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Hysteresis in the Mott transition between plasma and insulating gas

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We show that hysteresis can occur in the transition between a neutral plasma and the insulating gas consisting of neutral pairs bound by Coulomb attraction. Since the transition depends sensitively on the screening length in the plasma, regions of bistability occur in density-temperature phase space. We present numerical results which indicate where these regions occur for systems such as spin-polarized hydrogen, positronium gas, and excitons in a semiconductor.

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The system consisting of equal numbers of positively and negatively charged spin-1/2 particles provides a surprisingly rich subject for the study of phase transitions. At high density, the system is the well-known neutral Fermi plasma. As density decreases, the system becomes unstable to the formation of bound complexes which behave as bosons. Under certain conditions at low temperature, these composite bosons can form a Bose condensate. Presently, experimental searches are under way or proposed for observation of Bose condensation in several systems of this type, namely, excitons in semiconductors [1], hydrogen and alkali gases [2,3], and positronium [4]. Depending on the mass ratio and spin degeneracies of the positive and negative particles, other phases such as solid and Fermi liquid can arise.

The phase transition from conducting plasma to insulating bound-pair gas, known as the Mott transition, has been discussed in the literature for well over three decades. The general condition for this transition is that the screening length in the plasma be comparable to or less than the intrinsic bound-state Bohr radius. A point that has been less well appreciated is the possibility for *bistability and hysteresis* in this transition. The basic reason for this hysteresis is that neutral bound states will not contribute to long-range screening. Therefore, if the gas is initially in the insulating phase, a transition to conducting plasma will occur only when the number of free charged particles *created by thermal dissociation of bound pairs* becomes high enough that the screening due to these particles causes bound states to become unstable. In general, the density of this transition, called the "ionization catastrophe" [5], is not the same as the Mott transition in the reverse direction that occurs when the system is initially in the plasma state.

In this paper, we present a simple model that illustrates the hysteresis in this kind of system. Much of the discussion is in terms of equal-mass positive and negative particles (excitons or positronium) but the discussion can be generalized to apply to the large-mass-ratio (hydrogen atom) case as well. For the sake of discussion, the bound states will be called excitons. In all of the following we assume nondegenerate (Maxwell-Boltzmann) statistics for both bound states and free particles. This will limit the regions of phase space where the model is valid (i.e., it will not be valid near the Bose-Einstein phase transition or for the degenerate Fermi gas), but the primary effect of hysteresis does not depend on the statistics. We also ignore van der Waals interactions between bound states and the formation of bound-state complexes.

Rate equations. Instead of the usual partition function $Z = e^{\Delta/k_BT}$, the "Planck-Larkin" partition function [6,7], $Z = e^{\Delta/k_BT} - (1+\Delta/k_BT)$, is used, which takes into account the fact that states with $\Delta \ll k_BT$ are quasifree. This first-order correction to the Boltzmannian partition function was initially calculated in order to keep the density of states of atoms near the $n \to \infty$ continuum from an unphysical infinity. In the context of the neutral plasma system studied here, it enforces the physical result that when the binding energy is zero the population in bound states must become identically zero. Ebeling *et al.* [6] have used first-order perturbation theory to show that this partition function has a sound physical basis.

For species conversion via three-body collisions, the rate of change of the bound state (exciton) population n_{ex} is then given as follows:

$$\frac{\partial n_{ex}}{\partial t} = An_e\left[n_e^2 - \frac{n_{ex}n_Q}{e^{\Delta/k_BT} - (1+\Delta/k_BT)} \times\frac{g_eg_h}{g_{ex}}\left(\frac{\mu}{m}\right)^{3/2}\right] \tag{1}$$

where n_e is the free electron density, with $n_{ex} + n_e = n$, the total pair density; g_e, g_h, and g_{ex} are the electron, ion (hole), and exciton spin degeneracy, respectively, and m and μ are the total and reduced mass, respectively. The "quantum density of states" is given by

$$n_Q = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} \equiv 1/\lambda_D^3 \tag{2}$$

where λ_D is the de Broglie wavelength. Setting $\partial n_{ex}/\partial t = 0$ in (1) with $\Delta \gg k_BT$ gives the standard Saha equation [6] $(n_e^2/n_Q) = n_{ex}e^{-\Delta/k_BT}(g_eg_h/g_{ex})(\mu/m)^{3/2}$. The constant A, which

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depends on the cross section and may be temperature dependent, determines the absolute rate of conversion and does not enter into steady-state calculations.

The interesting dynamics in this system come from the dependence of Δ on n_e. The binding energy (Rydberg) of a single bound state (exciton) is given by $\Delta_0 = \hbar^2/2a^2\mu$, with the Bohr radius $a = \hbar^2\epsilon/e^2\mu$. (The dielectric constant ϵ is included in the case of a polarizable medium, e.g., for excitons in a semiconductor.) When screening is present, so that the particles do not interact with pure Coulomb attraction but with a Yukawa-type interaction, the binding energy decreases approximately according to [8]

$$\Delta(n_e,T) = \begin{cases} \Delta_0\left(1 - \frac{2}{1+(qa)^{-1}}\right), & qa < 1 \\ 0, & qa \geq 1. \end{cases} \tag{3}$$

For $1/q \sim a$, variational calculations give slight (20%) corrections to the above formula [9] which are not of interest here. The screening constant is given by the Debye-Huckel formula [10],

$$q^2 = \frac{4\pi e^2 n_e}{\epsilon k_B T}. \tag{4}$$

It is important to recognize that only free charged particles contribute to screening—the bound states are neutral.

Numerical results. It is convenient to set $n_e = ny^2$ and use $\dot{n}_{ex} = -\dot{n}_e$ to write the dynamics in dimensionless form:

$$\frac{dy}{d\tau} = \frac{y}{f(y)}\left[\alpha(1-y^2) - y^4 f(y)\right] \tag{5}$$

where $\tau = An^2t/2$ is a scaled time, and $f(y) = \exp[F(y)] - (1 + F(y))$ is the partition function in terms of

$$F(y) = \max\left[0, \frac{(g_e g_h/g)^2}{\pi\beta^2}\left(\frac{\sqrt{\alpha/\beta} - y}{\sqrt{\alpha/\beta} + y}\right)\right]. \tag{6}$$

The parameters α and β determine the temperature and density:

$$\left(\frac{a}{\lambda_D}\right)^2 = \frac{m}{\mu}\left(\frac{g}{2g_e g_h}\right)^2 \beta^2, \tag{7}$$

$$na^3 = \left(\frac{g}{g_e g_h}\right)^2 \left(\frac{\beta^3}{8\alpha}\right). \tag{8}$$

There is an equilibrium at $y = 0$ which is unstable due to thermal ionization of excitons. In addition, there is always at least one stable equilibrium described by

$$0 = \left[\alpha(1-y^2) - y^4 f(y)\right]. \tag{9}$$

For appropriate choices of n and T there can be three solutions; two stable and one unstable. The locus of points (n, T) defining the region of bistability has been determined numerically. When there is a fully ionized plasma state at $y = 1$ then $F(1) = 0$, and the model fails to quantitatively describe the approach to $y = 1$ due to the divergence of $f(y)^{-1}$ as $F \to 0$.

Figure 1 shows numerical results when $g_e = g_h = 2$ and $g_{ex} = 1$. The unitless pair density na^3 and the unitless temperature $(\mu/m)(a^2/\lambda_D^2)$ are control parameters; only the fraction of free carriers $y^2 = n_e/n$ can vary. The binding energy $\Delta(n_e)$ is calculated using a self-consistent value of n_e. The solid line marks the boundary between the region with *one* steady-state solution and the region with *three* steady-state solutions, one of which is unstable.

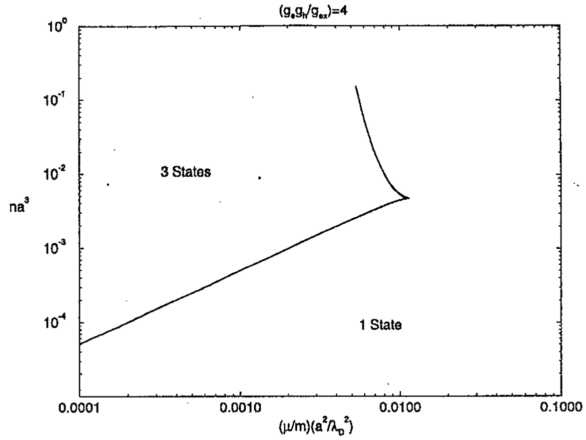

FIG. 1. The boundary between the regions of phase space with one steady-state solution and three steady-state solutions of Eq. (9) in the text, for the case $g_e = g_h = 2$, $g = 1$.

Figure 2 illustrates the behavior of the system in these regions, by plotting the ionized fraction as a function of total pair density at fixed temperature. For temperature well above the three-solution region [Fig. 2(a)], the system remains mostly ionized at all densities. At lower temperatures [Figs. 2(b) and 2(c)], a sharp transition appears between a pure plasma and exciton-rich phase. Finally, when the temperature is lowered further, a classic hysteresis curve occurs [Fig. 2(d)]. Two different solutions for the ionized fraction are stable against fluctuations.

Regions of phase space. By simple arguments, we can see how hysteresis occurs in this system. Figure 3 shows the relevant crossovers for the case $m = 4\mu$ and $g_e = g_h = 2, g_{ex} = 1$ of Figs. 1 and 2. If we assume that the system is in the plasma state, then we expect a Mott transition when $1/a = q$ where q is given by the Debye formula (4) with $n_e = n$. In terms of the unitless parameters na^3 (unitless pair density) and a^2/λ_D^2 (unitless temperature), this becomes

$$na^3 = \frac{1}{2}\left(\frac{\mu}{m}\right) a^2/\lambda_D^2, \tag{10}$$

shown as the heavy solid line in Fig. 3. On the other hand, if we assume the system is in the insulating gas (excitonic) phase, we would expect a transition when $1/a = q$ where q is given by (4), but instead of setting n_e equal to n, we would use the equilibrium value from (1), assuming $\Delta = \Delta_0$ and $n_e \ll n$. This yields

$$na^3 = \frac{1}{4}\left(\frac{a^2}{\lambda_D^2}\right)^{1/2}\left(\frac{g}{g_e g_h}\right)\left(\frac{\mu}{m}\right)^{1/2} e^{(\lambda_D^2/a^2)(m/\mu)/4\pi}, \tag{11}$$

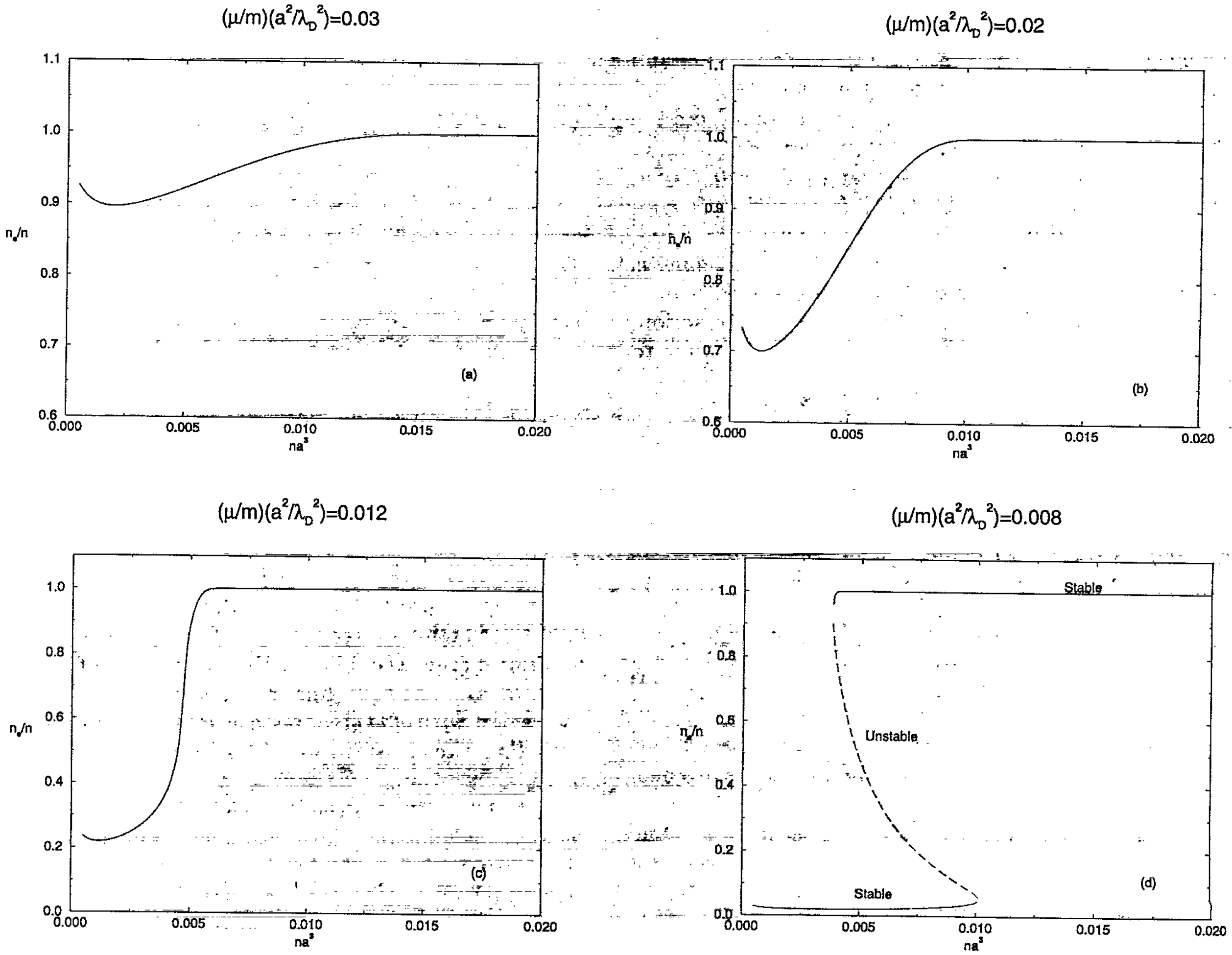

FIG. 2. Steady-state solutions of n_e/n from Eq. (9), as a function of na^3, for four temperatures.

shown as the light solid line in Fig. 3. Since at very low temperatures the number of thermally ionized particles becomes extremely small, the "ionization catastrophe" density becomes exponentially large at low temperature. For comparison, the conditions for a transition to a Fermi degenerate gas ($na^3 \sim 1$) and for a transition to a weakly interacting Bose condensate [$na^3 = 2.612(a^2/\lambda_D^2)^{3/2}$] are shown as the dashed and dotted lines in Fig. 1, respectively. Since the model presented here involves only Maxwellian statistics, it is only valid for densities well below both of these curves. The presence of the plasma state will prevent Bose condensation, however, so the proximity of the Mott transition to the Bose condensation boundary in certain regions of phase space merits attention in all composite-boson condensation experiments.

At low temperature and low density, the system is an insulating excitonic (bound-state) gas, assuming repulsive interactions between excitons. As density is raised, in the low-temperature limit the system remains an insulating gas until an ionization catastrophe occurs. As seen in Fig. 3, this can occur at substantially higher density than the Mott transition given by Eq. (10). If the sys-

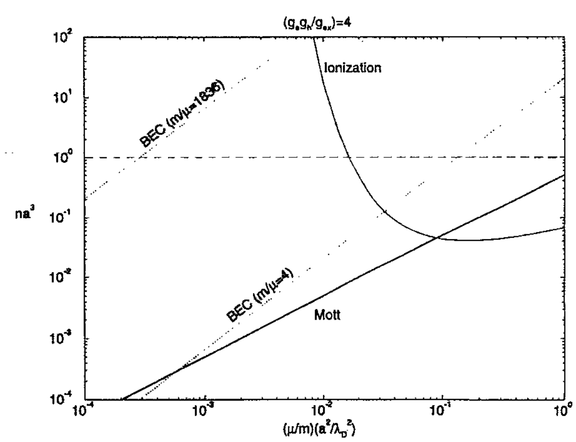

FIG. 3. The regions of phase space indicated by the simple equations (10) and (11) in the text. The model breaks down above the critical density for Bose condensation (dotted lines, for two different values of m/μ corresponding to excitons *and* hydrogen) and in the Fermi degenerate region ($na^3 \sim 1$, indicated by the dashed line).

tem starts in the plasma state in this temperature regime, however, it will remain a plasma indefinitely unless the density falls below the Mott density given by (10).

These two curves essentially form the boundaries of the region of hysteresis shown in Fig. 1. [The curve in Fig. 3 given by (11) lies above the phase boundary for an ionization catastrophe found numerically in Fig. 1 because it does not use a self-consistent value of the binding energy $\Delta(n_e)$.] At temperatures above the intersection of the solid curves, however, the system undergoes a single phase transition to a plasma state, since an ionization catastrophe occurs at lower density than the Mott transition given by (10). At very high temperature, the "ionization catastrophe" is not a clearly defined transition, since even at low density a substantial fraction of the system is ionized.

Application to experiment. Preliminary results from experiments with excitons in the semiconductor Cu_2O seem consistent with this picture. As reported in Ref. [11], excitons with binding energy $\Delta = 150$ meV exist in this material and have been observed at room temperature. In those experiments, the value of na^3 was roughly 0.003 (pair density $\sim 10^{19}$ cm^{-3}, excitonic Bohr radius 7 Å), a^2/λ_D^2 was approximately 0.04 (T =300 K, mass $m = 3m_0$), and $\mu/m \simeq 4$ (roughly equal electron and hole mass.) This puts the system right in the region of the crossover seen in Figs. 1 and 3. In the experiments, excitons appeared only when created resonantly by laser excitation. When free carriers were created by laser excitation with photon energy well above the band gap, no exciton luminescence ever appeared. In other words, two different stable states occurred at roughly the same temperature and pair density.

Clearly, there is room for more experiments and theory on this interesting system. Since the model presented here assumes spatial homogeneity, pattern formation and related nonlinear dynamical effects do not occur. The possibility exists that when the effects of spatial variations are taken into account regions of coexistence and very interesting chaotic behavior may be seen in the exciton-plasma phase transitions.

These results also relate to experiments on phase transitions of atoms with attractive interactions, e.g., the search for a metallic phase of hydrogen at high pressure [12]. Because of attractive interactions, the lower, insulating state may not be a *gas*, as assumed here, but instead a solid or liquid state. In many cases, however, screening is assumed to play an important role in a transition to a conducting phase. The results here indicate that the densities necessary for a *spontaneous* transition to such a phase may be much higher than expected from equilibrium calculations, since a metastable solid or liquid state comprised of bound pairs will have poor screening even at high density.

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