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Plasma Phase Transition in Fluid Hydrogen-Helium Mixtures

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Summary

The composition and the equation of state for a binary mixture of dense partially ionized hydrogen and helium are investigated on the basis of quantum statistical theory. Theoretical evidence for the existence of a hydrogen-like and helium-like plasma phase transition is found. Critical data for the phase transitions are given for the whole range of the mixing parameter.

I. Introduction

The thermodynamic and transport properties of hydrogen and hydrogen-helium mixtures are of high current interest for the investigation of astrophysical objects such as giant planets or stars. The helium contents, the degree of ionization as well as possible demixing of the hydrogen and helium components [1–3] are crucial for astrophysical evolution models. However, equally important is the question of the existence of phase transitions in H–He mixtures. The appearence of two coexisting phases would significantly change the mass and heat transport as well as electrical and optical properties of these systems.

The equation of state (EOS) and the resulting phase diagram for hydrogen and helium at low pressure are well investigated. However, more relevant for astrophysical problems is the high pressure behavior where the plasma is strongly correlated [4–16]. There are strong theoretical arguments for the existence of a plasma phase transition (PPT) at megabar pressures. The critical point is expected to be mainly determined by the Coulomb interaction of the free charge carriers. Though the PPT in ionized gases is still not accessible for systematic experimental study, its occurence in semiconductor electron-hole plasmas is well established, for a review cf. [17].

The PPT was first discussed in papers of NORMAN and STAROSTIN [4] and EBELING, KRAEFT and KREMP [5]. During the last 20 years the PPT then has been extensively studied theoretically for hydrogen, e.g. [7–10, 14–16]. It is interesting to note that the prediction of the PPT has been derived from quite different models. There are papers which use the grand canonical ensemble deriving the EOS in the physical picture and transforming it in the chemical picture [5, 10, 18–20]. Another approach departs from models for the free energy in the chemical picture, i.e. works in the canonical ensemble [11–15]. The latter is better known in astrophysics due to its relative conceptual simplicity. However, some problems, in particular the free-bound and bound-bound particle interaction, cannot be accounted for in a systematic way at this level of description.

The quantum statistical approach starting from the physical picture, is without doubt, the most general and systematic approach to thermodynamic properties of dense nonideal plasmas. Of course, a complicated problem has to be solved in this case, especially, if one is interested in a consistent and full description of the plasma state accounting for dynamical screening, phase space occupation effects, cluster formation and pressure ionization and dissociation. The way how to develop such a theory will be outlined in sections II and III.

Due to the complexity of the quantum statistical theory, in practice, additional simplifying assumptions are unavoidable. Substantial simplifications in the treatment of the Coulomb interaction were acchieved by the introduction of Pade approximations [7]. Improved Pade approximations have been presented in subsequent years [21, 22]. They give the correct limiting behavior, and they reproduce results for the thermodynamic functions obtained from Monte Carlo calculations for one-component plasmas. The contribution of the neutral particle interaction has so far been included, applying classical theories of dense fluids where the two-body interaction is described by the hard sphere potential with temperature-dependent diameters [6, 10, 23]. Improved theories have been applied working with density and temperature dependent hard sphere diameters [14, 15]. The interaction between charged particles and neutrals is usually treated on the level of third virial coefficients in first and second Born approximation [18, 10]. The third virial coefficient is frequently reduced to a second virial coefficient for a polarization potential.

Summarizing current results for the PPT in hydrogen according to different theories, one, first of all, has to admit surprisingly good agreement in the critical temperatures. The data range from 14000 K to 20000 K. Larger differences exist with respect to the critical pressure, the critical density and the coexistence line.

The question of a plasma phase transition in pure helium was investigated much less, [24, 25]. As in the case of hydrogen, a plasma phase transition is predicted for dense helium too. Recently FÖRSTER and EBELING [26] obtained for the critical temperature $T_c = 19000$ K and for the critical pressure $p_c = 0.5$ TPa. It is difficult to estimate the quality of these first results due to the lack of experimental data. There are EOS-data given by KOORTBECK et al. [27]. Unfortunately, these data don't cover the He-plasma region. Of course, specific properties of helium that are due to the more complex atomic structure should become important at high densities. In fact, FÖRSTER et al. predict a second phase transition in helium in connection with pressure ionization of He^+ with $T_{cr} = 61000$ K, $p_{cr} = 20$ TPa [26]).

For many problems of astrophysical interest, the system is mainly consisting of hydrogen and helium. Therefore, an interesting problem is, what will happen to the PPT in the binary mixture, i.e. what will be the influence of the helium component on the plasma phase transition. In this paper we make a first attempt to answer this question. Our calculations are based on a quantum statistical approach developed by EBELING, KREMP, KRAEFT and co-workers, e.g. [5, 9], that has been successfully applied to partially ionized hydrogen, e.g. [7, 10]. The aim of this paper is to extend this approach to hydrogen-helium mixtures. Our model covers the fully ionized plasma state and the atomic and molecular gas mixture as well. The charged particle interaction is considered in the framework of the two-fluid model, utilizing the Pade formulas of EBELING and RICHERT. For the charged particle-neutral interaction, the polarization potential model, and for the neutral-neutral interactions, effective hard sphere models are used. All approximations are given in section IV. The simplifying approximations are chosen to treat both components in a consistent manner. Certain better approximations that are known for hydrogen [15] should be applied to H—He mixtures after similar results for the helium component become available.

Focussing on the pressure ionization of helium atoms, it was sufficient to consider only that part of the phase diagramm where the twofold ionization of He can be neglected. Our analysis showed that this is possible for temperatures $T < 25000$ K and number densities below $10^{24}\,\mathrm{cm}^{-3}$. At the same time our calculations do not enter the region of limited solubility of helium in hydrogen at very high pressures ($p > 10$ Mbar) where phase separation is predicted (see e.g. STEVENSON [2], HUBBARD and DEWITT [3], KLEPEIS et al. [28]). Based on the previous results for pure hydrogen [7, 9, 10], we expect that the current model will give reasonable results for the critical point of the PPT in hydrogen-helium mixtures. Our main result is somewhat surprising: There is not one plasma phase transition of the binary mixture, but both the hydrogen and the helium PPTs survive. However, with an increase of the number fraction of the other component, the instability region is shifted to lower temperatures. This behavior of the critical temperatures of the PPTs resembles the freezing temperature curves of binary liquid alloys.

II. The Equation of State for Partially Ionized Plasmas

In the grand canonical ensemble using the Green's functions techniques, the thermodynamic properties can be calculated from the relation

$$n_a(\mu_a, T) = \int \frac{\mathrm{d}\omega}{2\pi} \frac{\mathrm{d}^3 p}{(2\pi)^3} f_a(\omega)\, A_a(p\omega) \tag{2.1}$$

which is of advantage because it allows, in a simple manner, to build up a quasiparticle picture summing up all the corresponding interaction contributions to the EOS. In (2.1) n_a is the number density of the elementary plasma particles ($a = e, i$) and $f_a(\omega)$ is the Fermi function

$$f_a(\omega) = [\exp \beta(\omega - \mu_a) + 1]^{-1}\,.$$

The spectral function $A_a(p\omega)$ is given by

$$A_a(p\omega) = \frac{-2\,\mathrm{Im}\,\Sigma_a(p\omega)}{\left(\omega - \dfrac{p^2}{2m_a} - \mathrm{Re}\,\Sigma_a(p\omega)\right)^2 + (\mathrm{Im}\,\Sigma_a(p\omega))^2} \tag{2.2}$$

where the self energy function $\Sigma_a(p\omega)$ is defined in well-known manner by the Dyson equation of the one-particle Green's function. With eq. (2.1), the EOS is determined quantum statistically in the physical picture. The two-particle Green's function or the self energy function are the central quantities which can be calculated using the diagram expansion or the methods based on the equations of motion. For details concerning Green's functions in quantum statistics, we refer to [9, 29].

In this paper we start from eq. (2.1). The chemical potentials μ_a can be obtained by inversion, and therefore all thermodynamic functions are available if the self energy is known. In order to derive approximate expressions for the EOS we will assume that the imaginary part of the self energy function is small compared to the real part. The physical meaning of this approximation is that we have weakly damped one-particle states (weakly interacting quasiparticles). From (2.1) then we get [30]

$$\begin{aligned} n_a(\mu_a T) = {} & \int \frac{\mathrm{d}p}{(2\pi)^3} f_a(E_a(p)) + \int \frac{\mathrm{d}\omega}{2\pi} \frac{\mathrm{d}p}{(2\pi)^3} 2\pi\delta(\omega - E_a(p))\, f_a(\omega) \frac{\partial}{\partial\omega} \mathrm{Re}\,\Sigma_a(p,\omega) \\ & - \int \frac{\mathrm{d}\omega}{\mathrm{d}\pi} \frac{\mathrm{d}p}{(2\pi)^3} \frac{\partial}{\partial\omega} \frac{P}{\omega - E_a} 2\,\mathrm{Im}\,\Sigma_a(p\omega)\, f_a(\omega) \end{aligned} \tag{2.3}$$

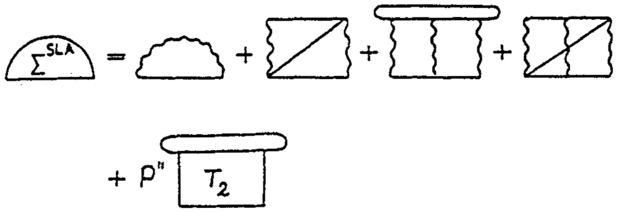
where P denotes the principal value, and $E_a(p)$ is the quasiparticle energy which follows from the solution of the dispersion relation

$$E_a(p) = \frac{p^2}{2m_a} + \mathrm{Re}\,\Sigma_a(p\omega)\,|_{\omega = E_a(p)}\,. \tag{2.4}$$

As can be seen, the real part of the self energy represents a correction to the kinetic energy describing the influence of the plasma medium on the one particle properties. With eq. (2.3) different contributions to the density are obtained: The first term on the r.h.s. is the contribution of an ideal Fermi system of quasiparticles with the energy given by (2.4). The second and the third terms in (2.3) are the contributions due to the interaction of quasiparticles. Of course, the renormalized description given by (2.3) can be turned into the usual formulation with "undressed" particles expanding the Fermi function with respect to Re Σ_a. In the nondegenerate case, then the well-known fugacity expansion of the EOS can be derived [30].

Let us start from the renormalized description given by eq. (2.3). In order to get explicit results, approximations for the self energy are necessary. In our case of a partially ionized plasma where the formation of bound state complexes is of importance, a cluster expansion of the self energy function has to be found. Such cluster expansions which follow from diagram techniques and from the equations of motion are given in [33, 31, 18, 10].

For demonstration of the approach we will restrict our discussion to the second order cluster expansion, that means, we consider the binary screened ladder approximation (SLA). Using the diagram representation the self energy reads [5, 30, 34]



(2.5)

where the full lines denote single particle Green's functions, the wavy line the dynamically screened potential in random phase approximation.

The first diagram on the r.h.s. of (2.5) represents the Hartree-Fock and the Montroll-Ward contributions. Then we have the second order exchange and the third order diagrams. The last diagram represents the in-medium two-particle T-matrix determined by a generalized Lippmann-Schwinger equation [36]. The P'' substracts the (divergent) lowest order terms. Explicit expressions of the diagrams in (2.5) can be found in [5].

Inserting the screened ladder approximation into eq. (2.3) one gets after transforming the energy variables

$$n_a(\mu_a T) = \int \frac{dp}{(2\pi)^3} f_a(E_a) - P'' \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \int \frac{dp}{(2\pi)^3} \frac{dp'}{(2\pi)^3} \frac{\partial}{\partial\omega} \frac{P}{\omega - E_a - E_b}$$

$$2 \operatorname{Im} < pp'|T_{ab}(\omega)|\, p'p > N_{ab}[n_B^{ab}(\omega) - n_B^{ab}(E_{ab})] \,. \tag{2.6}$$

Here $n_B^{ab}(\omega) = (e^{\beta(\omega - \mu_a - \mu_b)} - 1)^{-1}$ is the Bose function, $N_{ab} = 1 - f_a - f_b$ is the Pauli blocking factor and $E_{ab} = E_a + E_b$ is the two-particle energy.

For the further consideration it is convenient to split the quasiparticle shift into the part which contains the terms up to the third order and into the part of the higher orders. Then the quasiparticle distribution function is expanded according to

$$f_a(E_a) = f_a(E'_a) + P''\beta \operatorname{Re} \Sigma_a(p, E'_a)\, f_a(E'_a)\, [f_a(E'_a) - 1] \,. \tag{2.7}$$

E'_a denotes an approximation to the quasiparticle energy that takes into account the Hartree-Fock, the Montroll-Ward diagrams and the contributions of third order, that means the first four diagrams of (2.5).

With (2.7) it is possible to rewrite (2.6). Especially, one can separate the bound state and the scattering state contribution what gives [35, 30, 36]

$$n_a(\mu_a, T) = \int \frac{\mathrm{d}p}{(2\pi)^3} f_a(E'_a) + \sum_j \int \frac{\mathrm{d}P}{(2\pi)^3} n_B(E_{jP})$$

$$+ P'' \sum_b \int_{sc} \frac{\mathrm{d}\omega}{\pi} n_B(\omega)\, Tr \,\mathrm{Im}\,\{G_{ab}(\omega + i\varepsilon) - G^0_{ab}(\omega + i\varepsilon)\} \frac{1}{N_{ab}} \quad (2.8)$$

Here, Tr is the trace and E_{jP} is the energy of the two particle bound state where j denotes the set of internal quantum numbers and P the total momentum. G_{ab} is the retarded two-particle Green's function which is determined by the Bethe-Salpeter equation. G_{ab} describes the two-particle properties in the medium and is related to T-matrix by

$$G_{ab} = G^0_{ab} + G^0_{ab} T_{ab} G^0_{ab} \quad (2.9)$$

G^0_{ab} is the corresponding Green's function of free quasiparticles.

The first term in (2.8) gives the Fermi gas contribution of quasiparticles where the interaction with the surrounding plasma particles is accounted for by a self energy correction which includes dynamical screening and degeneracy effects. The second and the third terms can be considered as the bound state and the scattering part of a generalized second cluster coefficient, respectively. It gives the contribution of the two-particle interaction to the EOS taking into account in-medium effects. In particular, the bound states behave like Bose particles with Energies E_{jP}. These bound state energies are to be determined from an effective wave equation which follows from the homogeneous Bethe-Salpeter equation or from the ladder T-matrix equation [9, 37]. The effective wave equation can be written in the form

$$(H^0_{ab} + H^{pl}_{ab})\,|\Psi_{jP}\rangle = E_{jP}|\Psi_{jP}\rangle \,. \quad (2.10)$$

Here H^0_{ab} is the Hamiltonian of the isolated two-particle problem, and H^{pl}_{ab} takes into account all the corrections due to the influence of the surrounding plasma medium on the two-particle states. It contains self energy corrections, Pauli blocking and the effective interaction. Expressions for H^{pl}_{ab} can be found in [9]. The bound state energies which follow from (2.10) are then given by

$$E_{jP} = E^0_{jP} + \Delta_{jP} \quad (2.11)$$

where E^0_{jP} is the energy of the isolated atom and Δ_{jP} is the energy shift due to the influence of the many-body effects.

In first order perturbation theory the shift can be calculated from [9]

$$\Delta_{jP} = \langle \Psi^0_{jP}\,|H^{pl}_{ab}|\,\Psi^0_{jP}\rangle$$

with the $|\Psi^0_{jP}\rangle$ being the eigenstates of H^0_{ab}.

Let us now return to the EOS given by eq. (2.8). As already mentioned this is a very general EOS in the two-particle ladder approximation. But, there are many physical situations which allow to restrict to the nondegenerate case. Furthermore, if the second and the third terms of eq. (2.8) are taken in the static limit, we get

$$n_a(\mu_a\, T) = \int \frac{\mathrm{d}p}{(2\pi)^3} f_a(E'_a) + \sum_b z_a z_b\, 8\pi^{3/2} \lambda^3_{ab} \sum_{l=0}^{\infty} (2l + 1)$$

$$\times \left\{ \sum_n \mathrm{e}^{-\beta E_{nl}} + P'' \frac{1}{\pi} \int_0^{\infty} \mathrm{e}^{-\beta E} \frac{\mathrm{d}}{\mathrm{d}E} \eta_l(E)\, \mathrm{d}E \right\} \quad (2.12)$$

where $z_a = (2s_a + 1)\,\tilde{z}_a/\Lambda_a^3$ is the fugacity normalized to the density with $\tilde{z}_a = e^{\beta\mu_a}$ and $\Lambda_a = (2\pi\hbar^2/m_a k_B T)^{1/2}$. The second and the third terms on the r.h.s. represent the second cluster coefficient given by the Beth-Uhlenbeck-formula (the lowest order terms are substracted). Here, the E_{nl} are the bound state energies and the $\eta_l(E)$ are the scattering phase shifts which follow from the solution of the statically screened effective wave equation. In eq. (2.12) the thermal wave length is $\lambda_{ab} = (\hbar^2/2m_{ab}k_B T)^{1/2}$ with m_{ab} being the reduced mass. For simplicity of the notation, we have dropped the exchange term here. If higher order Levinson-theorems are applied the second cluster coefficient can be rewritten in the form [38, 39]

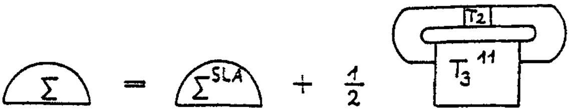
$$n_a(\mu_a, T) = \int \frac{dp}{(2\pi)^3} f_a(E_a') + \sum_b z_a z_b\, 8\pi^{3/2}\lambda_{ab}^3 \sum_l (2l + 1)$$
$$\left\{ \sum_n \{e^{-\beta E_{nl}} - 1 + \beta E_{nl}\} - \beta^2 \int_0^\infty dE\, e^{-\beta E} \int_E^\infty \vartheta^{(>3)}(E')\, dE' \right\}. \quad (2.13)$$

Here $\vartheta^{(>3)}$ is a reduced phase shift sum subtracting the Born terms up to the third order. The full phase shift sum is

$$\vartheta(E) = \frac{1}{\pi} \sum_l (2l + 1)\, \eta_l(E).$$

For systems with Coulomb interactions the representation (2.13) is of special interest. In particular, we obtain the Planck-Larkin-sum of bound states, given by the second term on the r.h.s. of (2.13). This quantity has the useful property to be convergent for plasmas in the zero density limit. In this approach, this sum is a straightforward result of the theory.

As already mentioned, we have restricted our theoretical considerations on the EOS in the screened ladder approximation taking into account two-particle correlations. Of course, generalizations are possible in order to include higher order clusters. Then further diagrams have to be included in the self energy function Σ_a as well as in the plasma-Hamiltonian H_{ab}^{pl} which describe the formation of more complex bound states and corresponding scattering processes. For instance, if we want to include the interaction of free charged particles with neutrals (two-particle bound states) the self energy function is given approximately by



As can be seen, the interaction between the free particles and the bound states is accounted for by a special three body T-matrix determined by the Lippmann-Schwinger equation [31, 32]

$$T_3^{kk'} = V_3^k + i^2 V_3^k \frac{1}{z - H_3} V_3^{k'} \quad (2.14)$$

where the notation of multi-channel scattering theory is used. In (2.14) V_3^k is the scattering potential in the channel k and H_3 is the three-particle Hamiltonian. In order to describe the influence of three-body interactions on the bound state energy shifts in eq. (2.10) one has to include the T_3^{33}-matrix contribution in the plasma Hamiltonian of the effective wave equation. With T_3^{33} the interaction of the two-particle bound state with a free particle is accounted for.

Further generalizations to higher order complexes can be achieved in similar manner by inclusion of corresponding T-matrix contributions in the self energy function and the plasma Hamiltonian.

III. Chemical Picture. Mass Action Law

The structure of the EOS given by (2.8) or by (2.12) shows that it is possible to transform the physical picture described up to now into a chemical picture. Applying the principle that bound states can be treated as new (composite) particles we define the fugacity of these new particles by [5, 34]

$$\tilde{z}_{Aj} = \tilde{z}_e \tilde{z}_i \, \mathrm{e}^{-\beta E_j^0} . \tag{3.1}$$

Eq. (3.1) represents a mass action law in terms of the fugacities of the free charged particles and the atoms in the state $|j\rangle$. Starting from (2.8) the fugacities of the atoms can be obtained by inversion from

$$n_{A_j} = \int \frac{\mathrm{d}P}{(2\pi)^3} \frac{1}{\tilde{z}_{Aj}^{-1} \, \mathrm{e}^{\beta\left(\frac{P^2}{2M} + \Delta_j\right)} - 1} \tag{3.2}$$

where n_{A_j} is the atomic number density.

The densities of the particles that are not in bound states are defined by the first and the third terms on the r.h.s. of eqs. (2.8). These terms represent the free quasiparticle and the reduced two-particle scattering contributions of the EOS. Since the quasiparticle density already contains major scattering contributions, in many cases, the reduced scattering part is small. If we neglect this contribution, the fugacities of the free particles follow from

$$n_a^* = \int \frac{\mathrm{d}p}{(2\pi)^3} f_a(E_a'(p)) \tag{3.3}$$

where $E_a'(p)$ is the quasiparticle energy.

For the further consideration we will apply the "rigid shift" approximation [37]. In this approximation the quasiparticle energy shifts are replaced by thermally averaged shifts which are determined by the normalization condition of the respective distribution function. It follows that this momentum independent shift coincides with the interaction part of the chemical potential. One gets for the free charged particles

$$\mu_a^{\mathrm{int}} = \Delta_a = \frac{\int \mathrm{d}p \, \mathrm{Re}\, \Sigma_a(p) \, f_a(p) \, [1 - f_a(p)]}{\int \mathrm{d}p \, f_a(p) \, [1 - f_a(p)]} . \tag{3.4}$$

If we consider the nondegenerate case, from (3.1) with (3.2) and (3.3) the following form of the mass action law can be derived

$$\frac{n_A}{n_e^* n_i^*} = 8\pi^{3/2} \lambda_{ei}^3 b_A^{\mathrm{bound}} \, \mathrm{e}^{-\beta(\mu_e^{\mathrm{int}} + \mu_i^{\mathrm{int}} - \mu_{A_j}^{\mathrm{int}})} \tag{3.5}$$

where n_A denotes the total number density of bound states. The sum of discrete atomic states reads

$$b_A^{\mathrm{bound}} = \sum_j \mathrm{e}^{-\beta E_j^0} .$$

In (3.5) the relation (3.4) was used.

In connection with the transformation into the chemical picture it should be mentioned that for the description of the ionization equilibrium it is useful to start from an EOS with a renormalized sum of bound states, i.e., we start from eq. (2.13) were we have extracted the Planck-Larkin formula avoiding divergencies in the zero density limit (Coulomb case) [39, 40]. For the transformation into the chemical picture it is now possible to define the new composite particles by

$$\tilde{z}_A = \tilde{z}_e \tilde{z}_i \sum_{nl} (2l + 1) \left(e^{-\beta E_{nl}} - 1 + \beta E_{nl}\right) \tag{3.6}$$

which results in a modified mass action law containing a sum of discrete atomic states according to (3.6).

The mass action law (3.5) has the well-known form of a Saha equation describing the ionization equilibrium of a nonideal nondegenerate plasma consisting of free charged particles and atoms. The interaction and therefore the nonideality is described by the energy shifts which are equal to the correlation part of the chemical potentials. If higher order bound state complexes have to be taken into account the chemical picture can be generalized and a system of mass action laws follows which determines the number densities of the different chemical species. Such a generalization is applied in the next section to the EOS for hydrogen helium plasmas.

IV. Application to Hydrogen-Helium Plasmas

We will now investigate the EOS for a partially ionized hydrogen-helium plasma for temperatures below $T = 25000$ K. We account for the formation of hydrogen and helium atoms as well as the formation of hydrogen molecules. As already mentioned, the twofold ionization of helium is negligible in the considered density temperature range. The plasma composition is determined then by a system of mass action laws describing the ionization and the dissociation equilibria in the plasma mixture. For the description of the ionization equilibria of the hydrogen and helium component we start from eq. (3.5) making some modifications. First, because of the relatively low temperatures, we approximate the sum of bound states by the ground state contribution (c = H, He)

$$b_c^{\text{bound}} \approx e^{-\beta E^0_{10}} .$$

Second, degeneracy is partially included for the free electrons via the ideal chemical potential determined by inversion of

$$n_e^* = \frac{2s_e + 1}{\Lambda^3} I_{1/2}(\beta \mu^{id}) \tag{4.1}$$

with the Fermi integral $I_{1/2}(\alpha)$

$$I_{1/2}(\alpha) = \int_0^\infty dx \, \frac{x^{1/2}}{e^{x-\alpha} + 1} .$$

Furthermore, taking into account that the thermally averaged shifts are equal to the correlation part of the chemical potential, the mass action law can be written as [10]

$$n_c = 2 n_i^* b_c^{\text{bound}}(T) \exp\left[\beta \mu_e^{id} + \beta\left(\mu_e^{\text{int}} + \mu_i^{\text{int}} - \mu_c^{\text{int}}\right)\right] \tag{4.2}$$

where n_c is the number density of the atoms (c = H, He) and n_i^* is the number density of the corresponding free ions (i = p, He$^+$).

Let us consider now the chemical equilibrium of molecular dissociation. It can be described by the following mass action law

$$n_{\mathrm{H}_2} = (n_{\mathrm{H}})^2\, b_{\mathrm{HH}}^{\mathrm{bound}}(T) \exp\,[\beta(\mu_{\mathrm{H}}^{\mathrm{int}} + \mu_{\mathrm{H}}^{\mathrm{int}} - \mu_{\mathrm{H}_2}^{\mathrm{int}})] \tag{4.3}$$

Here $b_{\mathrm{HH}}^{\mathrm{bound}}$ is the bound state part of the fourth cluster coefficient for the electronic singlet state Σ_g^1 of atom-atom interaction given in terms of all vibrational and rotational molecular states. It can be approximated by the following formula [10]

$$b_{\mathrm{HH}}^{\mathrm{bound}}(T) = \frac{1}{\sqrt{2}}\, \Lambda_{\mathrm{H}}^3\, \mathrm{e}^{T/T^D}\, \frac{T}{\Theta_r} \left[\frac{1 - \mathrm{e}^{-T^D/T}}{2 \sinh\,(\Theta/2T)} - \frac{T^D}{T}\, \mathrm{e}^{-T^D/T}\right] \tag{4.4}$$

with the characteristic temperatures $T^D = 51960.5$ K, $\Theta = 6160$ K, $\Theta_r = 85.6$ K and the thermal wavelength $\Lambda_{\mathrm{H}} = (2\pi\hbar^2/m_H k_B T)^{1/2}$.
In deriving (4.2) and (4.3) the factorization of the partition function of the discrete atomic and molecular states was assumed.

Let us now give a brief discussion of the approximations made in determining the correlation parts of the chemical potentials. The free charged particle chemical potentials are given by the respective self energy function according to (3.4). The lowest order diagrams which we have included in section II give the correct behaviour for low densities up to $O(n^2e^6)$ [5.42]. Because we are interested in a wide density temperature range to cover the partially ionized plasma region we have used Padé formulae given by EBELING and RICHERT [7, 10] which were constructed from the known limiting behaviour of low and high densities assuming the two-fluid model. Furthermore, numerical results, especially Monte Carlo data were taken into account. In order to treat the ionic mixture we have modified these formulae in a simple manner introducing an effective ion model with the free ion density $n_i^{\mathrm{eff}} = n_p^* + n_{\mathrm{He}^+}^*$ and the mass $m_i = (n_p^* m_p + n_{\mathrm{He}^+}^* m_{\mathrm{He}^+})/n_i^{\mathrm{eff}}$. This model works well as long as there are no multiply charged ions in the system. In the following we denote the free charged particle contributions by μ_e^{gas} and μ_i^{gas}. For the electron contribution we have

$$\mu_e^{\mathrm{gas}} = \frac{\mu_{eD} - \dfrac{1}{2}\,(\pi\beta)^{-1/2}\,\bar{n}_e + 8\mu_{GB}\bar{n}_e^2}{1 + 8 \ln\left[1 + \dfrac{1}{16\sqrt{2}}\,(\pi\beta)^{1/4}\,(\bar{n}_e)^{1/2}\right] + 8\bar{n}_e^2} \tag{4.5}$$

with the abbrevations $\bar{n}_e = n_e^*(4\pi\beta)^{3/2}$, $r_s = (3/4\pi n_e^*)^{1/3}$, $\mu_{eD} = -(\pi\beta)^{-1/4}\,\bar{n}_e^{1/2}$ and $\mu_{GB} = -1.2217/r_s - 0.08883 \ln\,(1 + 6.2208/r_s^{0.7})$.

For the ion contribution the following expression was used

$$\mu_i^{\mathrm{gas}} = k_B T\, \frac{(\mu_{iD}/k_B T)\,[1. - 2a\tilde{n}_i^{2/3}(\mu_{MC}/k_B T)]}{1 - 2a\tilde{n}_i^{1/2}\left[\tilde{n}_i^{1/2} \Big/ \dfrac{\mu_i D}{k_B T} + \tilde{n}_i^{1/6}\, \dfrac{\mu_{iD}}{k_B T}\right]} + \mu_i^{\mathrm{HS}} \tag{4.6}$$

with $\tilde{n}_i = 8\beta^3 n_i^{\mathrm{eff}}$, $\Gamma = (4/3\pi\tilde{n}_i)^{1/3}$, $\mu_{iD} = -3/2 \cdot 2.1605(\tilde{n}_i)^{1/2}$ and $\mu_{MC}/k_{BT} = -1.1928\Gamma + 3.5382\Gamma^{1/4} - 0.5012 \ln(\Gamma) - 2.9761 - r_s\tilde{n}_i^{1/3}/(1 + r_s^2)\,[0.0933 + 0.8206(\tilde{n}_i)^{-1/4} - 0.2287 \cdot (\tilde{n}_i)^{-1/3}]$. Furthermore, we have

$$a = \sqrt{\pi^3/\beta}\,\left\{\frac{1}{2}\left[1 + \frac{1}{\sqrt{4\pi\beta}} \exp\left(\frac{3\sqrt{\pi}}{\ln\,(4\beta) - 6\sqrt{4\beta}}\right)\right] - 0.29931\right\}.$$

The formulae (4.5) and (4.6) are written in Rydberg units. In eq. (4.6) μ_i^{HS} denotes the classical hard sphere contribution of the ions discussed below (only for the He-ions a nonzero diameter was assumed with $d_{He^+} = 3a_B/2$).

The charged particle neutral interaction is considered on the level of pair approximations of the higher order virial coefficients for the corresponding quantum mechanical few-body problem. Using the optical potential method of scattering theory it is possible to introduce local effective atomic potentials which allow to express the higher order virial coefficients by second virial coefficients [6, 10]. The interaction part of the charged particle chemical potential then can be written as (a = e, p, He$^+$)

$$\mu_a^{\text{int}} = \mu_a^{\text{gas}} + 2k_BT \sum_c n_c B_{ac}\,, \qquad c = \text{H}, \text{H}_2, \text{He} \tag{4.7}$$

where B_{ac} represents the virial coefficient of charged particle-neutral pair interaction which is given by

$$B_{ac} = 16\pi^{5/2}\beta\lambda^3 \int_0^\infty \mathrm{d}p p^2\, \mathrm{e}^{-\beta E_p} \operatorname{Re} \langle p\Psi_0| T_{ac} |\Psi_0 p\rangle\,. \tag{4.8}$$

Here $|\Psi_0\rangle$ is the atomic ground state vector and T_{ac} denotes the T-operator of the few-body scattering process between the charged particle and the atom. If we introduce the transition operator

$$t_{ac} = \langle \Psi_0| T_{ac} |\Psi_0\rangle$$

the following Lippmann-Schwinger-equation can be derived

$$t_{ac} = u_{ac}^{\text{opt}} + u_{ac}^{\text{opt}} G_a(E)\, t_{ac}$$

with the resolvent operator $G_a(E) = (E - p^2/2m_a + i\varepsilon)^{-1}$ and the optical potential

$$u_{ac}^{\text{opt}} = \langle \Psi_0| u_{ac} |\Psi_0\rangle\,. \tag{4.9}$$

The quantity u_{ac} is determined by

$$u_{ac} = V_{ac} + V_{ac} \sum_{j>0} \int \mathrm{d}p \frac{|\Psi_j p\rangle \langle \Psi_j p|}{E + E_0 - E_j - H_a + i\varepsilon}\, u_{ac}\,. \tag{4.10}$$

Here V_{ac} is the scattering potential in the considered channel, and H_a is the free charged particle Hamiltonian. In the simplest case of e-H-scattering one gets from eqs. (4.9) and (4.10), up to the second order assuming adiabatic and dipole approximation

$$u_{ac}^{\text{opt}} = -\mathrm{e}^2 \left(\frac{2}{r} + \frac{2}{a_B}\right) \mathrm{e}^{-2r/a_B} - \frac{\mathrm{e}^2\alpha_{pol}}{2} \left(\frac{1 + \varkappa r}{r^2 + r_0^2}\right)^2 \mathrm{e}^{-2\varkappa r} \tag{4.11}$$

The first term on the r.h.s. of (4.11) gives the static contribution and the second term represents the longer ranged polarization potential where α_{pol} is the polarizibility of the bound particle and r_0 is a fit radius for the behaviour at small distances. The parameters are chosen to be $\alpha_{\text{pol}} = 4.5a_B^3$, $r_0 = 1.456a_B$ for the e-H and $\alpha_{\text{pol}} = 1.39a_B^3$, $r_0 = 1.105a_B$ for the e-He polarization potentials. For the e-H$_2$ interaction the averaged polarizability $\alpha_{\text{pol}} = 5.5a_B^3$ is used and r_0 is fitted to be $r_0 = 1.4a_B$. In the calculation of the polarization potential static Debye screening was assumed with $\varkappa^2 = 4\pi\Sigma_{a=e,p}\, \mathrm{e}_a^2\, \mathrm{d}/\mathrm{d}\mu_a\, n_a(\mu_a)$ being the inverse screening length.

If the charged particle-neutral contributions in (4.8) are considered in quantum first Born approximation with respect to the optical potential one gets

$$B_{ac} = \beta \int \mathrm{d}^3 r u_{ac}^{\text{opt}}(r)\,.$$

In the case of the electron neutral interaction we have taken into account the polarization potential contribution only because it gives the main contribution. For the ion-neutral interaction the hard sphere potential model is used, and the B_{ic} are approximated by classical virial coefficients of hard spheres [10] whereas the corresponding He^+-contributions are extended to the same level as the hard sphere contribution of the neutral particles with the diameter given above.

The interaction part of the chemical potentials for the atoms and the molecules have been calculated from (c = H, H_2, He)

$$\mu_c^{\text{int}} = \mu_c^{HS} + 2k_BT\sum_a n_a^* B_{ac} \tag{4.12}$$

where μ_c^{HS} contains the neutral-neutral hard sphere interaction and the last term accounts for the charged particle-neutral interaction in μ_c^{int}. For the calculation of μ_c^{HS} the Mansoori-formulae valid for classical fluid mixtures of hard spheres was applied [41]. We use temperature dependent diameters of the atoms that are determined from second virial coefficients using Morse- and EXP-pair-potentials for the interaction of hydrogen atoms [23] and a EXP-6-pair potential for the He—He interaction [27]. The diameters of the H_2-molecules are obtained from the atomic ones by an addition rule including the atom-atom equilibrium distance. In Tab. 1 the atomic and molecular diameters are given for some temperatures.

We want to mention again that the model presented here is based on a level of description developed in earlier papers [21, 10]. The aim of this paper is to use this model as a first step in order to describe the main influence of the helium component on the plasma phase transition in H—He mixtures. Of course, improvements of the model are necessary in order to get more rigorous results. Better approximations must be used for the charged particle-neutral and the neutral-neutral correlations. Especially, the temperature dependent hard sphere interaction represents a crude model which allows a description on a qualitative level only. Because the plasma is considered up to very high densities, quantum many-body effects are of importance and one, in principle, has to carry out a rigorous quantum statistical calculation in a consistent manner according to the theory described above. However, this is a very complicated problem, and it is solved up to now only with many additional approximations [5, 9]. In the last time SAUMON and CHABRIER [15] are trying to improve the equation of state for dense hydrogen plasmas applying a free-energy model in a chemical picture for a mixture of electrons, protons, hydrogen atoms and hydrogen molecules. Especially, the hard sphere contribution of the neutral-neutral interaction was treated with higher accuracy using the WCA perturbation theory and interatomic potentials modified according to available experimental results. In their calculations the plasma phase transition could be found and a detailed discussion was given about the influence of the different contributions in their free-energy model.

Let us discuss now the results concerning the plasma phase transition for hydrogen-helium mixtures which follow from the simple model used in this paper.

Table 1. Hard sphere diameters for different temperatures

T(K)	$d_H(A)$	$d_{H_2}(A)$	$d_{He}(A)$
10000	1.56	2.31	1.46
15000	1.44	2.19	1.37
20000	1.36	2.11	1.30
25000	1.30	2.05	1.25

V. Numerical Results

Figs. 1–4 show the results of the numerical solution of the coupled set of three mass action laws eqs. (4.2), (4.3), for different values of the mixing parameter γ. The mixing parameter is defined as $\gamma = (n^*_{He^+} + n_{He})/n_i$ with $n_i = n^*_p + n_H + 2n_{H_2} + n^*_{He^+} + n_{He}$ being the total ion density. The number fraction coefficients are $\alpha_e = n^*_e/n_i$, $\alpha_H = n_H/n_i$, $\alpha_{H_2} = 2n_{H_2}/n_i$, $\alpha_{He} = n_{He}/n_i$ and $\alpha_{He^+} = n^*_{He^+}/n_i$.

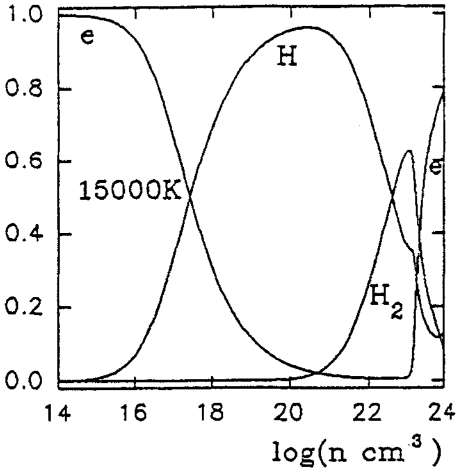


Fig. 1

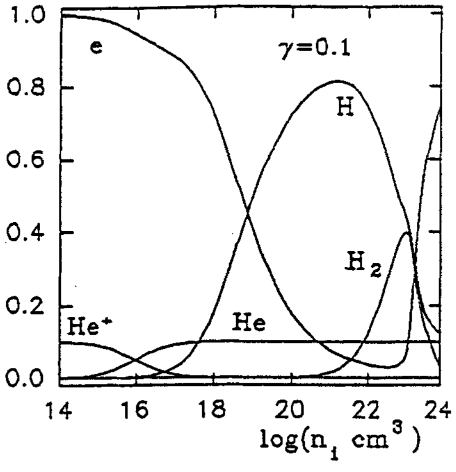


Fig. 2

Fig. 1. Plasma composition of pure hydrogen ($\gamma = 0$) vs. total ion density for $T = 15000$ K.

Fig. 2. Plasma composition of a H–He mixture with $\gamma = 0.1$ vs. the total ion density for $T = 20000$ K.

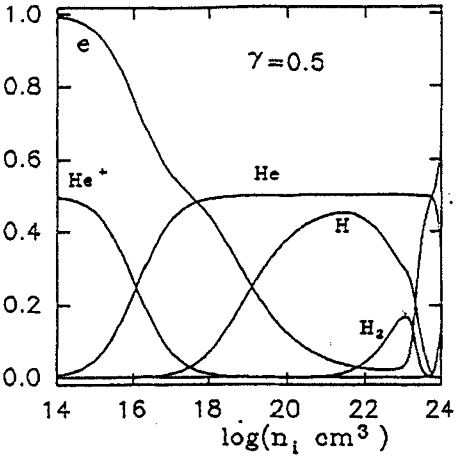


Fig. 3

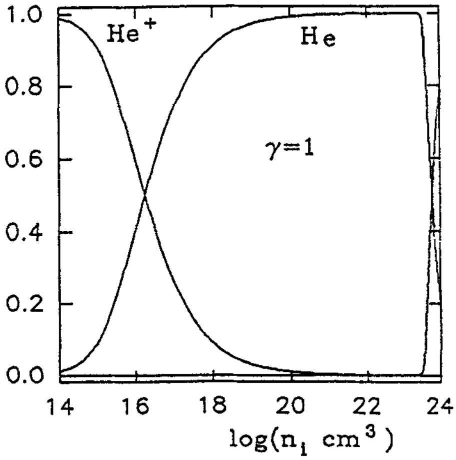


Fig. 4

Fig. 3. Plasma composition of a H–He mixture with $\gamma = 0.5$ vs. total ion density for $T = 20000$ K.

Fig. 4. Plasma composition of pure He ($\gamma = 1$) vs. total ion density for $T = 20000$ K.

Consider first pure hydrogen. Fig. (1) shows the plasma composition for $T = 15000$ K, i.e. close to the critical point of the PPT (see below). At low densities the plasma is fully ionized. With increasing density, hydrogen atoms are formed. The atom fraction decreases again for densities above 10^{21} cm^{-3} due to the formation of hydrogen molecules. Around 10^{23} cm^{-3}, we observe a strong increase of the degree of ionization, what describes the Mott transition in the dense hydrogen plasma. Notice that in our model, pressure ionization and pressure dissociation occur nearly at the same density, in contrast to previous results [10]. Figs. 2, 3 show the composition of H – He mixtures at $T = 20000$ K. At low densities, our model describes the partially ionized plasma mixture. First, we observe the formation of helium atoms because of their higher binding energy. In the region from $n_i \approx 10^{21}$ cm^{-3} to $n_i \approx 10^{23}$ cm^{-3} the plasma mixture mainly consists of neutrals. As in the case of pure hydrogen, pressure ionization and pressure dissociation of hydrogen occur nearly at the same density $n_i \gtrsim 10^{23}$ cm^{-3}.

It can be seen that the pressure ionization of the helium component is separated from that of the hydrogen and occurs at higher total ion densities depending on the helium number fraction. By reducing the helium number fraction, pressure ionization of the helium component is shifted to higher densities. For comparison, we show in Fig. 4 the plasma composition of pure helium in the region of one-fold ionization for $T = 20000$ K.

Let us now consider the results for the EOS which can be calculated using the formula

$$p = \int_{-\infty}^{\mu} n_i(\mu', T)\, \mathrm{d}\mu' . \tag{5.1}$$

Here, p denotes the pressure and $\mu = \mu_e + (1 - \gamma)\,\mu_p + \gamma\mu_{\mathrm{He}^+}$ the plasma chemical potential, respectively. Comparing our results obtained for the plasma composition and the equation of state with available data for pure hydrogen and pure helium [15, 27], we found good agreement up to densities $\varrho \sim 0.2$ g/cm^3 for hydrogen and $\varrho \sim 0.6$ g/cm^3 for helium.

Consider now the pressure isotherms as a function of the total ion density. We clearly observe Van-der-Waals-like loops below a critical temperature indicating the existence of the plasma phase transition in the hydrogen-helium mixture for all values of the mixing parameter. For pure hydrogen, we find that the critical data are close to those of SAUMON and CHABRIER [15]. There are deviations with respect to the behavior of the coexistence line $p(T)$ (Fig. 7a), which, in our opinion, is mainly a consequence of our simplified treatment of neutrals. For pure helium we get a critical temperature of the plasma phase transition (cf. Tab. 2) significantly lower as compared to the results of FÖRSTER et al. [24]. Their later

Table 2. The critical points of the plasma phase transition in mixtures of hydrogen and helium. Two critical points are given for the helium number fractions $\gamma = 0.8$ and $\gamma = 0.9$, first line corresponds to the H-like transition and second one to the He-like transition, respectively

γ	T_{cr} (10^3 K)	p_{cr} (Mbar)	n_{cr} (10^{23} cm^{-3})
0.0	14.90	0.723	1.74
0.1	14.75	0.750	1.80
0.2	14.55	0.790	1.85
0.3	14.30	0.825	1.90
0.4	14.00	0.865	1.94
0.5	13.50	0.920	1.98
0.6	12.80	0.970	2.02
0.7	11.80	1.050	2.06
0.8	10.30	1.160	2.10
	5.90	5.100	3.98
0.9	7.80	1.310	2.14
	10.30	6.050	3.90
1.0	17.00	7.220	3.76

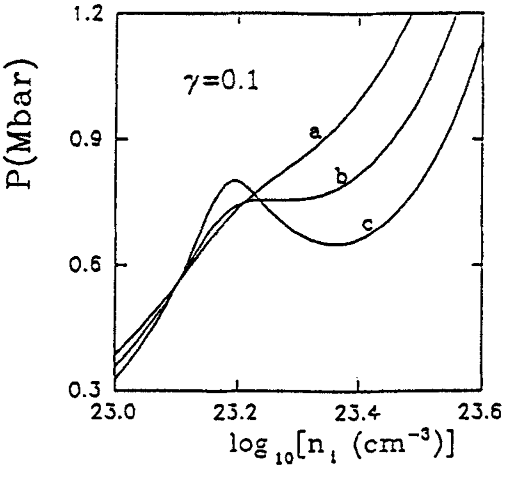


Fig. 5. Pressure isotherms of a H – He mixture with $\gamma = 0.1$ vs. total ion density. The temperatures are $T = 18000$ K (a), 14750 K (b), 12000 K (c).

improved result [26] is quite close to our data. The critical temperature of pure helium is higher than that for pure hydrogen, due to the higher binding energy. However, the finite size of the helium ions results in an additional lowering of the effective binding energy.

The pressure isotherms in H-He mixtures with low values of the mixing parameter show small deviations from the pure hydrogen result. Fig. (5) gives the result for $\gamma = 0.1$, relevant for conditions in giant planets. Obviously, the phase transition is here mainly dominated by the hydrogen component. We now consider plasmas with larger He fractions. One can see that there is not a single phase transition of the mixture. Both, the hydrogen and the helium phase transitions survive, and we, therefore, will call them hydrogen-like and helium-like plasma phase transition, respectively. There even exists an interval of mixing parameters, where both transitions can occur for the same temperature. The corresponding pressure isotherms exihibit two Van der Waals loops, cf. Fig. (6). Consequently, there are now two coexistence lines, shown in Fig. (7). The critical data for the H-like and He-like phase transitions are listed in Tab. 2. With increasing He fraction we observe a strong decrease of the critical temperature and an increase of critical density and pressure of the "H-like" phase transition. Similarly, for the "He-like" transition the critical temperature

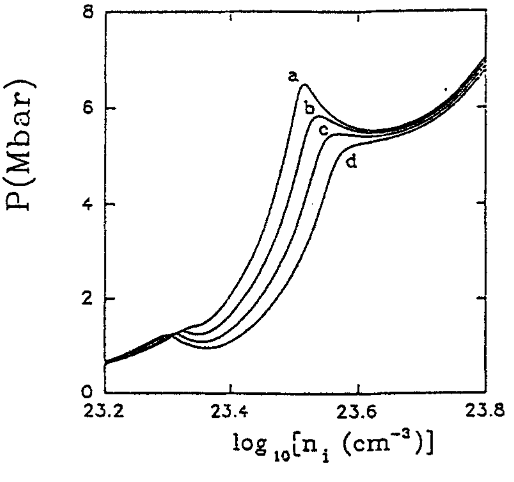


Fig. 6. Pressure isotherms for mixtures of hydrogen and helium with $\gamma = 0.95$ (a), 0.9 (b), 0.85 (c) and 0.8 (d) as a function of the total ion density for $T = 7000$ K.

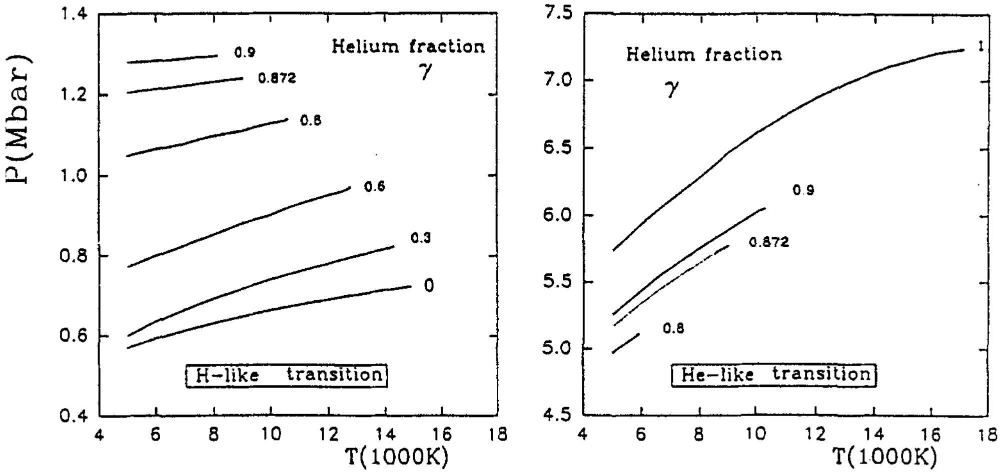


Fig. 7. Coexistence pressure for H—He mixtures for different values of the mixing parameter, for the hydrogen-like plasma phase transition and for the helium-like plasma phase transition.

decreases with growing hydrogen fraction. The critical density increases too, however the critical pressure is decreasing. This behavior is due to the change of the degree of ionization if one varies the mixing parameter at constant total ion density. The degree of ionization α_e at the critical point of the H-like transition decreases with growing helium fraction, starting with $\alpha_e = 0.25$ in the case of pure hydrogen. This is due to the fact that at the critical point the helium component is in the atomic phase. For the He-like transition, α_e is increasing with growing hydrogen fraction (for pure helium $\alpha_e = 0.11$). The critical temperatures of the two phase transitions are of major interest and are, therefore, plotted in Fig. (8) vs. the mixing parameter. One clearly sees the strong decrease of T_{cr} if one departs from the one-component situation. The crossing of both curves occures at $T_{cr}(\gamma) \approx 9000$ K and $\gamma \approx 0.872$. For a given temperature below this value, both phase transitions can be observed, as already discussed in Fig. (6). At the crossing point, the degree of ionization is $\alpha_e = 0.07$ and $\alpha_e = 0.28$ for the H-like and He-like transitions, respectively.

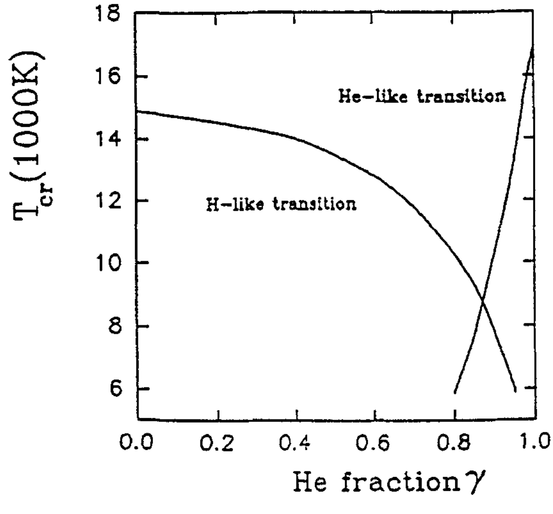


Fig. 8. Critical temperatures of the plasma phase transitions as a function of the mixing parameter γ.

In view of the rather simplified treatment of the neutrals in our model, we checked the influence of the chosen parameters on our final results. It turned out, in particular, that variations of the effective hard sphere diameters within substantial range, has only little impact on the critical temperatures of the plasma phase transitions. This confirms the mentioned in the introduction expectation, that the critical temperature of the PPT is determined mainly by the Coulomb interaction. On the other hand we found that variations of the hard sphere diameters significantly influences the critical pressure as well as the form of the coexistence line. Therefore, an improved treatment of the neutrals will certainly affect these results. However, we expect that the critical temperatures will not change drastically compared to the results from our model.

As a concluding remark we want to notice that Fig. (8) reminds the behavior of a classical binary liquid alloy if one considers its freezing temperature versus the mixing parameter.

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