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DOES THE PHASE TRANSITION EXIST IN THE ONE - COMPONENT PLASMA MODEL ?

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Explanations are given why there is no real first order phase transition in the one - component plasma model (OCP). Fluid (liquid) and crystalline states of the OCP observed in computer experiments are not in equilibrium due to instability of the system. However specific features of the free energy suggest that some sort of a " virtual " phase transition happens in the model. That kind of a transition can be turned real by choosing a right form of the background energy.

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The purpose of this note is to clarify some delicate features connected with existence and properties of the phase transition in the so called one-component plasma model (OCP). The one-component plasma model is a system of identical charged point particles, immersed in a homogeneous neutralizing background of opposite charge. Properties of the classical OCP can be described in terms of a single dimensionless parameter $\Gamma = (Ze)^2/r_s T$, where Ze is a particle charge, r_s is the radius of a sphere containing one particle and T is the temperature. In the quantum case one more parameter r_s or T is needed to characterize the system.

First indications of existence of a crystalline phase in the quantum model of OCP were obtained by Wigner in his classical paper devoted to correlation effects in an electron gas [1]. The terms " Wigner solid "and " Wigner crystallization " became common in physics since that time. Later on Brush, Sahlin, and Teller in their pioneering Monte-Carlo simulation of the OCP discovered that the radial distribution function $g(r)$ indicates existence of crystalline structure in the classical OCP at $\Gamma > 120$ [2]. Probably Brush, Sahlin, and Teller used for the first time the term " phase transition ", when discussed two states of the OCP: liquid and solid. Then Hansen [3] and Pollock and Hansen [4] carried out extensive study of the OCP using improved Monte-Carlo technique and again they observed existence of liquid and solid states in the OCP model and announce that the liquid - solid transition in OCP occurred at $\Gamma = 155 \pm 10$. It should be emphasized here that by this time nobody was in doubt about the existence of the phase transition in the OCP and the most of subsequent work were devoted to determination of the more precise value of Γ_m, the quantum effects, etc. Current estimates of Γ_m are confined in the interval 172–178 [5]. Quantum Monte-Carlo simulation of the OCP should be mentioned here [6, 7]. In general their results are considered to have confirmed the expectations of so called " cold " melting in quantum Coulomb systems [1, 8]. The result of the latest simulation data of this sort [7] is shown in the Fig.1. It would seem that the all OCP calculation and simulation data obtained create a very reliable ground for discussing numerous problems in condensed matter physics in various way connected with the existence of solid and liquid phase in the OCP. The state of plasma in the interior of white dwarfs is one of the most intriguing problems [8, 9]. But first we should have better understanding of

what actually occurs in the OCP at the critical value of Γ_m. Let's see how the numbers for Γ_m are being obtained. Normally all calculations in the OCP model are carried out in the canonical ensemble, and natural output is Helmholtz free energy F for various values of Γ. The intersection of two branches of Helmholtz free energy is taken as the phase transition coordinate Γ_m (Fig.2). As a matter of fact it is a wrong procedure, a phase transition occurs when Gibbs free energies of two phases are equal, one has to use the double tangent construction in $F - V$ plane or equivalent to get a correct result (Fig.3). But usually it was said that the volume change at the transition is too small to distinguish between the two mentioned procedures. Moreover the subsequent claim that volume change at the liquid-solid transition in the OCP always equal to zero eliminated any potential inquiry [10].

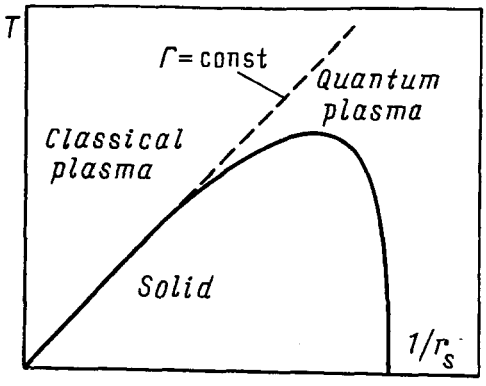

Fig.1. The " phase " diagram of the OCP after Jones and Ceperly [7]. The condition Γ =const corresponds to the classical " transition ". The strong deviation of the " transition " curve from the Γ =const line at high density is a result of the quantum effects. From the numerical data [7] it follows that at the curve maximum $\lambda_T/L \approx 0.5$, where λ_T – thermal de Broglie wavelength, L – average interparticle distance

Meanwhile the fact that the double tangent construction is wrong in principle in the case of the OCP was missed by the whole generation of researchers in the field. Fig.3, where the "impossible" double tangent construction is depicted, illustrates the situation. The point is that the OCP is thermodynamically unstable at $\Gamma \geq 3$ and pressure and compressibility of the system are negative (Fig.2,3) [11]. Due to the negative value of compressibility the free energy F of the OCP is a convex function of volume V and hence a common tangent to two branches of free energy does not make any sense. The conclusion is that there is not any kind of first order phase transition in the system at least for the reason that one of the necessary conditions, which is equality of pressure in coexisting phases, can not be satisfied. So a question arises what does take place at the intersection point when $F_{liq} = F_{sol}$ (See Fig. 2, 3). A slope change is obvious at this point and because $(\partial F/\partial V)_T = -p$, where p is pressure, liquid and solid at the intersection point have different pressures and can not be in equilibrium. But for the reason, which will be explained below, the intersection point, we discuss, may be called the point of a "virtual" phase transition. Note that the density is not changed at the intersection point by definition and the long discussion of this problem in Ref.[10] is senseless.

From the equality $F_{liq} = F_{sol}$ one can get an analog of the Clausius–Clapeyron equation in the form: $dT/dV = \Delta P/\Delta S$, which describes behavior of the intersection point in $T - V$ plane. This equation is applicable to the quantum case as well , where a temperature maximum is observed (Fig.1). As follows from the above equation the temperature maximum is reached when pressure difference in liquid and solid $\Delta P = 0$, of course, if one assumes that the corresponding entropy difference ΔS is finite at finite temperatures.

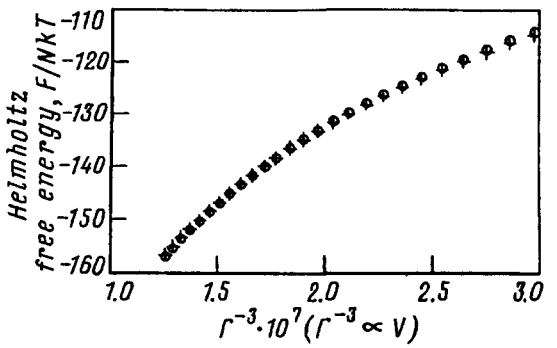

Fig.2. Helmholtz free energy, F divided by NkT of the OCP as a function of Γ^{-3} ($\Gamma^{-3} \propto V$) as follows from the Monte-Carlo calculations (H.E.DeWitt – privite communication). V is the specific volume. The plot contains two systems of data which are almost on top of each other. The crosses and circles correspond to the fluid phase and the solid phase respectively. The intersection point occurs at $\Gamma \approx 175$ (H.E.DeWitt – privite communication)

This situation is illustrated by Fig.4, where the temperature of the virtual phase transition as a function of pressure, which is of course negative, is shown in qualitative way.

It is obvious that the OCP model is not quite physical, but as was emphasized earlier if one would think of a neutralizing background as a degenerate electron gas and would add the corresponding Fermi energy to the total energy of the system, then the situation would change drastically [4]. The pressure and the compressibility would become positive and the tangent construction would be feasible. That is why we may call the transition in the OCP by the virtual phase transition. Fig.5 illustrates the transformation of the compression isotherm of the OCP with the quantum effects taken into account, when Fermi energy of the background is added. However one should keep in mind that in the given case the role of the electronic background is restricted to the charge compensation and Fig.5*b* is drawn with the assumption that there is no other interaction between the point charges, which could be ions, and electrons. We also assume that the quantum kinetic energy of ions is not influenced by nature of the background. As a result the intersection points of the free energy curves do not change their volume coordinates (Fig.5).

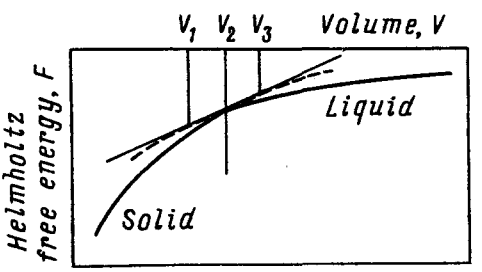

Fig.3. The exaggerated version of the diagram of Fig.2. It is seen the correct double tangent construction is impossible for convex potentials

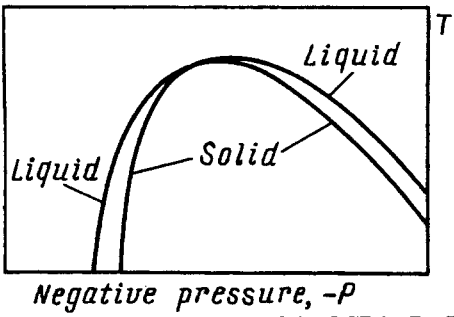

Fig.4. The " phase " diagram of the OCP in $P-T$ plane (compare with Fig.1)

Both of the assumptions are valid in high density limit, which almost exactly correspond to the interior of white dwarfs. However the free energy difference of liquid and solid in the OCP is so small (see Fig.2) that hardly any certain prediction about quantum (cold) melting at very high positive pressure can be made on the basis of the OCP

calculations not taking into account the realistic structure of the background. In this connection it is instructive to refer to the papers [12, 13], where proofs were found that in case of metallic hydrogen the zero point energy favored highly symmetrical structures in certain density range. In other words one may expect that the quantum effects not necessarily decrease melting temperature of a Coulomb system on compression and further and more sophisticated studies are needed to reach a definite conclusion.

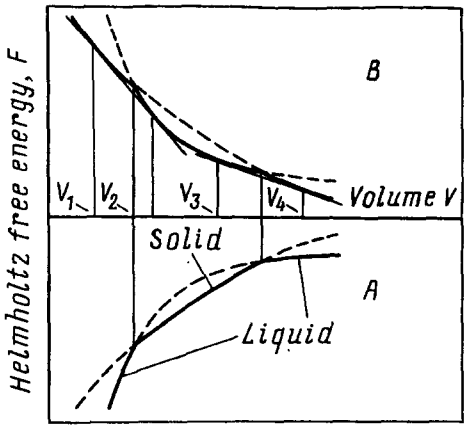

Fig.5. The double crossing of free energy curves in case of strong quantum effects in the OCP model: *a* – standard OCP model (see Fig. 1), *b* – OCP model with a realistic background, the double tangent constructions reveal two phase transitions with volume change $V_1 - V_2$ and $V_3 - V_4$. The second high density crossing is due to the fact that the quantum contribution appears to be structure sensitive and increase the solid energy in respect to the liquid one

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