NONIDEAL PLASMA

Suppression of the Dissociative Phase Transition in Plasma Mixtures of Molecular and Noble Gases

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Abstract—The thermodynamic properties of a hydrogen–helium plasma are calculated both by the quantum Monte Carlo method and by using a chemical model. It is shown that the previously observed anomalous behavior of the isotherms of superdense molecular gases (the so-called dissociative phase transition) is suppressed in plasma mixtures of molecular and noble gases. © 2002 MAIK "Nauka/Interperiodica".

1. INTRODUCTION

In [1, 2], the thermodynamic parameters of a superdense plasma of molecular gases were calculated both by the quantum Monte Carlo method [3] and by using the chemical model of a nonideal chemically reacting plasma [4, 5]. In both cases, simulations showed the anomalous behavior of the isotherms of a superdense hydrogen plasma in the submegabar and megabar pressure ranges. Calculations by the chemical model showed that, under certain conditions, a van der Waals loop characteristic of the gas-liquid phase transition appears in the phase diagram of a molecular gas plasma. The typical values of the critical temperature T_c turned out to be on the order of the dissociation energy of molecules or molecular ions, depending on what particles are dominant in the region where the temperature is close to the critical temperature. Numerical simulations by the quantum Monte Carlo method also showed the presence of a loop typical of phase transitions. It should be noted that an abrupt change in density is accompanied by an abrupt change in the plasma composition. The anomalous behavior observed was called the dissociative phase transition, because, when going over along the spinodal from the rarified phase to the dense one, the molecule density decreases sharply (by nearly five to seven orders of magnitude) due to the intense dissociation caused by the high pressure.

At the same time, for noble-gas plasmas, calculations by the chemical model demonstrate the monotonic behavior of the isotherms as the specific volume decreases. Although the interaction between plasma particles is rather strong, the calculated values of the thermodynamic parameters differ only slightly from those predicted by the ideal-gas model, as was pointed out in [5]. Since there are no molecules in a noble-gas plasma, no anomaly is observed in the isotherms of this plasma. In this context, the question arises as to the character of the phase diagrams of mixtures containing molecular and noble gases. Intuitively, it is clear that the anomalous effects observed in [1, 2] should disappear as the mole fraction of the noble gas in the mixture increases.

The objective of this paper is to illustrate how the dissociative phase transition in the plasma mixture of a molecular and noble gas is suppressed as the noble gas fraction in the mixture increases. As an example, the thermodynamic properties of a superdense hydrogen-helium plasma are calculated both by the quantum Monte Carlo method and by using the chemical model of a multicomponent plasma. An analysis of the calculation results obtained by using both approaches allows us to conclude that the phase transition gradually disappears as the helium fraction in the mixture increases.

2. RESULTS OF ANALYTICAL AND NUMERICAL CALCULATIONS

In this paper, we do not describe the calculation procedures, because they are described in detail in [3-5]. We only note their basic points.

When calculating by the quantum-mechanical Monte-Carlo method, we selected a system of 100 nuclei; the number of seed electrons was given by the ratio of the hydrogen and helium mole fractions in the mixture. The thermodynamic quantities were calculated as the logarithmic derivatives of the statistical sum [6]. The statistical sum of the quantum system was expressed through the density matrix, which was approximately represented in the form of integrals over trajectories [3, 6].

The chemical model is based on the separation of the spectrum of free and bound states of the Coulomb and neutral subsystems of the plasma. The Coulomb corrections to the thermodynamic functions were calculated as exact asymptotic expansions in terms of the activity powers in the grand canonical ensemble [4]. When calculating the atomic statistical sum, we used the nearest neighbor approximation. The corrections for the interactions with the participation of neutrals were written as a series expansion in terms of the densitv with allowance for all the types of charge-neutral and neutral-neutral binary and triple interactions [5]. The second and third virial coefficients due to the interaction of different types of free particles were calculated in [7] for the Hill pseudopotentials [8] constructed on the initial Lennard-Jones potentials (12-6) and (12-4).

By using previously developed procedures of calculating the thermodynamic properties of a nonideal plasma, we analyze their behavior on the phase diagram for a hydrogen-helium mixture over a wide range of densities and temperatures. First, we present the results of calculations obtained by the chemical model. Their analysis seems to be more convenient and simple and provides the possibility of obtaining a large body of information. Then, we compare these results with the quantum-mechanical Monte Carlo method. The results of the latter are most important and demonstrative, because they can be regarded as a numerical experiment. However, in this method, it is rather difficult to obtain a large body of numerical data because of serious computational problems. For this reason, calculations were performed for some isotherms with certain specified compositions (He : H = 7 : 93 and 33 : 67).

We consider a nonideal muticomponent hydrogenhelium plasma. We specify the plasma components as e^{-} , H, H⁺, H⁻, H₂, H₂⁺, He, He⁺, He⁺⁺, He₂⁺, and HeH⁺. The other possible components can be omitted because of the low probability of their formation. In calculations, we varied the mass density ρ , the plasma temperature T, and the mole fractions of hydrogen and helium in the mixture, $c_{\rm H}$ and $c_{\rm He}$. As in [1, 2], the region of the phase diagram with an anomalous behavior of isotherms is studied by moving along the isotherm with a small step in the density. As was mentioned above, the isotherms of noble gas plasmas have no singularities because, in this case, there is no molecular components in the plasma. Hence, it is convenient to begin calculations for a helium plasma and, then, to increase the hydrogen fraction in the mixture. The results of calculations of the plasma composition along each preceding isotherm can be used as an initial approximation when calculating the next one. The main parameter distinguishing one curve from another is the hydrogen or helium mole fraction in the mixture ($c_{\rm H} + c_{\rm He} = 100\%$).



Fig. 1. Isotherm $T = 10^4$ K for a hydrogen-helium plasma. The mole fraction of the components in the mixture (H : He, %): (*1*) pure helium, (2) 10 : 90, (3) 20 : 80, (4) 25 : 75, (5) 30 : 70, (6) 50 : 50, (7) 90 : 10, and (8) pure hydrogen.

Figure 1 shows the isotherm $T = 10^4$ K of the hydrogen-helium mixture at different values of $c_{\rm H}$ and $c_{\rm He}$. The isotherm of pure helium is the monotonic curve 1. As the hydrogen mole fraction in the mixture increases, the behavior of the isotherm gradually changes (curves 2, 3) and a distinct inflection point appears at $c_{\rm H} = 25\%$ (curve 4). This point corresponds to a mass density of \approx 4 g/cm³ and a pressure of \approx 4.25 Mbar. At a temperature of $T = 10^4$ K, the molar concentrations (25% H and 75% He) in curve 4 can be considered to be critical for the phase transition studied in [1, 2] in pure hydrogen. As the hydrogen mole fraction increases further, a characteristic van der Waals loop appears (curves 5, 6). Then, this loop degenerates into instability (curves 7, 8), which means that a stable solution for the dense phase is absent. Hence, according to calculations by the chemical model, the dissociative phase transition at T = 10^4 K is suppressed when the helium concentration in the mixture is higher than $c_{\text{He}} = 75\%$. Similar dependences for the isotherms $T = 3 \times 10^4$ K and 4×10^4 K are shown in Figs. 2 and 3. It is seen that, as the plasma temperature increases, the critical helium concentration required for suppressing the phase transition decreases rapidly (from 56% for $T = 3 \times 10^4$ K to 10% for $4 \times$ 10^4 K). The critical temperature for the dissociative transition in pure hydrogen calculated by the chemical model is about 5×10^4 K [1, 2].

Now, we compare the results of calculations by the chemical model with the data from quantum-mechanical Monte Carlo calculations. An analysis of the diagrams shows that, over a wide range of temperatures for different helium concentrations in the range of low and moderate pressures, the results obtained with these two methods almost coincide (see Figs. 4–9). This agreement means that the quantum Monte Carlo method not only provides the reliable values of thermodynamic quantities for the specified ensemble of 100 nuclei, but also allows one to qualitatively trace the plasma com-



Fig. 2. Isotherm $T = 3 \times 10^4$ K for a hydrogen-helium plasma. The mole fraction of the components in the mixture (H : He, %): (*1*) pure helium, (2) 10 : 90, (3) 20 : 80, (4) 30 : 70, (5) 44 : 56, (6) 50 : 50, (7) 70 : 30, (8) 80 : 20, (9) 90 : 10, and (*10*) pure hydrogen.



Fig. 4. Comparison of the results of calculations of the pressure for the isotherm $T = 10^4$ K by the chemical model (curves) and the Monte Carlo method (squares) for different helium mole fractions in the mixture: (a) 7 and (b) 33%.

position. In other words, these calculations account (at least qualitatively) for the formation of bound states (atoms, molecules, etc.).



Fig. 3. Isotherm $T = 4 \times 10^4$ K for a hydrogen-helium plasma. The mole fraction of the components in the mixture (H : He, %): (1) pure helium, (2) 10 : 90, (3) 20 : 80, (4) 90 : 10, and (5) pure hydrogen.



Fig. 5. Comparison of the results of calculations of the internal energy for the isotherm $T = 10^4$ K by the chemical model (curves) and the Monte Carlo method (squares) for different helium mole fractions in the mixture: (a) 7 and (b) 33%.

Moreover, for $T = 10^4$ K and a low helium concentration, both methods result in the appearance of the phase transition (Figs. 4, 5), whose positions in the

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Fig. 6. Comparison of the results of calculations of the pressure for isotherms $T = (a) 3 \times 10^4$ and (b) 5×10^4 K by the chemical model (curves) and the Monte Carlo method (squares) for a helium mole fraction of 7%.

phase diagrams calculated by the two methods are in qualitative agreement. However, there is a significant quantitative difference. According to the Monte Carlo calculations, the helium concentration at which the phase transition is suppressed turns out to be $\sim 40\%$, whereas the calculations by the chemical model give 75%.

At higher temperatures of $T > 3 \times 10^4$ K, the quantum-mechanical Monte Carlo calculations (Figs. 6, 7) do not result in the appearance of anomalies in the phase diagram even at a low helium concentration, whereas the calculations by the chemical model show the existence of anomalies at least up to $T = 5 \times 10^4$ K. It should also be noted that the agreement between the calculations with respect to the internal energy is, of course, worse than that with respect to the pressure.

At $T > 5 \times 10^4$ K (the critical temperature of the dissociative phase transition obtained by the chemical model), the results of calculations of the plasma pressure obtained with both methods agree well up to 10^8 atm (Fig. 8). In this case, the plasma mass density is on the order of 10 g/cm³. The density range in which the data on the internal energy obtained with both meth-



Fig. 7. Comparison of the results of calculations of the internal energy for isotherms $T = (a) 3 \times 10^4$ and (b) 5×10^4 K by the chemical model (curves) and the Monte Carlo method (squares) for a helium mole fraction of 7%.



Fig. 8. Same as in Fig. 4 for isotherm $T = 10^5$ K.



Fig. 9. Same as in Fig. 5 for isotherm $T = 10^5$ K.

ods are in good agreement expands significantly (Fig. 9).

3. CONCLUSION

A substantial quantitative difference between the results obtained by the Monte Carlo method and by using the chemical model at high pressures and low temperatures is related to the fact that the calculations were performed in the parameter range in which the chemical model is no longer applicable. Under these conditions, computations by the quantum Monte Carlo method are also characterized by poor stability. Nevertheless, an important result is that, in both cases, we observed the specific anomaly in the isotherms in the phase diagrams of hydrogen-helium plasma mixtures. The anomaly observed is of the same nature as that for pure hydrogen (the dissociative phase transition [1, 2]). The phase transition disappears gradually as the helium fraction in the mixture increases. Although both methods give different numerical values of the critical helium concentration above which the phase transition is suppressed, both of these methods indicate that the anomaly disappears as the He mole fraction in the mixture increases.

As a rule, noble gases are atomic. In our opinion, this fact confirms the dissociative nature of this phase transition [1, 2], because, according to our calculations, the phase transition in noble gases is absent due to the low concentration of molecular components.

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