

Coulombic Phase Transitions in Dense Plasmas¹

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We give a survey on the predictions of Coulombic phase transitions in dense plasmas (PPT) and derive several new results on the properties of these transitions. In particular we discuss several types of the critical point and the spinodal curves of quantum Coulombic systems. We construct a simple theoretical model which shows (in dependence on the parameter values) either one alkali-type transition (Coulombic and van der Waals forces determine the critical point) or one Coulombic transition and another van der Waals transition. We investigate the conditions to find separate Van der Waals and Coulomb transitions in one system (typical for hydrogen and noble gas-type plasmas). The separated Coulombic transitions which are strongly influenced by quantum effects are the hypothetical PPT, they are in full analogy to the known Coulombic transitions in classical ionic systems. Finally we give a discussion of several numerical and experimental results referring to the PPT in high pressure plasmas.

KEY WORDS: Plasma phase transition; Coulombic interactions; ionization equilibrium.

1. FIRST ORDER VAN DER WAALS AND COULOMB TRANSITIONS

The theory of gases developed in the dissertation of van der Waals in 1873 may be considered as the starting point of the modern theory of phase transitions. Van der Waals' approach is based on a simple physical model

¹ Dedicated to the 70th birthday of Michael Fisher.

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of interactions between particles which takes into account short range repulsive as well as long range attractive forces. The van der Waals model predicts below the critical temperature the possibility of coexistence of two phases which differ from each other by the density of molecules. In connection with the development of more strict theories it became clear that van der Waals approach is restricted to relatively weak attractive forces which either decay faster than $1/r^3$ or fulfil the ac conditions. Therefore the applicability to Coulomb forces remained open.

In 1943 Landau and Zeldovich discussed new possibilities of phase transitions connected with metal-insulator transitions in metal fluids in the vicinity of critical points.⁽¹⁾ We have to mention in this connection also the work of Mott on metal-insulator transitions in Coulomb systems. A first systematic study of Coulombic transitions in plasmas was given by Norman and Starostin in 1968.⁽²⁾ The first order transition predicted by these authors was named plasma phase transition (PPT). The PPT was predicted as a possible result from the competition between effective Coulomb attraction and quantum repulsion in the partially ionized dense plasma.^(2,3) The qualitative picture was similar to the van der Waals model where the phase transition is a result from the long-range attraction between neutral molecules and their short-range repulsion. We remember that the two phases in the van der Waals model differ from each other by the density of molecules. The two phases in PPT have different number densities of charged particles and different degrees of ionization. Atoms, which are present in both coexistent phases, were treated originally as an ideal gas.⁽²⁾

To get the first estimate of the critical temperature Norman and Starostin⁽²⁾ used the thermodynamic functions available at that time, namely Debye-Hückel expressions for the chemical potential of the charges with quantum corrections.⁽⁴⁾ The expressions described an effective Coulomb attraction and an effective quantum repulsion due to the uncertainty principle. In the linear approximation in the density a critical temperature $T_{cr} = 2660$ and with the more realistic nonlinear Debye-Hückel expression the value $T_{cr} = 10640$ was obtained. We mention that both expressions are valid only in the limit of small quantum repulsion ($\lambda/r_D) \ll 1$ (here λ is the electron thermal wavelength and r_D is the Debye radius), and small non-ideality parameter $\gamma = e^2 n_i^{1/3} / kT \ll 1$, where n_i is the ion number density, T is the temperature. Later estimates of the PPT in hydrogen plasmas lead to higher values of the critical temperature.⁽⁵⁻¹⁴⁾

The hypothetical phase transitions in multiple ionized plasmas were treated first in ref. 15. A detailed study of He-plasmas was given in ref. 16. Here we will consider only single-charged ions in gaseous plasmas.

Since up to now the PPT in plasmas is not yet clearly identified experimentally we plan to make as clear as possible the definition, the properties and the conditions for a PPT. For this reason we develop a simple model (a combination of the Debye–Hückel with the Van der Waals theory) which shows a separate Coulombic transition—which is a PPT. Other related phenomena in plasma systems are discussed only in brief.

Plasma-like phase transitions in the optically excited electron-hole system in semiconductors were studied with similar methods.^(5, 6, 17–19) The experimental observations seem to point out that these instabilities of the theory correspond to a real phase transition in semiconductors, this topic will not be considered here in detail.

In more detail we will discuss comparison of the PPT to the known transitions in classical Coulombic systems. The first results on phase transitions in ionic systems go back to the late sixties. In 1970 Voronzov *et al.*⁽²⁰⁾ found a coexistence line and a critical point in the course of Monte Carlo studies of charged hard spheres imbedded into a dielectric medium. An analytical estimate of the critical point and the coexistence line for electrolytes based on the Debye–Hückel theory was given in a short note by one of the authors.⁽²¹⁾ However a systematic theory of classical Coulombic phase transitions including a comparison with numerical and experimental data was given only in the pioneering work of Michael Fisher and his coworkers.⁽²²⁾ These authors have also made an extensive investigation of the state of art in this field.⁽²³⁾ Summarizing these results for classical systems we may say that theory and experiment (Monte Carlo data as well as measurements on electrolytes) are in quite good agreement. There is no doubt any more that a Coulombic phase transition in classical systems exists. We will not repeat here all the arguments but refer to the careful investigations of Fisher *et al.*^(22, 23)

The classical Coulombic transition is due to a balance between a hard-core repulsion and a Coulombic attraction. We will show here that the PPT is a balance between quantum repulsion between point charges and Coulombic attractions. In this respect PPT is a kind of quantum variant of the classical Coulombic transition. If on one hand the existence of a Coulombic transition in ionic systems is now well confirmed, there is on the other hand no proof yet for the existence of a PPT in plasmas. At present the problem of the existence of a PPT is still open. From the point of view of the theory this is connected with the difficulties to derive an accurate equation of state for nonideal quantum plasmas. From the experimental point of view the difficulties are connected with the very high pressures where the PPT could occur. However as we will point out here there are now several experimental and numerical data which point to the existence of a PPT in real plasmas.

2. DEBYE HÜCKEL APPROXIMATION FOR CLASSICAL AND QUANTUM SYSTEMS

In order to describe Coulombic phase transitions one needs good approximations for the thermodynamic functions in the regions where—according to the first estimates—the phase transition is to be expected. As we have learned from the theory of phase transitions in neutral gases, already simple expressions as the van der Waals equation might give qualitatively correct results. We will show here that the Debye–Hückel expressions for the thermodynamic functions together with the mass action law provide an approximation which might serve as a zeroth approximation for the description of Coulombic phase transitions. In their first work Norman and Starostin⁽²⁾ proposed for a first estimate of the critical temperature, to use Debye–Hückel-type expressions $(1 - c\lambda/r_D)$ for the chemical potential. Here λ is electron thermal wavelength, r_D is a Debye radius, $c \simeq 0.1$ is a numerical coefficient. The Debye–Hückel term describes an effective Coulomb attraction, the (λ/r_D) -term represents in this approach an effective quantum repulsion due to the uncertainty principle. Norman and Starostin⁽³⁾ used also the original expression of Debye–Hückel for the chemical potential $(1 + c\lambda/r_D)^{-1}$ which has the same accuracy if (λ/r_D) tends to zero.

We will give now a systematic discussion of the Debye–Hückel approximation for the classical and quantum cases. We consider a binary Coulomb system with n_+ positive ions (cations) and n_- negative charges (anions or electrons) per cubic centimeter $n_+ = n_-$. The density of neutrals is n_0 . The total density is $n = n_+ + n_0 = n_- + n_0$. In the following we will use the plasma notations, i.e., we call the negative charges “electrons” and the positive charges simply “ions”. In the Debye–Hückel theory for charged hard spheres with the diameter a the excess chemical potential of the charges of species i is given by the simple expression

$$\mu_i^{ex} = -\frac{e_i^2}{2D_0 kT(r_D + a)} \quad (1)$$

The densities of free and bound particles are connected by the mass action law (Saha equation)

$$\frac{n_0}{n_i n_e} = K(T) \exp\left(\frac{\mu_{ex}}{k_B T}\right) \quad (2)$$

where $K(T)$ is the mass action constant which is given by Bjerrum's formula or certain modifications^(5,24) in the classical case. The osmotic pressure is given by the formula

$$P/kT = n_i + n_e + n_0 - \frac{1}{24\pi} \kappa^3 \phi(\kappa a) \quad (3)$$

Here the Debye-Hückel function $\phi(x)$ is defined by

$$\phi(x) = \frac{3}{x^3} \left[1 + x - \frac{1}{1+x} - 2 \log(1+x) \right] \quad (4)$$

The easiest way to transfer the Debye-Hückel approximation to quantum plasmas is the replacement of the hard sphere diameter by an effective quantum diameter of charges. According to the Heisenberg principle a point particle with the thermal momentum

$$\hat{p} = \sqrt{\frac{8mkT}{\pi}} \quad (5)$$

corresponds to a wave packet of size

$$\delta x = \frac{\hbar}{\hat{p}} = \frac{\pi\hbar}{4\sqrt{2\pi mkT}}. \quad (6)$$

Identifying this with the effective diameter of the charges we get

$$a \rightarrow a(T) = \frac{\Lambda}{8} = \frac{h}{8\sqrt{2\pi m_e kT}} \quad (7)$$

In this so-called Lambda approximation^(7,10) quantum effects are expressed by just one characteristic length, the thermal de Broglie wavelength Λ in combination with Debye-Hückel type approximations. The Lambda approximation agrees very good with the exact quantum-statistical results for small densities for $T < 10^5 K$.^(7,9) This approximation requires that the plasma is nondegenerate i.e., $n^* \Lambda^3 \ll 1$ (where n^* denotes the density of free particles). Furthermore only a small fraction of the atoms should be bound in molecules $\beta_2 \ll 0.5$. The standard choice of the mass action constant for quantum plasmas is the Brillouin-Planck-Larkin expression

$$K(T) = \Lambda^3 \sigma(T) \quad (8)$$

where

$$\sigma(T) = \sum_{s=1}^{\infty} s^2 (\exp(-\beta E_s) - 1 + \beta E_s) \quad (9)$$

In this way the classical and the quantum case might be treated in the present rough approximation by the same procedure. The easiest way to check for stability of the system is the investigation of the sign of the derivative of the pressure. The region where

$$\frac{\partial \beta P}{\partial n} < 0 \quad (10)$$

corresponds to thermodynamic instability. Equivalent is the condition^(2,3)

$$\left(\frac{\partial n_i}{\partial n} \right)_T < 0 \quad (11)$$

which is valid only if atoms are treated as ideal gas. Instability is restricted to temperatures below the critical one which is defined by

$$T \leq T_{\text{cr}} = 16 \frac{e^2}{D_0 k_B a} \quad (12)$$

In the case of classical ionic solutions the parameter a is to be identified with the diameter of ions. In the case of dense quantum plasmas we have to introduce the quantum effective diameter $a(T) = \lambda/8$. This way we have shown that the PPT is the analogue of the known classical Coulombic transition in ionic solutions. At least in the simplified theory given above the classical transition in ionic solutions and the quantum PPT in dense plasmas are in full analogy. In both cases the spinodal curve is given by

$$\mu_{1,2} = \left(\frac{b^2}{8} - b \right) + / - \left[\left(\frac{b^2}{8} - b \right)^2 - b^2 \right]^{1/2} \quad (13)$$

where $b = e^2/k_B T a(T)$ and $\mu = e^2 \kappa/k_B T$. In the quantum case we find the corresponding estimate for the critical temperature

$$T_{\text{cr}} \simeq 12570 \text{ K} \quad (14)$$

In the case of electrolytic solutions or semiconductors the critical temperature is much lower due to the appearance of the dielectric constant

in the denominator. Another effect which decreases T_{cr} is the finite size of ions. In order to describe the size of the ion cores in alkali or noble gas plasmas we introduce an effective ion radius R , e.g., we have $R \simeq 1.69A$ for Cs -ions. Further we replace $\Lambda/8$ by

$$a(T) = \Lambda/8 + R \quad (15)$$

Assuming that R is temperature-independent we find now from Eq. (15)

$$T_{\text{cr}} = 12570 \text{ K} \frac{2}{1 + (1 + (6R/\pi a_B))^{1/2}} \quad (16)$$

where $a_B = \hbar/e^2 m_e$ is the Bohr radius. We see that a finite ion size may lead to an essential decrease of the critical temperature to values far below 10000 K. For Cs -plasmas this estimate gives, e.g., $T_{\text{cr}} \simeq 6000$ K. Since this value is still far above the observed critical point $T_{\text{cr}} \simeq 2000$ K we have to search now for additional effects, which might reduce the critical temperature.

3. COMBINATION OF VAN DER WAALS AND DEBYE-HÜCKEL APPROXIMATION

In the Debye-Hückel type approximation derived in the previous section the interaction of charges with neutrals and the neutral-neutral interaction was not taken into account. This model might fail if the interactions with neutrals have an essential influence. In the following we consider for concreteness a plasma system. We treated the neutrals as ideal particles in the simple approach given above which is analytically solvable. The system of mass action laws might become rather difficult if one includes the interactions with neutrals or/and chemical equilibria between neutrals as, e.g., between atoms and molecules. A better starting point for such more complicated cases is as a rule the expression for the free energy, including a minimization procedure.

Combining the Debye-Hückel model with a van der Waals expression and a contribution which takes into account the polarization of neutrals we get for the free energy

$$\begin{aligned} F = & n_0 k_B T \left[\ln \left(\frac{n_0 \Lambda_0^3}{\sigma(T)} \right) - 1 \right] + n_i k_B T \left[\ln \left(\frac{n_i \Lambda_i^3}{g_i} \right) - 1 \right] \\ & + n_e k_B T \left[\ln \left(\frac{n_e \Lambda_e^3}{g_e} \right) - 1 \right] - k_B T V \frac{\kappa^3}{12\pi} \tau \left(\frac{\kappa \Lambda}{8} \right) \\ & - k_B T n_0 \ln(1 - n_0 B) - A n_0^2 - W n n_0 \end{aligned} \quad (17)$$

Here the last three terms denote the contributions from the short range van der Waals interactions and the contributions from polarization terms. The polarization terms are of particular importance for the description of alkali and mercury plasmas.^(25, 26)

Three free constants characterize now our model

- the repulsion of atoms: B
- the attraction of atoms: A
- the strength of atomic polarizability: W

In order to reduce the number of free parameters we assume in the following $W = 0$. We note that the free energy in this form defines a model plasma with properties intermediate between van der Waals gas and a Debye–Hückel plasma. The equilibrium composition is given by the non-ideal Saha equation

$$\frac{1-\alpha}{\alpha^2} = n A^3 \sigma(T) \exp\left(-\frac{\Delta I(\alpha)}{k_B T}\right) \quad (18)$$

Here

$$\begin{aligned} \Delta I(\alpha) = & \frac{e^2 \kappa \sqrt{\alpha}}{k_B T (1 + \kappa a(T) \sqrt{\alpha})} - \frac{(1-\alpha) n B}{1 - (1-\alpha) n B} \\ & + \log(1 - (1-\alpha) n B) + (1-\alpha) n A - W n (2\alpha - 1) \end{aligned} \quad (19)$$

is the lowering of the ionization energy.

As well known, real gases with attractive interactions show a first-order phase transition described in the p – T plane by a critical point C_1 and a coexistence line ending in C_1 . Assuming that the Coulombic terms are omitted in our expressions for the free energy a simple van der Waals type expression is obtained with the critical point

$$T_{\text{vdW}} = \frac{8a}{27k_B b}, \quad n_{\text{vdW}} = \frac{1}{3b} \quad (20)$$

The critical temperature is about $10^1 < T_{\text{cr}} < 10^3$ for realistic values of the parameters. For example $T_{\text{cr}} \simeq 33$ K for hydrogen. The degree of ionization is practically zero in this region, i.e., there is no interference with the PPT. On the other hand, at least for hydrogen, the PPT occurs in a region where the number density of neutrals is rather low. We may assume therefore that the assumption $a = 0, b = 0$ is justified in this case. Then, as

shown above, the PPT may be treated in an analytical way. In the Lambda-approximation we got in the previous section an analytical expressions for the critical point of the PPT.^(7, 19) By introducing the Bohr radius a_B we may transform the expression for the critical temperature to the form

$$T_{\text{ppt}} = \frac{e^2}{8k_B a_B} \quad (21)$$

Further the critical density of the free electrons may be written as

$$n_{\text{ppt}} = a_B^{-3} \quad (22)$$

What happens in a system where both types of interactions are present? Evidently now besides the classical first-order phase transition typical for neutral gases a second first-order phase transitions due to Coulomb forces may appear. The second one which might occur only at rather high temperatures $T > 10^4$ K is the PPT. In Fig. 1 we give the pressure isotherm of hydrogen plasmas at $T = 10000$ K.

In the unstable region of the isotherm the plasma is separated into two phases. The dense phase is highly ionized and the Coulomb interaction dominates over the van der Waals forces. The less dense phase is only weakly ionized and van der Waals interactions dominate. A more realistic calculation of the coexistence line for hydrogen plasmas was given recently.⁽²⁸⁾ A coexistence pressure of $p \simeq 115$ GPa was found in the cited

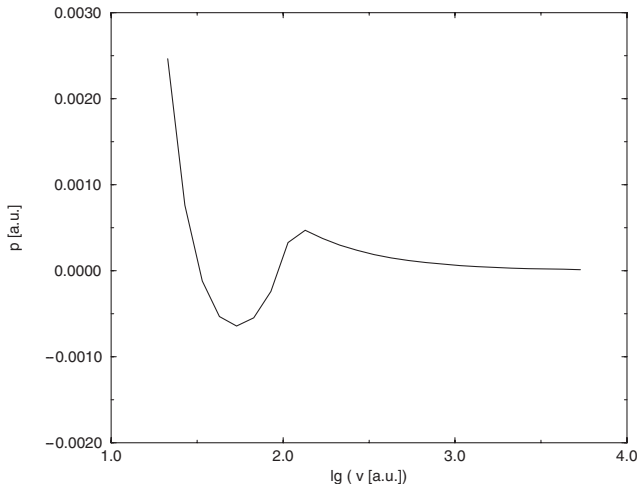


Fig. 1. The isotherm $T = 10000$ K for hydrogen plasmas showing the PPT instability.

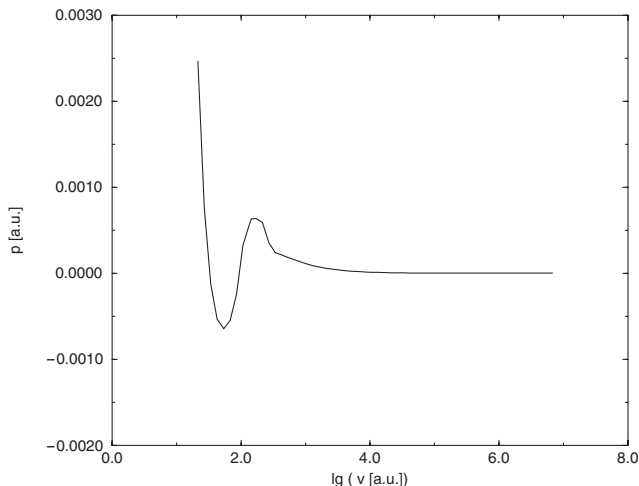


Fig. 2. The isotherm $T = 0.07$ a.u. for an alkali-like model plasma with one transition of mixed PPT-van der Waals type (van der Waals parameters of the model: $a = 30$ a.u., $b = 30$ a.u.).

work for $T = 10000$ K; the corresponding mass densities of the coexisting phases are $\rho_1 \simeq 0.62$ g/cm³ and $\rho_2 \simeq 0.82$ g/cm³.

In order to investigate the qualitative influence of the van der Waals forces we studied a model plasma with increasing values of the parameters a and b . Fig. 2 shows the isotherm $T = 0.07$ a.u. and $a = b = 30$ a.u.

In spite of the fact that these values are rather large we cannot detect a separate van der Waals wiggle. Both attracting forces support each other and lead to one phase transition approximately in the same density region as the PPT. This is the situation we observe in nature for alkali plasmas. At further increase of the values of the van der Waals parameters to $a = b = 100$ a.u. we observe two separate van der Waals loops as shown in Fig. 3. This is the situation we observe for real noble gas plasmas. We emphasize, that Figs. 2 and 3 have just illustrative character; in reality we do not see two wiggles in one isotherm due to the drastic difference between the critical temperatures.

Summarizing these findings we may state that in dependence on the values of the van der Waals parameters we may obtain either a phase diagram with two first order transitions (hydrogen and noble gas plasmas) or a phase diagram where both transitions fuse to just one (alkali plasmas). The existence of a phase diagram including a van der Waals type transition and a separate metal-insulator phase transition was discussed for the first

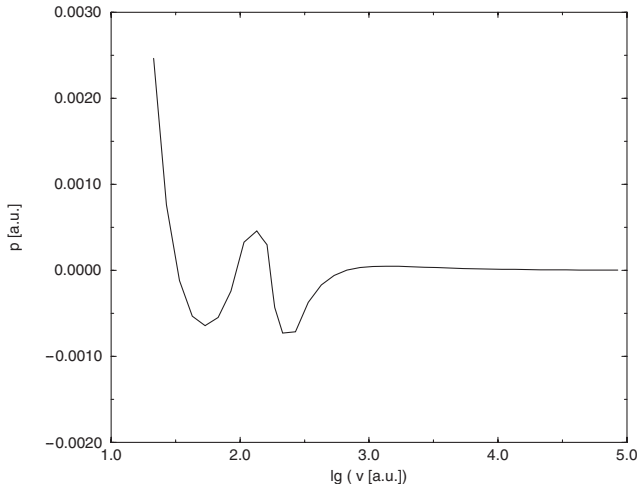


Fig. 3. The isotherm $T = 0.07$ a.u. for a noble gas-like model plasma with a PPT and a separate van der Waals transition (van der Waals parameters of the model: $a = 100$ a.u., $b = 100$ a.u.).

time in 1944 by Landau and Zeldovich.⁽¹⁾ We repeat that the existence of two separate phase transitions requires the validity of the inequalities

$$T_{\text{vdW}} \ll T_{\text{ppt}}; \quad \rho_{\text{vdW}} \ll \rho_{\text{ppt}} \quad (23)$$

This is fulfilled for hydrogen and for noble gas plasmas. In the case of alkali plasmas the van der Waals and the PPT transition have about the same critical density and temperature. Therefore both transitions fuse just to one with very specific properties.^(14, 25–27)

4. DISCUSSION OF PLASMA PHASE TRANSITIONS

Considerable efforts were applied to obtain better plasma thermodynamic functions for larger range of the nonideality parameter. We will not go into the details of the theory here which are explained elsewhere.^(7, 9, 10, 11) The critical temperatures derived from more refined versions of the theory lay in the region $T_{\text{cr}} = 14000\text{--}19000$ K.^(7, 8, 11) There is a scatter in the values of T_{cr} , p_{cr} and n_{cr} , since the procedure of getting the thermodynamic functions for large nonideality is not a unique one. Instead of going into details on the several theoretical approaches we concentrate here on the physics and the relation to experiments, to numerical simulations and to related phenomena.

Let us start with the experimental aspects. The existence of a PPT in dense plasmas is still less clear than in classical Coulombic systems. This is mainly due to the fact that pressures predicted for the coexistence line are above 1 Mbar what is still hardly reachable in experimental situations. However in the last time more and more experiments were performed which cover the region of interest.^(29,36) Experiments with shock-compressed hydrogen and deuterium plasmas have verified that around 140 GPa and 3000 K a transition to a highly conducting state occurs.^(29,31) This is approximately the pressure region where the coexistence line of the PPT is expected.⁽²⁸⁾ A corresponding behavior of conductivity data has been reported.⁽³⁰⁾ Pressure dissociation and ionization, which almost do not depend on the temperature, become a dominant factor at 10^4 K and below in hydrogen and deuterium fluid studied experimentally at high pressures.^(31,34-36)

In order to compare theory and experiment in a more quantitative way refined treatments of the phase transition induced by pressure dissociation and ionization were given.^(7,8,11,13,14,28) Most of the possible species and various interactions were taken into account to calculate the equations of state. There is a certain discussion whether the model equations of state reproduce reasonably well the recent experiments. However the theory predicts in all variants a phase transition. with $T_{cr} = 14000-19000$ K. Excited states do not contribute significantly to the hydrogen partition function in the intermediate range of temperatures.

Path integral Monte Carlo calculations and wave packet dynamics also give some hints to the existence of the plasma phase transition.⁽³⁷⁻⁴³⁾ For example the validity of the thermodynamic expressions used was tested by comparison with molecular simulation and experimental data for non-ideal plasmas and limiting expansions for weakly nonideal plasmas.⁽⁴³⁾ The problem continues to attract remarkable attention, for example at the recent (June 2-7, 2002) "International Conference on Warm Dense Matter and FEL Experiments" in Hamburg, Filinov *et al.*^(44,45) claim that they "present results of direct path integral Monte Carlo simulations which, for the first time, provide first-principle support of such a phase transition in dense hydrogen". It should be noted, however, that these particular PIMC simulations yield rather low energy values for the "droplets" that appear in the simulations. Kohanoff and Scandolo⁽⁴⁶⁾ discussed on this workshop the same problem in a softer manner and presented their results of ab initio molecular dynamics simulations. We mention these works as part of the ongoing effort to simulate the PPT.

Let us discuss now in brief the phase transitions observed in alkali-plasmas. As pointed out in previous sections the theory predicts for this case that the PPT and the van der Waals transition fuse just to one

transition. Near to the critical point the degree of ionization is low but different from zero. Coulombic interactions are present and influence the critical behavior, in spite of the fact that they do not play the dominant role. The area of parameters close to the critical point of cesium was carefully investigated.⁽²⁵⁾ It was shown that near to the critical point the ionization landscape changes quickly and has a quite complicated structure. The theoretical predictions which take into account the charge-atom interaction (polarization effects) are in rather good agreement with the data.^(26, 14)

The existing experiments for argon plasmas based on shock wave data are also in satisfactory agreement with the theory.^(34, 47, 48)

We will discuss now the problem of critical behavior and the critical indices. For the classical case much attention has been devoted to this problem.^(23, 49, 50) For the PPT where quantum effects influence the critical point, the problem of critical indices is still open. So far no experiments are available which give reliable information about the critical properties of hydrogen and noble gas plasmas. Experimental studies of classical electrolyte solutions revealed that Coulomb liquids characteristics differ from those of simple liquids. Even if crossover was observed from classical scaling laws to Ising scaling, it takes place much closer to the critical point. The Ginzburg parameter, which characterizes the size of the Ising region, turns out to be of 1–2 and more orders of magnitude less than for simple liquids. So there is a remarkable difference in crossover range between simple and Coulomb liquids.^(23, 49, 50) Experimental study of crossover phenomena in real plasmas and in particular in cesium plasmas might help to find out if the critical point is of the plasma or gas-liquid kind. Additional factors, which do not exist in electrolytes, namely, quantum effects and charge-atom interaction can influence the crossover phenomena in PPT.

Michael Fisher⁽⁴⁹⁾ formulated clearly the challenge to the critical phenomena theory: “Critical behavior is thoroughly understood in Ising models alias lattice gases: But how far does that help our insight into the critical region of continuum models and real fluids? In particular, what causes some ionic solutions to exhibit van der Waals or “classical” critical exponents, while other, so-called “solvophobic” systems are of Ising—type?”. It is evident that the difference between properties of various liquids under similar external conditions can be attributed principally only to the interaction potentials between the particles. However the Kadanoff–Wilson theory of critical phenomena, which is based on the universality hypothesis, neglects interaction potential peculiarities and appeals only to large-scale properties, such as system dimension and Hamiltonian symmetry. So other approaches are needed.

First of all Fisher points to the integral equation approach. But most of the standard approaches to the theory of critical phenomena based on

integral equation method fail.⁽⁴⁹⁾ Though both the Kadanoff–Wilson theory and the integral equation approach are on equal rights, the first is based on global treatment whereas the latter is related to the local Ornstein–Zernike equation. For this reason Fisher puts the integral equation approach on the first place in his hope to solve the problem of Coulomb criticality. However there is a specific difficulty in the local approach which is connected with the choice of closing relation in the integral equation approach. This difficulty was attacked recently by Martynov.⁽⁵¹⁾ He suggested an integral equation which depends on the interaction potential and permits in principle to define the critical indices and their dependence on the interaction potential. Martynov⁽⁵¹⁾ applied his local approach to the system of charged particles. The critical indices obtained differ almost as much as twice from van der Waals and Kadanoff–Wilson predictions. However the results cannot be applied directly to electrolyte solutions since they do not take into account solvent molecule influence, neither it can be applied directly to dense plasma, since quantum effects are not taken into account.

Let us finally discuss several special problems connected with Coulombic phase transitions. At first we mention the magnetic field influence. It was shown recently that strong magnetic fields increase the critical temperature.^(52, 12) Another important effect is connected with non-equilibrium phenomena. It was noted⁽⁵³⁾ that nonideal plasmas are usually generated in non-equilibrium state with respect to plasma wave excitation. This might complicate the theory⁽¹⁴⁾ and the analysis of experiments.

At third we would like to discuss a new class of phenomena observed in Cs-plasmas.⁽⁵⁴⁾ Though the standard cesium phase diagram is well known⁽²⁷⁾, Recently a new phase state of Cs was observed by Holmlid *et al.*^(54–56) In experiments with thermoionic converters clusters were observed first at 1300 K. These cluster were cooled and associated in microdroplets. The microdroplets formed were fixed and measured at 70 K. The number density obtained was about 1018 atoms/cm³. Holmlid⁽⁵⁴⁾ considered his results as an observation of the Rydberg matter predicted by Manykin *et al.*^(55, 56) Generally speaking Rydberg matter exists only at 0 K temperature. At higher temperatures Manykin's approach can and should be combined with our non-ideal plasma treatment. In fact both approaches enhance each other. The phenomenon might be connected with the idea of isolated segment of metastable nonideal plasmas which was introduced into the plasma thermodynamics long ago.⁽⁵⁷⁾ Supercooled nonideal plasma states were a direct consequence of the PPT.⁽⁵⁸⁾ Manykin's Rydberg matter,^(55, 56) Holmlid's microdroplets⁽⁵⁴⁾ and plasma phase transitions^(2, 3, 59) are various facets of Coulombic phenomena. The existence of isolated regions of metastable nonideal plasmas is not an exceptional feature of cesium. Several authors^(55–58) suggested that this might be a more general feature. In fact Holmlid⁽⁵⁴⁾

observed his clusters in many other substances as well. The isolated region of metastable nonideal plasmas is possibly an inherent part of the phase diagram. This part complements the standard diagram and is superimposed on it.

5. CONCLUSIONS

This work is devoted to plasma phase transitions (PPT) which are determined by attractive Coulombic interactions and quantum repulsion. The PPT occurs in the region of high pressures and temperatures, where matter is at least partially ionized. At least in principal the PPT is an analogue of the known Coulombic transition in classical ionic solutions. In both cases the mechanisms are the same, the transition is due to the interference between a Coulombic attraction of the charges and repulsive forces. The classical repulsion of ions at small distances is in the quantum case replaced by Heisenberg and Pauli repulsion effects. We have shown above for dense gaseous plasmas that in dependence on the values of the van der Waals parameters of the neutral component we may obtain either a phase diagram with two first order transitions (hydrogen and noble gas plasmas) or a phase diagram where both transitions fuse to just one (alkali plasmas). In spite of considerable efforts there is no final proof yet that the PPT really exists, however new theoretical and experimental results seem to confirm this hypothesis. One strong theoretical argument in favor of the PPT is the analogy to the Coulombic phase transition in classical systems. For ionic solutions theory and experiment (Monte Carlo data as well as measurements on electrolytes) show a corresponding Coulomb transition. Therefore there is no doubt any more that a Coulombic phase transition in classical systems exists.^(22, 23, 49) For quantum systems as, e.g., hydrogen plasmas the problem of the existence of a PPT is still open. The main reason for still unsolved problems are

- the theory of the PPT requires an accurate theory of dense quantum plasmas, and
- the pressures where the PPT occurs are in the Mbar region what leads to very difficult experimental problems.

We discussed here several results of theory and experiment which point to the existence of a PPT in real plasmas and discussed the conditions and parameter regions where the PPT is expected.

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