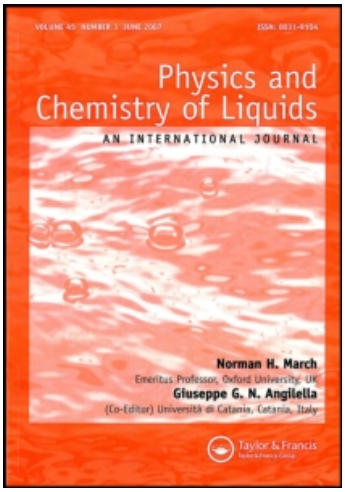

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Approximate Melting Curve of Wigner Electron Crystal

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Expressing the melting curve of the Wigner lattice in reduced temperature T/T^* and reduced density ρ/ρ^*, the simplest realistic assumptions allow the Clausius–Clapeyron equation to be integrated to yield

$$\frac{T}{T^*} = \left(\frac{\rho}{\rho^*}\right)^{(d-2)/d}\left(1 - \frac{\rho}{\rho^*}\right)^{1/2}$$

where d is the dimensionality. The melting curve then has its maximum at a density given by $2(d-2)/(3d-4)$ of the critical density ρ^* for electron crystallization in the ground-state.

1 INTRODUCTION

Electron crystallization is a topic that continues to attract considerable attention.[1] Though it is hard to find a system in nature to simulate jellium, in which Wigner[2] originally showed that electron crystallization would occur at sufficiently low densities in the ground-state, this problem remains of importance in both many-electron theory and in the theory of phase transitions.

More recently, Parrinello and March[3] discussed the thermodynamics of Wigner crystallization, while we have earlier[4] considered the limiting forms of the melting curve of the three-dimensional Wigner lattice in (a) the classical regime and (b) in the region near the critical density for the crystallization to occur in the ground state.

In the present paper, we obtain an approximate theory for the entire melting curve of the Wigner electron crystal. It will be helpful, in doing so, to develop the theory for a general dimensionality d, though in practice we shall be interested in the explicit results for three dimensions. In terms of reduced temperature T/T^* and reduced density ρ/ρ^*, it is shown below that the simplest realistic assumptions allow the Clausius-Clapeyron equation to be integrated to obtain an approximate analytic form for the reduced melting curve over the entire density range from zero to the critical density ρ^* at which electron crystallization takes place in the ground state. This allows an estimate to be made of the magnitude of the melting temperature at the maximum of the melting curve in terms of the density ρ^*.

2 DEPENDENCE OF MELTING CURVE ON DIMENSIONALITY

We consider the melting curve in the temperature-density plane. The equality of the Helmholtz free energy in the two phases yields

$$\Delta E = T\Delta S \tag{2.1}$$

and the Clausius-Clapeyron equation is

$$-\frac{dV}{dT} = \frac{\Delta S}{\Delta p}. \tag{2.2}$$

Here ΔE is the change in internal energy across the melting line, ΔS is the entropy change, p is the pressure and V the volume, related to the number density ρ by

$$\rho = N/V \tag{2.3}$$

for N electrons in a volume V.

Following Parrinello and March,[3] the virial theorem relates the kinetic energy K, potential energy U and pressure p through

$$2K + (d-2)U = dpV \tag{2.4}$$

where d is the dimensionality. Using $\varepsilon = 4 - d$, this becomes, when written in terms of changes across the melting curve

$$2\Delta E - \varepsilon\Delta U = (4-\varepsilon)V\Delta p \tag{2.5}$$

since $E = K + U$. Hence the quantity $\Delta E/\Delta p$ needed in Eqs. (2.1) and (2.2) is given by

$$\frac{\Delta E}{\Delta p} = \frac{\varepsilon}{2}\frac{\Delta U}{\Delta p} + \left(2 - \frac{\varepsilon}{2}\right)V \tag{2.6}$$

Then Eqs. (2.1), (2.2) and (2.6) yield

$$-\frac{\partial V}{\partial T} = \frac{2V}{T} + \frac{\varepsilon V}{2T}(g - 1) \tag{2.7}$$

where we have simply defined g as $1/V(\Delta U/\Delta p)$. In terms of the density ρ, the differential equation (2.7) determining the melting curve becomes

$$\frac{\partial \rho}{\partial T} = \frac{2\rho}{T} + \frac{\varepsilon \rho}{2T}(g - 1) \tag{2.8}$$

This is quite general, but, of course, some assumptions must now be introduced for $g = 1/V(\Delta U/\Delta p)$ before the differential equation (2.8) can be integrated to yield the melting curve. Fortunately, as we shall see below, g can be discussed exactly, as a function of dimensionality d, in two limiting cases, the first of which is the classical limit.

3 MELTING CURVE IN CLASSICAL LIMIT

Returning to the virial theorem (2.4), we note that in the classical limit the kinetic energy K is determined solely by the temperature T and hence the change $\Delta K = 0$. We immediately obtain in this case

$$g = \frac{1}{V}\frac{\Delta U}{\Delta p} = \frac{d}{d-2} = \frac{4-\varepsilon}{2-\varepsilon} \tag{3.1}$$

Inserting this into Eq. (2.8) yields

$$\frac{\partial \rho}{\partial T} = \frac{\rho}{T}\frac{4-\varepsilon}{2-\varepsilon} \tag{3.2}$$

which has the integral

$$T = \text{const}\, \rho^{2-\varepsilon/4-\varepsilon} \tag{3.3}$$

or

$$\rho = \text{const}\, T^{4-\varepsilon/2-\varepsilon} \tag{3.4}$$

In three dimensions, this yields $T \propto \rho^{1/3}$ and the constant of proportionality is known from computer experiments.[5]

4 MELTING CURVE NEAR CRITICAL DENSITY FOR CRYSTALLIZATION IN GROUND-STATE

We next work near the quantum mechanical ground state transition density, or more specifically for ρ near to ρ^*, T near to absolute zero. We have first from Eq. (2.5)

$$\frac{\Delta E}{\Delta p} = \frac{\varepsilon}{2}\frac{\Delta U}{\Delta p} + \left(2 - \frac{\varepsilon}{2}\right)V \tag{4.1}$$

or

$$\frac{1}{V}\frac{\Delta E}{\Delta p} = \frac{\varepsilon}{2}\frac{1}{V}\frac{\Delta U}{\Delta p} + \left(2 - \frac{\varepsilon}{2}\right). \tag{4.2}$$

Now as $T \to 0, \Delta E \to 0$ from Eq. (2.1) and hence from Eq. (4.2) we have near ρ^*

$$g = \frac{1}{V}\frac{\Delta U}{\Delta p} = -\frac{2\left(2 - \frac{\varepsilon}{2}\right)}{\varepsilon} = -\frac{d}{\varepsilon} \tag{4.3}$$

Thus, in two limits the quantity g in the Clausius-Clapeyron Eq. (2.8) is known from Eqs. (3.1) and (4.3) as a function of dimensionality. Our next task is to use physical assumptions to find an approximate form of g, as a function of density, which includes correctly these exact limits.

5 APPROXIMATE FORM OF MELTING CURVE THROUGH WHOLE DENSITY RANGE

The theory of the melting curve of the electron crystal evidently depends on judicious approximation of g in Eq. (2.8). To see how to proceed, we make the assumption that g can be Taylor expanded around $\rho = 0$ as

$$g = \frac{4 - \varepsilon}{2 - \varepsilon} + \rho c(\varepsilon) + 0(\rho^2) \tag{5.1}$$

where use has been made of the classical limiting form (3.1).

The second assumption is that, around the quantum-mechanical transition density ρ^*, we can also Taylor expand as

$$g = -\frac{d}{\varepsilon} + (\rho^* - \rho)q(\varepsilon) + 0(\{\rho^* - \rho\}^2) \tag{5.2}$$

Unfortunately, to date, there is no microscopic theory developed which will enable us to calculate c or q in Eqs. (5.1) and (5.2).

Therefore, we shall construct the simplest possible form having realism which incorporates the forms (5.1) and (5.2), but which can be utilized to cover the entire density range of interest, namely $0 < \rho < \rho^*$. This we achieve by writing

$$g = \frac{1 + b_1\left(\frac{\rho}{\rho^* - \rho}\right)}{\frac{2-\varepsilon}{4-\varepsilon} - b_2\left(\frac{\rho}{\rho^* - \rho}\right)} \tag{5.3}$$

It is obvious that in writing Eq. (5.3) we have used the limiting result (3.1) as ρ tends to zero. To incorporate the limit (4.3), as $\rho \to \rho^*$, we must have

$$b_1 = \frac{b_2\, d}{\varepsilon} \tag{5.4}$$

It is the one-parameter form (5.3) which now allows us to solve the Clausius-Clapeyron Eq. (2.8) without further approximation, as a function of the single parameter b_2. It is readily verified that

$$\frac{T}{T^*} = \left(\frac{\rho}{\rho^*}\right)^{(2-\varepsilon)/(4-\varepsilon)}\left(1 - \frac{\rho}{\rho^*}\right)^{b_2}. \tag{5.5}$$

The final task is to choose b_2 on physical grounds. For three dimensions, we have argued elsewhere that near the quantum mechanical density ρ^* for the electron crystallization, the form of the melting curve is $T \propto (\rho^* - \rho)^{1/2}$. This utilized the fact that the liquid was metallic and that single-particle excitations at low temperatures lead to an entropy $S \propto T$ in the metallic liquid, which dominates the Debye T^3 specific heat contribution to the entropy in the three dimensional insulating crystal. Though this latter insulating form is dependent on dimensionality, in fact the metallic term is not dependent on dimensionality and we obtain $b_2 = \frac{1}{2}$, independent of dimensionality. We emphasize that this choice of b_2 depends on microscopic theory at low temperatures.

Two final points now follow. The first is that the melting curve has a maximum which is readily shown from Eq. (5.5) to occur at

$$\frac{\rho_{\max}}{\rho^*} \equiv m = \frac{2-\varepsilon}{4-\varepsilon}\Big/\left\{b_2 + \frac{2-\varepsilon}{4-\varepsilon}\right\} \tag{5.6}$$

which for $b_2 = \frac{1}{2}$ yields the density corresponding to the maximum in the melting curve as

$$\frac{\rho_{\max}}{\rho^*} \equiv m;\ m = 2(2-\varepsilon)/(8-3\varepsilon). \tag{5.7}$$

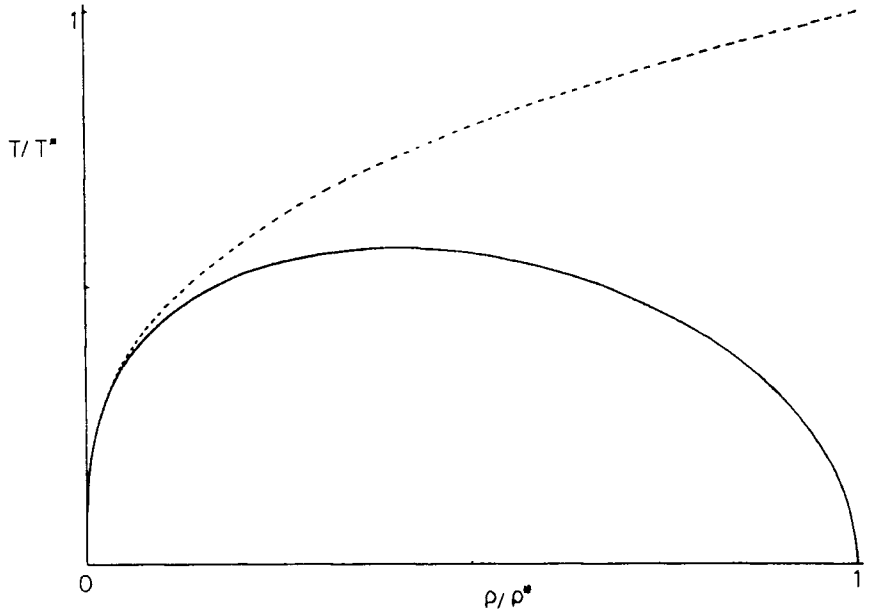

FIGURE 1 Reduced melting curve of three-dimensional Wigner electron crystal using the form (6.1). The dashed curve is the classical asymptote (5.8) in similar reduced form.

This result is readily traced back to the fact that it corresponds to the zero in the denominator of the form of g in Eq. (5.3). The presence of a maximum in the melting curve; inevitable from the asymptotic properties, means of course from Eq. (2.8) that $\partial\rho/\partial T$ must be infinite there and hence that g must be infinite.

Secondly, for the three-dimensional case, our main interest, we know the constant A in the classical melting curve

$$T = A\rho^{1/3} \tag{5.8}$$

from machine calculations.[5] Hence the temperature T^* is related to the density ρ^* and A by

$$T^*\rho^{*-1/3} = A, \tag{5.9}$$

from Eq. (5.5) with $\varepsilon = 1$.

If we use Eq. (5.9) to estimate the melting temperature at the maximum of the melting curve plotted in Figure 1, which from Eq. (5.7) occurs at $(2/5)\rho^*$, then we find for a critical density ρ^* corresponding to a mean interelectronic spacing $r_s \sim 200a_0$, where a_0 is the Bohr radius, $T \sim 5°K$, whereas for $r_s \sim 100a_0$ we get $\sim 10°K$. Naturally, near the critical density for melting at

$T = 0$, i.e., ρ^*, one can use the above scaling to read off from Figure 1 the melting temperatures. The broken curve in Figure 1 is merely the classical asymptote (5.8), scaled with T^* and ρ^*.

6 SUMMARY

We have constructed an approximate theory of the melting curve of the Wigner electron crystal over the entire density range of interest, namely $0 < \rho < \rho^*$. The reduced melting curve we obtain is

$$\frac{T}{T^*} = \left(\frac{\rho}{\rho^*}\right)^{(2-\varepsilon)/(4-\varepsilon)} \left(1 - \frac{\rho}{\rho^*}\right)^{1/2} \tag{6.1}$$

where $\varepsilon = 4 - d$ with d the dimensionality. This result contains the classical limit correctly, as well as the form given by microscopic theory near $\rho = \rho^*$, and T therefore near to zero. In three dimensions, the melting curve in the present approximation has its maximum at 2/5 of the quantum-mechanical zero temperature transition density ρ^*. The magnitude of the melting temperature is then determined in terms of ρ^*.

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