 + 10 - 4\eta_1 \eta_2 + (10/\alpha)(\eta_1 \eta_2 - \eta_2) + (\eta_2^2 - 2\eta_2 - 4\eta_1 \eta_2)/\alpha^2], \\ G_{12} &= 15(\eta_2 - \eta_1)(1/\alpha - 1)2\alpha/(1+\alpha) - 30(1+\eta) + (2\alpha/1+\alpha)^2 [\eta_1^2 - 2\eta_1 + 10 - 4\eta_1 \eta_2 + 20\eta_2 + 10(\eta_1 \eta_2 + \eta + 2)/\alpha + (\eta_2^2 - 2\eta_2 + 10 - 4\eta_1 \eta_2 + 20\eta_1)/\alpha^2], \end{aligned} \quad (9)$$

$$\eta_1 = (1-x)\alpha^3 \eta/d, \quad \eta_2 = x\eta/d$$

and G_{22} is obtained from G_{11} by replacing $1/\alpha$ by α and η_1 by η_2 . Corrections to the hard-sphere approximation are contained in ΔF_{int} , discussed below.

We next consider the "band-structure" energy E_{BS} , resulting from the nonuniformity of the electron gas. In general, it is possible to expand $\rho_{ind}^i(\vec{k})$, the Fourier transform of the electron-den-

sity change induced by the ions of species i , in powers of the electron-ion interaction.¹⁷⁻¹⁹

$$\begin{aligned} \rho_{\text{ind}}^i(\vec{k}) &= \sum_{n=1} \rho_{\text{ind}}^{i(n)}(\vec{k}) \\ &= \chi_1(\vec{k}) V^i(\vec{k}) \rho_{\text{ion}}^i(\vec{k}) + \sum_{i=1,2} \sum_{\vec{q}} \chi_2(\vec{k}, \vec{q}) V^i(\vec{k} \\ &\quad + \vec{q}) \rho_{\text{ion}}^i(\vec{k} + \vec{q}) V^i(-\vec{q}) \rho_{\text{ion}}^i(-\vec{q}) + \text{higher order}, \end{aligned} \quad (10)$$

where

$$\rho_{\text{ion}}^i(\vec{k}) = \sum_m e^{i\vec{k} \cdot \vec{r}_m^i}$$

and

$$V^i(\vec{k}) = (8\pi Z_i / k^2), \quad (11)$$

where $8\pi Z_i / k^2$ is in Ry a_0^3 .

We have retained terms up to third order in the electron-ion interaction, so that $E_{\text{BS}} \approx E^{(2)} + E^{(3)}$, where

$$E^{(n)} = \frac{1}{nN\Omega} \sum_{\vec{k} \neq 0} \left\langle \sum_{i,j=1,2} \rho_{\text{ind}}^{i(n-1)}(\vec{k}) V^j(-\vec{k}) \rho_{\text{ion}}^j(-\vec{k}) \right\rangle. \quad (12)$$

Note that in Eqs. (7) and (12), the zeroth Fourier components are omitted from the summation since they are exactly compensated by the divergent electron-electron interaction energy.

The lowest order term in $\rho_{\text{ind}}^i(\vec{k})$ is the linear response result^{17,20}

$$\rho_{\text{ind}}^{i(1)}(\vec{k}) = \frac{k^2}{8\pi} \left(\frac{1}{\epsilon(k)} - 1 \right) V^i(\vec{k}) \rho_{\text{ion}}^i(\vec{k}), \quad (13)$$

where $\epsilon(k)$ is the static dielectric function. In our calculations, the Hubbard approximation has been used.²⁰ This is a more realistic form for the linear response than the Lindhard expression used in the Monte Carlo studies.^{5,6} Corrections for the *dynamic* response of the electron gas appear to be negligible²¹ and have not been included.

From the definitions of the partial structure factors, it can then be shown that²²

$$\begin{aligned} E^{(2)} &= \frac{2}{\pi} \int_0^\infty [Z_1^2(1-x)S_{11}(k) + 2Z_1Z_2x^{1/2} \\ &\quad \times (1-x)^{1/2}S_{12}(k) + Z_2^2xS_{22}(k)] \\ &\quad \times \left(\frac{1}{\epsilon(k)} - 1 \right) dk \text{ Ry/ion}, \end{aligned} \quad (14)$$

where k is in units of a_0^{-1} . This contribution is evaluated numerically using the hard-sphere structure factors.

The theory for $E^{(3)}$ is not given in detail here, since it is an obvious generalization of the results for crystalline metals.¹⁷⁻¹⁹ (For example, the only change to equation 4.8 of Lloyd and Sholl¹⁷ is the insertion of ensemble averages.) The appropriate generalization of Eq. (90) of Hammerberg and Ash-

croft¹⁹ is

$$\begin{aligned} E^{(3)} &= -\frac{16}{\pi^3} \left(\frac{4}{9\pi} \right)^{1/3} \gamma_s \sum_{i,j,k=1,2} \int d\vec{\xi} d\vec{\xi}_1 W^i(-\vec{\xi}) \\ &\quad \times W^j(\vec{\xi} - \vec{\xi}_1) W^k(\vec{\xi}_1) H^{(3)}(\vec{\xi}, \vec{\xi}_1) T_{ijk}(\vec{\xi}, \vec{\xi}_1) \end{aligned} \quad (15)$$

where

$$\begin{aligned} T_{ijk}(\vec{\xi}, \vec{\xi}_1) &= \left\langle \frac{1}{N\Omega} \sum_{m,n,p} \exp[i2k_F \right. \\ &\quad \left. \times (-\vec{\xi} \cdot \vec{r}_m^i + (\vec{\xi} - \vec{\xi}_1) \cdot \vec{r}_n^j + \vec{\xi}_1 \cdot \vec{r}_p^k) \right\rangle. \end{aligned} \quad (16)$$

$W^i(\xi) = [Z_i / \xi^2 \epsilon(\xi)]$, $\xi = k/2k_F$, k_F is the Fermi wave vector, and $H^{(3)}$ is the three-vertex function defined by Hammerberg and Ashcroft. Since m, n, p do not have to be different in the summation for T_{ijk} , it is clear that $E^{(3)}$ contains not only three-body interactions, but also corrections to two-body interactions and (structure independent) corrections to the screening of single ions. The evaluation of T_{ijk} can only be approximate since there is no accurate theory for three-body correlation functions. We have chosen a convolution approximation (see Appendix A).

We have not evaluated the *fourth-order* contribution to the band-structure energy, but some semi-quantitative assertions can be made. First, it is clear from the work of Hammerberg and Ashcroft¹⁹ that there are additional complications at fourth order that can only be encompassed by the use of finite-temperature perturbation theory. Second, their formal results can be easily extended to liquids and liquid mixtures. In particular, the terms which they ascribe to the nonsphericity of the Fermi surface in the solid, are nonzero (and comparable in magnitude) in the liquid phase. It seems that the substantial cancellation of fourth-order terms that they found for crystalline metallic hydrogen, persists in the liquid. The cancellation is also substantial for helium, since the dominant fourth-order contributions have similar Z dependence. Thus it is hoped that our omission of $E^{(4)}$ is not a serious deficiency.

In the above calculations, we have used an effective ion-ion interaction, the accuracy of which is limited only by uncertainties in the dielectric function of the electron gas. We have not, however, evaluated the ionic configuration appropriate to that interaction. This is corrected by the optimized random-phase approximation method of Andersen and Chandler (see Appendix B). To second order in the electron-ion interaction.

$$\begin{aligned} \Delta F_{\text{int}} &= \frac{k_B T}{16\pi^3 N} \int [\ln(\det |\tilde{I} + N\tilde{S}\tilde{\phi}/k_B T|) \\ &\quad - N\text{Tr}\tilde{S}\tilde{\phi}/k_B T] d\vec{k}, \end{aligned} \quad (17)$$

where \det means determinant, Tr means trace, \tilde{I} is the unit 2×2 matrix; and $\tilde{S}, \tilde{\phi}$ are the 2×2 ma-

trices, the elements of which are

$$\begin{aligned}\bar{S}_{ij} &= S_{ij}(\vec{k}), \\ \bar{\phi}_{ij} &= (x_i x_j)^{1/2} \phi_{ij}(\vec{k}),\end{aligned}\quad (18)$$

where x_i, x_j are the number fractions of ion species i and j , and $\phi_{ij}(\vec{k})$ is the Fourier transform of the optimized potential $U_{ij}(r)$, given by

$$U_{ij}(r) = \begin{cases} -k_B T C_{ij}(r), & r < R_{ij} \\ v_{ij}^{\text{eff}}(r), & r \geq R_{ij}, \end{cases} \quad (19)$$

where R_{ij} is the minimum hard-sphere separation and $v_{ij}^{\text{eff}}(r)$ is the effective ion-ion interaction, the Fourier transform of which is $4\pi e^2/k^2 \epsilon(k)$. The functions $C_{ij}(r)$ are chosen variationally

$$[\delta \Delta F_{\text{int}} / \delta C_{ij}(r)] = 0, \quad r < R_{ij}. \quad (20)$$

A quadratic function of r was found to be adequate for approximating each $C_{ij}(r)$.

Finally, we have included the lowest-order high-temperature quantum correction

$$\begin{aligned}F_Q &= \frac{\hbar^2 N}{24 k_B T} \sum_{i,j=1,2} \frac{x_i x_j}{M_{ij}} \int g_{ij}(r) \nabla^2 v_{ij}^{\text{eff}}(r) d\vec{r}, \\ 1/M_{ij} &= \frac{1}{2} (1/M_i + 1/M_j),\end{aligned}\quad (21)$$

where $g_{ij}(r)$ is the pair correlation function for ion species i and j , and M_i is the mass of ion species i . This result was first derived by Wigner²³ and is the effect of including the uncertainty principle for the ions to lowest order in $\hbar^2/Ma_0^2 k_B T$. Unlike F_Q , the next term in the Wigner expansion depends on whether the ions are bosons or fermions, but it can be shown to be negligible ($\sim 10^{-3}$ Ry) for our present purposes.

Notice that F_Q does *not* scale as $r_s^{-3/2}$, the result that one might expect for zero-point motion.²⁴ The Wigner expansion is rapidly convergent provided

TABLE I. Parameter $c = (1/Nk_B)(dP/dT)_{V,x}$ as a function of $r_s, r_s T$, and x .

r_s	$r_s T$	x						
		0.0	0.1	0.2	0.4	0.6	0.8	1.0
1.2	4000	1.07	1.12	1.18	1.40	1.60	1.46	1.30
	7000	1.24	1.30	1.41	1.67	1.86	1.78	1.70
	12000	1.22	1.25	1.30	1.39	1.52	1.69	1.83
	20000	1.23	1.25	1.27	1.32	1.41	1.47	1.55
	30000	1.25	1.30	1.31	1.35	1.44	1.47	1.55
0.9	4000	1.01	1.04	1.05	1.02	0.83	0.77	0.69
	7000	1.12	1.16	1.19	1.32	1.43	1.51	1.48
	12000	1.17	1.23	1.28	1.46	1.56	1.59	1.65
	20000	1.17	1.19	1.24	1.32	1.40	1.49	1.60
	30000	1.19	1.21	1.25	1.33	1.40	1.45	1.59
0.7	4000	0.65	0.60	0.57	0.59	0.61	0.64	0.65
	7000	1.03	1.05	1.10	1.12	1.12	1.09	1.08
	12000	1.14	1.18	1.25	1.37	1.48	1.54	1.56
	20000	1.18	1.24	1.30	1.36	1.41	1.47	1.50
	30000	1.20	1.25	1.30	1.35	1.40	1.44	1.47

TABLE II. Parameter $\gamma = (d \ln T / d \ln \rho)_{S,x}$ as a function of $r_s, r_s T$ and x .

r_s	$r_s T$	x						
		0.0	0.1	0.2	0.4	0.6	0.8	1.0
1.2	4000	0.61	0.62	0.62	0.65	0.66	0.61	0.55
	7000	0.61	0.62	0.66	0.67	0.68	0.61	0.56
	12000	0.61	0.61	0.65	0.65	0.66	0.65	0.65
	20000	0.63	0.64	0.64	0.65	0.66	0.65	0.65
	30000	0.64	0.64	0.65	0.65	0.66	0.65	0.65
0.9	4000	0.58	0.58	0.59	0.58	0.55	0.53	0.53
	7000	0.60	0.61	0.60	0.59	0.60	0.61	0.61
	12000	0.63	0.63	0.62	0.62	0.62	0.63	0.62
	20000	0.64	0.63	0.63	0.63	0.64	0.63	0.63
	30000	0.64	0.63	0.63	0.63	0.64	0.63	0.63
0.7	4000	0.56	0.56	0.55	0.55	0.55	0.53	0.53
	7000	0.59	0.60	0.59	0.59	0.59	0.56	0.56
	12000	0.63	0.62	0.62	0.62	0.62	0.62	0.63
	20000	0.63	0.64	0.63	0.63	0.63	0.63	0.64
	30000	0.63	0.64	0.64	0.63	0.64	0.63	0.63

$$\hbar^2 / M \sigma^2 k_B T \ll 1, \quad (22)$$

where σ is roughly the range of the strongly repulsive part of the effective interaction. Detailed calculations indicate $r_s T \gtrsim 1500^\circ \text{K}$ is a sufficient condition for F_Q to represent accurately the quantum correction.

III. THERMODYNAMIC PROPERTIES

The free energy given by Eq. (1) was evaluated as a function of density, temperature, and relative concentration. The procedure is to minimize $F_{\text{hs}} + E_M + E^{(2)} + E^{(3)} + F_Q$ as a function of η and α . (The best choice for α is found to be insensitive to all other parameters and varied between 0.73 and 0.77 only.) The remaining contributions to F are then added. Since ΔF_{int} effectively corrects the hard-sphere approximation, to *second* order in the electron-ion interaction, the minimization procedure would be unnecessary, were it not for $E^{(3)}$. If $E^{(3)}$ is excluded, then the total F is indeed very weakly dependent on η and α and this encourages confidence in our calculation. The minimization procedure is justified by a result of the thermodynamic perturbation theory which states that the exact free energy is bounded above by the free energy calculated using the hard-sphere model.²⁵

Rather than tabulate F , we have tabulated various derivatives that are particularly useful in constructing planetary models (see Tables I–III). Note that the heat capacity per nucleus, at constant volume, can be determined from Tables I and II since

$$c_V / k_B = c / \gamma, \quad (23)$$

where

TABLE III. Entropy S (in k_B /nucleus) at $r_s = 0.9$. (For extrapolation to other densities, use Table II.)

T (°K)	x						
	0.0	0.1	0.2	0.4	0.6	0.8	1.0
3500	4.3	4.8	5.15	5.6	5.9	6.0	5.75
6000	5.25	5.75	6.1	6.5	6.75	6.85	6.55
9000	6.0	6.55	6.95	7.45	7.75	7.85	7.55
12500	6.6	7.2	7.6	8.2	8.6	8.75	8.6
17500	7.25	7.85	8.3	8.9	9.4	9.6	9.5
25000	7.95	8.55	9.0	9.65	10.15	10.45	10.45
35000	8.55	9.2	9.65	10.35	10.85	11.25	11.25

$$c = \frac{1}{Nk_B} \left(\frac{dP}{dT} \right)_{V,x},$$

$$\gamma = \left(\frac{d \ln T}{d \ln \rho} \right)_{S,x}.$$

The equation of state $P(V, T, x)$ has not been tabulated but has been fitted to a polynomial in x and r_s for $T = 6000$ °K. (Pressures at other temperatures can be found by using Table I.)

$$\begin{aligned}
 P &= (51.6/\gamma_s^5) [1 + a(x)r_s + b(x)r_s^2 + c(x)r_s^3] \text{ Mbar}, \\
 a(x) &= -0.654 - 0.200x + x(1-x) \\
 &\quad \times (-0.182 + 0.370x - 0.288x^2), \\
 b(x) &= 0.085 - 0.054x + x(1-x) \\
 &\quad \times (-0.086 - 0.530x + 0.573x^2), \\
 c(x) &= -0.008 + 0.028x + x(1-x) \\
 &\quad \times (0.077 + 0.254x - 0.321x^2).
 \end{aligned} \tag{24}$$

This interpolation formula is accurate to 0.3% for $0.6 \leq r_s \leq 1.3$. For $x=0$ (metallic hydrogen) our results for P are in good agreement with previous workers. For example, at $r_s = 1.0$ we obtained $P = 21.8$ Mbar whereas Hubbard and Slattery⁵ obtained 22.0 Mbar. This agreement is not surprising, since the pressure is determined mainly by E_{eg} and E_M , terms that are common to both treatments. (For example, $E^{(3)}$ contributes only $0.35/\gamma_s^2$ Mbar to P for hydrogen.) We believe that our equation of state is the best available for liquid metallic hydrogen and is probably accurate to better than 1%. The accuracy for $x \neq 0$ is more difficult to assess, since the perturbation expansion is much less valid for helium (as we discuss in the final section.)

The parameter c (Table I) would be 1.0 for an ideal gas and 1.5 for a high-temperature Debye solid. The actual behavior is more complicated than either of these limiting cases. For example, c is reduced by the quantum corrections at low T , but increased by the free energy of the electron gas at high T . The Monte Carlo results⁵ are too incomplete for a detailed comparison. To give a sample comparison: at $x=0$, $r_s = 1.0$; they obtained 1.49 at 4200 °K, 1.42 at 6300 °K, 1.32 at 10500 °K and

1.16 at 31500 °K. Our results for the same temperatures are 1.04, 1.15, 1.18, and 1.21, respectively.

The parameter γ (Table II) would be $\frac{2}{3}$ for an ideal monatomic gas and 0.5 for a high-temperature Debye solid (neglecting screening). The actual value usually lies between these limiting cases. For comparison, the Monte Carlo result for $x=0$, $r_s = 1.0$ was $\gamma \approx 0.64$, for $4 \times 10^3 \leq T \leq 3 \times 10^4$ °K.

The specific entropy (Table III) differs surprisingly little from the Monte Carlo results. For example, at $x=0.143$, $\rho = 5$ g/cm³ Hubbard²⁶ finds $T = 23400$ °K for $S = 8.4$ k_B /nucleus. Our results predict $T = 20500$ °K. (For a fully adiabatic, homogeneous Jupiter, this would be roughly the central temperature of the planet.)

Our calculations enable us to assess accurately the "volume additivity" approximation that has often been made. Let $\Omega(x, P)$ be the volume per ion. We can always write

$$[1 + \delta(x, P)] \Omega(x, P) = x\Omega(1, P) + (1-x)\Omega(0, P), \tag{25}$$

where $\delta(x, P)$ is a measure of the deviation from volume additivity in the alloy. Figure 1 shows that δ is significantly nonzero, in contrast to Thomas-Fermi theory where it is natural to assume $\delta \equiv 0$.²⁷ This nonadditivity is not attributable to any particular term in the free energy. It is comparable to (but usually somewhat larger than) the nonadditivity observed in liquid alloys in the laboratory.²⁸

This result indicates a small modification to models for giant planets. For example, a model constructed using the exact equation of state and $x=0.1$, would require $x \approx 0.12$ if volume additivity were assumed. Correct allowance for nonadditivity slightly *reduces* the amount of helium required in giant planet models.

IV. PHASE SEPARATION

There are two ways of testing for incomplete miscibility in a fluid mixture calculation. One way

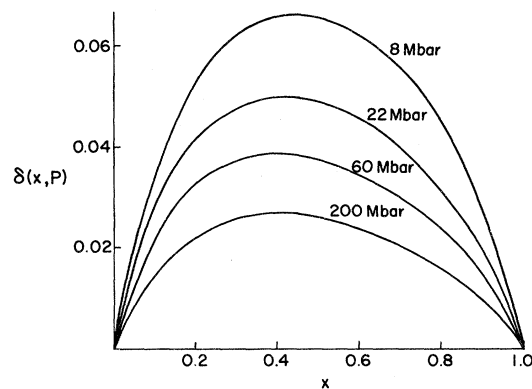


FIG. 1. Extent of volume nonadditivity [Eq. (25)] at $T = 10^4$ °K and for various pressures.

is to look for divergent behavior in the long-wavelength limit of a partial structure factor, corresponding to the onset of macroscopic concentration fluctuations. This method has been applied by Stroud²⁹ to the alkali metals with some success, but his mean-field approach would predict complete miscibility in the H-He system. The more exact calculation described below indicates that this must be a failure of the mean-field approximation. (Our inability to find divergent behavior indicates a lack of self-consistency in our calculation. It is hoped that this inadequacy is serious only near the critical point.)

The second test is to evaluate the Gibbs energy $G(P, T, x)$ and then determine whether $\partial^2 G / \partial x^2 < 0$ in any region of (P, T, x) space. Such regions are unstable towards phase separation.³⁰ This method has been used²² to predict, with considerable success, the miscibilities and phase separation curves for several alkali metal mixtures.

Figure 2 shows the Gibbs energy of mixing, defined as

$$\Delta G(P, T, x) = G(P, T, x) - xG(P, T, 1) - (1-x)G(P, T, 0). \quad (26)$$

At low temperatures, the unstable region is easily discernable. Near the critical temperature, a careful common tangent construction must be made (see the curve at 9000°K, for example). Since ΔG is much smaller than G , it is clear that even small errors can dramatically affect an estimate of T_c , the critical temperature. Nevertheless, there is little doubt that the unstable region exists for T

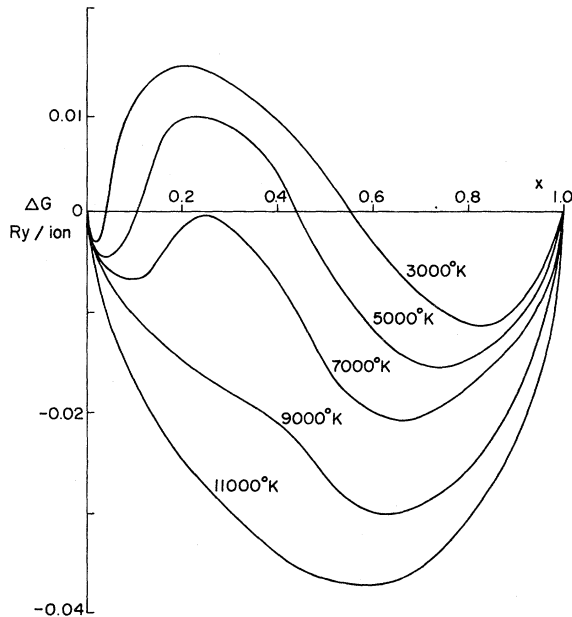


FIG. 2. Gibbs energy of mixing ΔG , as a function of T and x at $P=8$ Mbar.

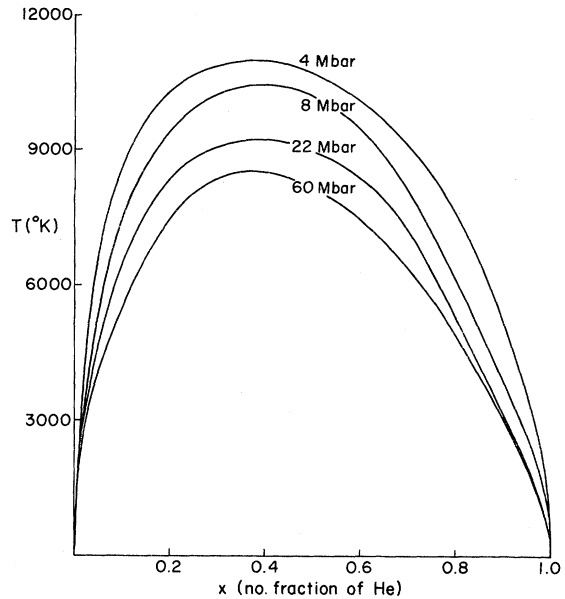


FIG. 3. Phase separation curves for various pressures. The phase-excluded region (miscibility gap) is below the curve in each case.

$\leq 7000^\circ\text{K}$.

In Figure 3, we show the phase separation curves constructed from several plots like Figure 2. (Not shown are the results at $P=200$ Mbar, for which $T_c \approx 10000^\circ\text{K}$.) The regions near T_c are interpolations and may be inaccurate. Away from $T \approx T_c$, the curves are likely to be accurate to about $\pm 20\%$. The results may also be incorrect at low temperatures ($T \leq 2000^\circ\text{K}$) where solid phases may exist. We found no evidence in the calculations for the more complicated phase diagrams that are permitted by the Gibbs phase rule.³¹

The results indicate that a H-He mixture of solar composition ($x \approx 0.1$) separates into hydrogen-rich and helium-rich phases at temperatures less than about 8000°K and pressures in the range 4–200 Mbar. It is not surprising that this phase transition did not clearly manifest itself in Hubbard's Monte Carlo calculations, because of the small number of particles he used.³² The immiscibility is not attributable to any particular contribution to F .

The effect of separation in a planet such as Jupiter is to retard the cooling rate and evolution.⁴ This will be discussed elsewhere.

V. DISCUSSION

We have assumed throughout that it is valid to consider the helium as fully pressure ionized, even at a few megabars pressure. There may be serious objections to this.

It should be emphasized, however, that the validity of our approach has nothing to do with the pres-

sure at which pure solid helium becomes metallic. We have evaluated the band structure of face-centered-cubic helium using plane waves as a basis set for the electronic wave functions. We obtain a transition pressure of 70 Mbar, similar to the result of Trubitsyn.³³ However, a calculation of the band gaps to third order in the electron-ion interaction is accurate even at 10 Mbar. This is a more relevant criterion, since our calculation of F relies on the convergence of a plane wave expansion and not on the existence of metallic conduction in the helium fluid. We have also used the methods outlined in this paper to calculate the free energy of *molecular* hydrogen at $r_s \leq 1.7$ to an accuracy comparable to that achieved using semiempirical H_2 - H_2 pair potentials. We mention this to emphasize the power of the perturbation technique used.

Contrary to what has been stated in the literature,³ there is no good reason for supposing that helium becomes less soluble at pressures lower than those considered in this paper. Indeed, the screened interaction between a neutral helium atom and a proton has a large attractive region, which suggests miscibility.³⁴ In contrast, the solubility of helium in alkali metals at near-zero pressure is very low³⁵ because of the repulsive electron-helium pseudopotential.³⁶ As the pressure increases and the wavelength of a conduction electron becomes comparable to the size of a helium atom, the pseudopotential becomes less repulsive and the solubility increases. It is not correct to compare the H-He system with any large r_s system (such as Na-He) that is accessible in the laboratory.

In this paper, we have shown how a judicious mixture of perturbation techniques enables us to evaluate the thermodynamics of a nonideal system that was previously thought to require Monte Carlo techniques. It is likely that other, similar systems will yield to a comparable analysis. One candidate is the H_2 -He mixture that is present at lower pressures ($P \leq 2$ Mbar) in the giant planets.

ACKNOWLEDGMENTS

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APPENDIX A: EVALUATION OF $T_{ijk}(\vec{q}_1, \vec{q}_2)$

The calculation of $E^{(3)}$ requires an approximation for

$$T_{ijk}(\vec{q}_1, \vec{q}_2) = \left\langle \frac{1}{N\Omega} \sum_{m,n,p} \exp i[-\vec{q}_1 \cdot \vec{r}_m^i + (\vec{q}_1 - \vec{q}_2) \cdot \vec{r}_n^j + \vec{q}_2 \cdot \vec{r}_p^k] \right\rangle. \quad (\text{A1})$$

For simplicity, we consider a pure liquid so that the subscripts i, j, k can be omitted. There are

numerous papers in the theory of liquid metals^{37,38} in which $T(\vec{q}_1, \vec{q}_2)$ is approximated by $T_c(q_1, q_2)$, where

$$T_c(\vec{q}_1, \vec{q}_2) = S(-\vec{q}_1) S(\vec{q}_1 - \vec{q}_2) S(\vec{q}_2), \quad (\text{A2})$$

and $S(q)$ is the usual liquid structure factor. This is often called the "geometric approximation." As discussed by Ballentine and Heine,³⁷ it treats clusters of three atoms approximately, but is otherwise exact. However, it can be readily demonstrated³⁹ that (A2) is identical to the well-known *convolution* approximation in real space. This approximation states that⁴⁰

$$g^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) \simeq g_{KS}^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) - [g^{(2)}(\vec{r}_1, \vec{r}_2) - 1] \\ \times [g^{(2)}(\vec{r}_2, \vec{r}_3) - 1] [g^{(2)}(\vec{r}_1, \vec{r}_3) - 1] \\ + N \int [g^{(2)}(\vec{r}_1, \vec{r}_4) - 1] [g^{(2)}(\vec{r}_2, \vec{r}_4) - 1] \\ \times [g^{(2)}(\vec{r}_3, \vec{r}_4) - 1] d\vec{r}_4, \quad (\text{A3})$$

where $g^{(2)}$ and $g^{(3)}$ are the two-body and three-body correlation functions, respectively, and $g_{KS}^{(3)}$ is the Kirkwood superposition approximation

$$g_{KS}^{(3)}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = g^{(2)}(\vec{r}_1, \vec{r}_2) g^{(2)}(\vec{r}_1, \vec{r}_3) g^{(2)}(\vec{r}_2, \vec{r}_3). \quad (\text{A4})$$

To prove the equivalence of (A2) and (A3) we note that by definition

$$\left\langle \frac{1}{N\Omega} \sum_{m,n,p}^* \exp i[-\vec{q}_1 \cdot \vec{r}_m + (\vec{q}_1 - \vec{q}_2) \cdot \vec{r}_n + \vec{q}_2 \cdot \vec{r}_p] \right\rangle \\ = \int d\vec{r} d\vec{s} d\vec{t} \exp i[-\vec{q}_1 \cdot \vec{r} + (\vec{q}_1 - \vec{q}_2) \cdot \vec{s} + \vec{q}_2 \cdot \vec{t}] \\ \times N^3 g^{(3)}(\vec{r}, \vec{s}, \vec{t}), \quad (\text{A5})$$

where \sum^* means $m, n,$ and p are all unequal in the summation. The proof is then straightforward.

As discussed by Feenberg,⁴⁰ the convolution approximation is an exact solution of the hierarchy equation that links $g^{(2)}$ and $g^{(3)}$, whereas the superposition approximation is not. Moreover, the convolution approximation is a natural consequence of diagrammatic analyses, such as that made by Abe.⁴¹ However, it does not necessarily satisfy the physical requirement, $g^{(3)} > 0$, whereas the superposition approximation does. This could lead to serious errors for strongly repulsive potentials.

Nevertheless, we have used the convolution approximation since the superposition approximation is very cumbersome in Fourier space:

$$T_{KS}(\vec{q}_1, \vec{q}_2) = T_c(\vec{q}_1, \vec{q}_2) - [S(-\vec{q}_1) - 1] \\ \times [S(\vec{q}_1 - \vec{q}_2) - 1] [S(\vec{q}_2) - 1] \\ + \frac{1}{(2\pi)^3 N} \int d\vec{k} [S(\vec{k}) - 1] \\ \times [S(\vec{k} + \vec{q}_1) - 1] [S(\vec{k} + \vec{q}_2) - 1]. \quad (\text{A6})$$

We have made one test evaluation of $E^{(3)}$ using T_{KS} instead of T_c , for $\eta=0.3$ and $r_s=1.0$ in pure hydrogen. The results agreed to within 10%, although T_{KS} and T_c often differed by more than 10%. This is also expected to be comparable to the error that is incurred when either approximation is used, rather than the "true" $T(\vec{q}_1, \vec{q}_2)$ that would be deter-

mined by Monte Carlo or molecular-dynamics techniques. For larger η (closer packing), the error may be larger, since it is observed in machine calculations that $g_{KS}^{(3)}$ deviates more from the true $g^{(3)}$ as η increases.^{42, 43}

The generalization of (A2) to mixtures is straightforward (but not trivial). The result is

$$T_{ijk}(\vec{q}_1, \vec{q}_2) = [S_{ij}(-\vec{q}_1) - \delta_{ij}] [S_{jk}(\vec{q}_1 - \vec{q}_2) - \delta_{jk}] [S_{ki}(\vec{q}_2) - \delta_{ki}] + (x_k x_i)^{1/2} [S_{ij}(-\vec{q}_1) - \delta_{ij}] [S_{jk}(\vec{q}_1 - \vec{q}_2) - \delta_{jk}] \\ + (x_j x_k)^{1/2} [S_{ij}(-\vec{q}_1) - \delta_{ij}] [S_{ki}(\vec{q}_2) - \delta_{ki}] + (x_i x_j)^{1/2} [S_{jk}(\vec{q}_1 - \vec{q}_2) - \delta_{jk}] [S_{ki}(\vec{q}_2) - \delta_{ki}] \\ + \delta_{ij} (x_i x_k)^{1/2} S_{ik}(\vec{q}_2) + \delta_{ik} (x_i x_j)^{1/2} S_{jk}(\vec{q}_1 - \vec{q}_2) + \delta_{jk} (x_i x_j)^{1/2} S_{ij}(-\vec{q}_1) - 2x_i \delta_{ij} \delta_{jk}, \quad (A7)$$

where δ_{ij} is the Kronecker delta.

APPENDIX B: OPTIMIZED-RANDOM-PHASE APPROXIMATION (ORPA)

The object of a liquid perturbation theory is to approximate the true pair interaction by a very simple interaction for which the corresponding ionic configuration is well known. The free energy is then expanded about the free energy of the well understood reference system, in powers of the difference between the actual and reference interactions. The ORPA was devised by Anderson and Chandler^{7, 44} so that this perturbation expansion would rapidly converge. In briefly discussing our application of this method, we restrict ourselves to a pure system.

The first step is to approximate the real interaction $v^{eff}(r)$ by a trial interaction $v_T(r)$ given by

$$v_T(r) = \begin{cases} \infty & r < R \\ v^{eff}(r), & r > R, \end{cases} \quad (B1)$$

where R is the variationally determined hard-sphere diameter. The error in F that is incurred by this replacement is

$$\Delta F_T = \frac{Nk_B T}{2} \int_{r < R} C_T(\vec{r}) \exp[-v^{eff}(\vec{r})/k_B T] d\vec{r}, \quad (B2)$$

where $C_T(r)$ is the direct correlation function, evaluated by equation (B5) below. Since $v^{eff}(r) \gg k_B T$ when $r < R$, this error is found to be negli-

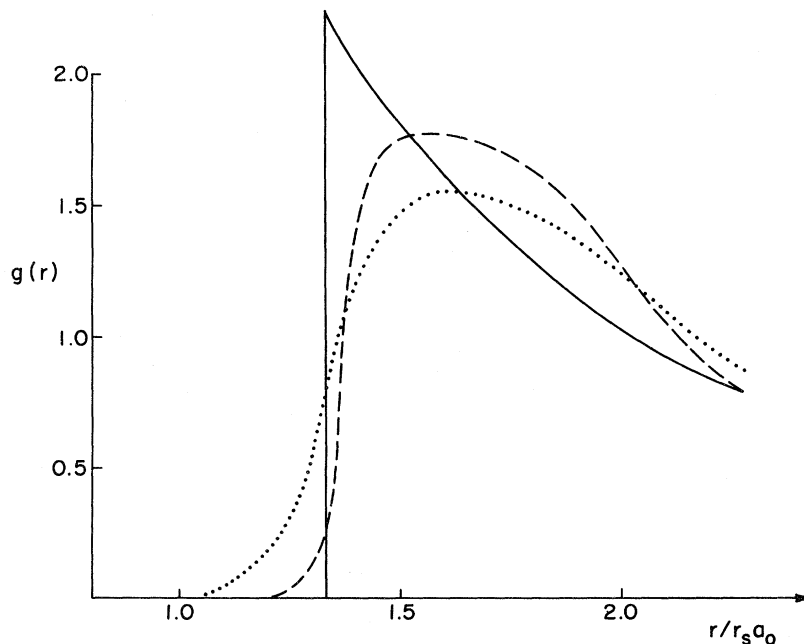


FIG. 4. Pair correlation functions for $Z=1$, $r_s=1.0$ and $T=4200^\circ\text{K}$. Solid line, optimized hard spheres; dashed line, ORPA; dotted lines, Monte Carlo [Hubbard (Ref. 5)].

gible (it corresponds to neglecting infrequent high-energy collisions between ions).

The trial interaction is then decomposed into a reference and a perturbation part

$$\begin{aligned} v_T(r) &= v_0(r) + u(r), \\ v_0(r) &= \begin{cases} \infty, & r < R \\ 0, & r > R, \end{cases} \\ u(r) &= \begin{cases} -k_B T c(r), & r < R \\ v^{\text{eff}}(r), & r > R. \end{cases} \end{aligned} \quad (\text{B3})$$

An exact calculation of F for this interaction must be independent of $c(r)$, since it is defined in the physically inaccessible region. However, the result of an approximate calculation does depend on $c(r)$. Andersen and Chandler showed that ΔF_{int} , the change in the free energy from a hard-sphere system, can be accurately approximated by the

lowest-order term

$$\Delta F_{\text{int}}^{(1)} = \frac{k_B T}{16\pi^2 N} \int \left[\ln \left(1 + \frac{NS(k)\varphi(k)}{k_B T} \right) - \frac{NS(k)\varphi(k)}{k_B T} \right] d\vec{k}, \quad (\text{B4})$$

where $\varphi(k) = \int e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) d\vec{r}$, provided

$$\delta \Delta F_{\text{int}}^{(1)} / \delta c(r) = 0, \quad r < R. \quad (\text{B5})$$

They also showed that $c(r) \approx C_T(r) - C_{\text{hs}}(r)$ for $r < R$, where C_{hs} is the hard-sphere direct correlation function.

In our calculations $|\Delta F_{\text{int}}| \leq k_B T$, but is large enough to have a significant effect on the entropy, as the Monte Carlo calculations by Ross⁴⁵ would have predicted.

In Fig. 4, a comparison is made of the pair correlations for ORPA, hard spheres and Monte Carlo.⁵ The similarity of our ORPA result and the machine simulation is very satisfactory.

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²¹One consequence following from the inclusion of dynamic response is the replacement of terms such as $[1/\epsilon(k) - 1]S(k)$ in $E^{(2)}$ by

$$\int_{-\infty}^{\infty} [1/\epsilon(k, \omega) - 1] [S(k, \omega) d\omega / 2\pi]$$

where by definition $\int_{-\infty}^{\infty} S(k, \omega) d\omega / 2\pi = S(k)$. Expansion of $\epsilon(k, \omega)$ about $\omega = 0$ [F. Toigo and T. O. Woodruff, *Phys. Rev. B* **4**, 4312 (1971)] and the use of sum rules for $\int_{-\infty}^{\infty} S(k, \omega) \omega^2 d\omega$ [A. Rahman, K. S. Singwi and A. Sjölander, *Phys. Rev.* **126**, 986 (1962)] show that this dynamical correction to $E^{(2)}$ is of order $10^{-3}k_B T$ (for $T \geq 10^3$ °K and $r_s \sim 1$) and hence negligible. Since no completely dynamic theory exists, we cannot rigorously prove that *all* dynamic corrections are negligible.

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