VOLUME 64, NUMBER 3 PHYSICAL REVIEW LETTERS 15 JANUARY 1990

Density-Functional Theory of Freezing for Quantum Systems: The Wigner Crystallization

G. Senatore
Dipartimento di Fisica "A. Volta," Università di Pavia, Pavia, Italy

G. Pastore
International School for Advanced Studies, Trieste, Italy

(Received 21 June 1989)

We present a density-functional approach to the freezing of quantum systems which emphasizes the role of the liquid phase. The key ingredient of this theory is the static response function of the homogeneous liquid. From this quantity one constructs the difference of the relevant free energy between the liquid and a given crystalline phase and hence locates the melting curve. As an illustration we study the Wigner crystallization.

PACS numbers: 64.70.Dv, 05.30.−d, 71.10.+x

Density-functional theory[1,2] (DFT) exploits the fact that a many-particle system can be described through a suitable thermodynamic potential, which is a functional of the one-body density and attains its minimum at the equilibrium density. For a quantum system, it shifts the emphasis from the complicated many-body wave function to the much simpler one-body density (*the density*). It appears natural, therefore, to use DFT to investigate the phenomenon of crystallization, which in equilibrium conditions is characterized by the behavior of the density—changing from a positionally independent constant to a periodic form at the liquid-to-crystal transition. Practical implementations of a density-functional theory of freezing, however, require the ability to construct suitable approximations to the relevant thermodynamic functionals, since these are not known exactly for interacting particles.

To be specific let us consider the Helmholtz free energy F for a system with only one type of particle, whose density we denote by $n(\mathbf{r})$, the generalization to multicomponent systems being straightforward. In the presence of an external potential $v_{\text{ext}}(\mathbf{r})$ acting upon the particles F can be decomposed into[3]

$$F[n]=F_0[n]+F_I[n]+\int d\mathbf{r}\, n(\mathbf{r})v_{\text{ext}}(\mathbf{r})\,, \tag{1}$$

with F_0 being the Helmholtz free energy of the noninteracting particles at density $n(\mathbf{r})$. Hence the excess free energy F_I contains effects due to particle-particle interaction and—in the quantum case—to exchange. It is this functional that is not exactly known and requires approximations to perform practical calculations. However, rather than making an approximation to the whole F_I—as is done in the local-density approximation[1,3] (LDA)—we propose here to approximate the difference of excess free energy between the inhomogeneous system and a homogeneous liquid at density n_l. This is achieved by functionally expanding $\Delta_I=F_I[n_s]-F_I[n_l]$ around the liquid in powers of the density difference $\delta n(\mathbf{r})=n_s(\mathbf{r})-n_l$ between the two phases. In the absence of an external field,

$$\Delta_I=\int d\mathbf{r}\,\mu_I\delta n(\mathbf{r})+\tfrac{1}{2}\int\!\!\int d\mathbf{r}\,d\mathbf{r}'[-\chi^{-1}(\mathbf{r}-\mathbf{r}')+\chi_0^{-1}(\mathbf{r}-\mathbf{r}')]\delta n(\mathbf{r})\delta n(\mathbf{r}')+\cdots\,. \tag{2}$$

Such an expansion involves as coefficients inverse static response functions of the liquid phase of all orders, which arise from the nonideal free energy. In particular, μ_I and χ are, respectively, the excess chemical potential and the linear-response function of the liquid, the subscript zero indicating ideal (i.e., noninteracting particle) quantities. Use of Eqs. (1) and (2) together with the extremum condition for the appropriate thermodynamic potential allows the calculation of free-energy differences between the solid and the liquid, once the properties of the liquid are known. A nontrivial theory is obtained by carrying out the expansion of Δ_I up to second order,[4] which yields all the terms explicitly shown in Eq. (2). The theory that we have outlined above is the natural extension to quantum systems of a DFT approach to the freezing of classical fluids,[5,6] which has been applied with success to many systems—from neutral[7] and charged[8] hard spheres to Lennard-Jones fluids,[9] the one-component classical plasma,[10] mixtures,[11] and a model description of water.[12]

In this Letter we intend to show that calculations based upon a density-functional approach such as the one described above are indeed feasible for quantum systems. Clearly, the technology involved in the calculations is quite different from that required for classical systems,[6] but existing band-structure computer codes can be easily adapted. As an illustration, we consider below the freezing of *jellium* in three dimensions at $T=0$, within the second-order theory.

Jellium[13] is a model system of electrons in a uniform neutralizing background, whose density n_0 is usually specified by the parameter $r_s\equiv(4\pi n_0/3)^{-1/3}/a_B$—the Wigner sphere radius measured in units of Bohr radii.

Wigner,[14] more than fifty years ago, introduced the idea that electrons could crystallize into a regular lattice under the effect of their mutual Coulomb repulsion. A wide variety of theoretical estimates was then produced over the years[15] for the coupling strength[16] r_s at the phase transition. The best current estimate of the location of the Wigner crystallization comes from quantum Monte Carlo (QMC) simulations of Ceperley and Alder,[17] who have established that the freezing into a bcc lattice takes place at $r_s = 100 \pm 20$, from a liquid which is fully spin polarized. Therefore, in the following we shall restrict our investigation to the freezing of a spin-polarized electron fluid. We notice that, owing to the rigidity of the background and to charge neutrality, the electronic crystallization is at constant density.

At zero temperature the Helmholtz free energy goes into the simpler ground-state energy $E[n]$. Thus, to investigate the stability of a chosen crystalline phase with respect to the liquid, one has to construct the difference in energy of the two phases, $\Delta E = E_s - E_l$. By taking advantage of Eq. (2) and using charge neutrality [i.e., $\int d\mathbf{r}\, \delta n(\mathbf{r}) \equiv 0$] one readily obtains

$$\Delta E = T_0[n_s] - \tfrac{3}{5} N \epsilon_F + \tfrac{1}{2} \int\!\!\int d\mathbf{r}\, d\mathbf{r}' [-\chi^{-1}(\mathbf{r}-\mathbf{r}') + \chi_0^{-1}(\mathbf{r}-\mathbf{r}')]\, \delta n(\mathbf{r})\, \delta n(\mathbf{r}') , \qquad (3)$$

with T_0 denoting the noninteracting particle kinetic energy, ϵ_F being the Fermi energy of the liquid phase, and N the number of electrons. It is apparent from Eq. (3) that the nonideal part of the response function of the liquid plays the role of an effective interaction which might favor the modulation of the electron density despite the increase of ideal kinetic energy. To measure the departure of such an effective interaction from the bare interparticle potential it is customary to define—in reciprocal space—a local field factor[13] $G(\mathbf{q})$ by

$$v(\mathbf{q})[1 - G(\mathbf{q})] = -\chi^{-1}(\mathbf{q}) + \chi_0^{-1}(\mathbf{q}) , \qquad (4)$$

with $v(\mathbf{q}) = 4\pi e^2/q^2$. Imposing the extremum condition on the approximate energy functional of Eq. (3) is equivalent to solving a problem of independent electrons in an effective self-consistent potential[3] whose Fourier components are explicitly given by

$$v_{\text{eff}}(\mathbf{q}) = \delta n(\mathbf{q}) v(\mathbf{q}) [1 - G(\mathbf{q})] . \qquad (5)$$

However, periodicity implies that

$$n_s(\mathbf{r}) = n_0 + \sum_{\mathbf{G} \neq 0} n_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}} , \qquad (6)$$

where the G's are reciprocal-lattice vectors (RLV) of the chosen structure. It follows that the effective potential is also periodic. Hence, one has to self-consistently solve Kohn-Sham equations[3]

$$[-(\hbar^2/2m)\nabla^2 + v_{\text{eff}}(\mathbf{r})]\psi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) \qquad (7)$$

for the Bloch orbitals $\psi_{\mathbf{k}}$, the density being given by $n_s(\mathbf{r}) = \sum_{\mathbf{k},\text{occ}} |\psi_{\mathbf{k}}(\mathbf{r})|^2$.

It is instructive to rewrite the energy difference of Eq. (3) by making use of Eqs. (4)-(6) and of charge neutrality. One immediately gets

$$\Delta E = T_0[n_s] - \tfrac{3}{5} N \epsilon_F + \tfrac{1}{2} V \sum_{\mathbf{G} \neq 0} v(\mathbf{G})[1 - G(\mathbf{G})] \, |n_{\mathbf{G}}|^2 , \qquad (8)$$

with V the total volume. As we have already noted, the ideal kinetic-energy difference is always positive and therefore in the second-order theory the crystalline phase may become stable if and only if $G(\mathbf{G}) > 1$ for some G and the contribution from such vectors is dominant in the potential-energy sum on the right-hand side of Eq. (8). The coexistence point, characterized by the vanishing of ΔE, locates the critical r_s for crystallization. At larger r_s one should find $\Delta E < 0$, since the crystal should be stable, while $\Delta E > 0$ at smaller r_s, the liquid being stable.

The calculation that we have been outlining requires the knowledge of the static response function of the homogeneous electron liquid, whereas to date QMC results are available only for the static structure. To make use of this information, in the absence of an exact expression giving $\chi(\mathbf{q})$ in terms of $S(\mathbf{q})$, we resort to the following approximate decoupling scheme,[13]

$$G(\mathbf{q}) = -\frac{1}{n_l} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\mathbf{k}\cdot\mathbf{q}}{k^2} [S(\mathbf{q}-\mathbf{k}) - 1] . \qquad (9)$$

We note that combined with the fluctuation-dissipation theorem the above relation would yield the so-called Singwi-Tosi-Land-Sjolander theory.[13,18] Though being one of the simplest of the many approximate theories proposed to study the electron liquid, this method apparently provides more accurate correlation energies than other approximations.[13] The static local field factor that one obtains for spin-polarized electrons by making use of Eq. (9) and of the available QMC data for the static structure is shown in Fig. 1. It is apparent that, with increasing r_s, $G(\mathbf{q})$ develops a peak just before $2q_F$—exceeding 1 in that region of wave vectors. Here, $q_F \equiv (6\pi^2 n_0)^{1/3}$ is the Fermi wave vector for spin-polarized electrons. Also, for a given value of the reduced wave vector q/q_F the residual dependence of $G(\mathbf{q})$ on r_s is reasonably smooth, which allows for extrapolation[19] at all relevant values of r_s.

The calculation of the energy difference ΔE requires, for a given r_s, the solution of Kohn-Sham equations for the Bloch orbitals $\psi_{\mathbf{k}}$ of a single fully occupied energy band since there is one electron per unitary cell and we are interested in the spin-polarized state. We have performed state-of-the-art, fully converged band-structure calculations based on the plane-wave expansion of Bloch orbitals at each of the special points chosen to perform

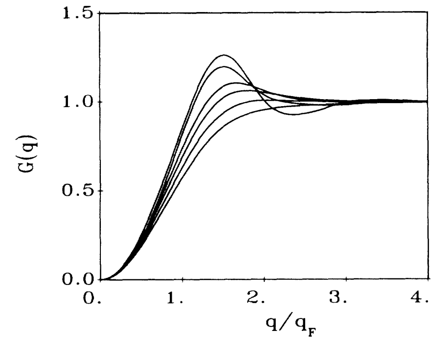

FIG. 1. The local field factor $G(q)$ for the spin-polarized electron fluid at increasing values of the coupling strength parameter r_s. In order of increasing peak height the curves refer to $r_s = 2,5,10,20,50,100$.

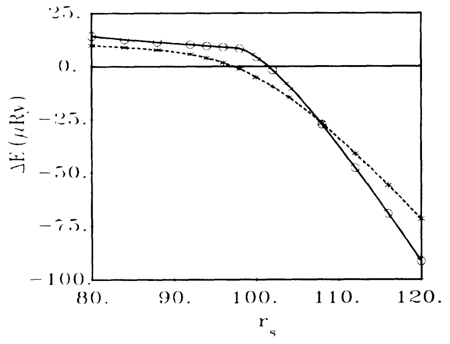

FIG. 2. The energy of the bcc (circles) and fcc (stars) electron crystals relative to that of the polarized electron liquid in microrydbergs (μRy), around freezing. The lines are only a guide to the eye.

sums over the Brillouin zone. We have investigated the stability with respect to the spin-polarized homogeneous liquid of both bcc and fcc electron crystals. We find that the bcc crystal becomes stable at $r_s = 102$, in excellent agreement with the QMC value $r_s = 100 \pm 20$. We also find that around freezing there is a competition between the bcc and the fcc structure, as can be seen in Fig. 2. In particular, the fcc crystal becomes stable first at $r_s = 97$ and remains the stable phase up to $r_s = 108$, where the bcc lattice finally becomes lower in energy.

Thus, our results are in agreement with the findings of QMC simulations,[17] which were concerned only with the bcc structure. On the other hand, they are not inconsistent with calculations based on the harmonic approximation, which establish[20] that at $T = 0$ the bcc electron lattice is always stable with respect to the fcc one. Clearly, such a conclusion is only valid at couplings where the harmonic approximation applies, i.e., for values of r_s somewhat larger than the critical value. In fact, we find that for $r_s > 108$ the bcc is the stable phase. We should also mention that in our investigation we have encountered none of the difficulties found in studying the freezing of classical jellium.[10] In fact, in testing the convergence of our calculations, we have included in the sums of Eqs. (6) and (8) all the stars of RLV below a given cutoff—to include up to 74 stars. We believe that the differences between classical and quantum jellium arise in part from the presence of much less structure in the local field function $G(\mathbf{q})$, as compared with its classical counterpart.

According to QMC[17] in the crystalline phase near freezing the quantum particles are well localized around the lattice sites, with a Lindemann ratio γ (rms deviation about a lattice site divided by the nearest-neighbor distance) of 0.30 ± 0.02. In the present calculations we estimate a slightly larger Lindemann ratio at freezing, namely, we find for the bcc crystal $\gamma = 0.34$, with the electrons, however, still well localized.

An analysis of our calculated crystal densities reveals that for a given r_s the Fourier components $n_{\mathbf{G}}$ are well reproduced by a simple Gaussian form, $n_{\mathbf{G}} = \exp(-A|\mathbf{G}|^2)$. Considering the good localization of the electrons at freezing, this would suggest that instead of solving the Kohn-Sham equations for the $\psi_{\mathbf{k}}$'s one might try an *Ansatz* in which Bloch sums are constructed from a single Gaussian orbital ϕ per site, $\phi(r) = (2C/\pi)^{3/4}\exp(-Cr^2)$, with C a variational parameter. This simpler approach, which introduces an additional approximation, yields results that are not much different from those presented above. In particular, one finds a critical r_s of 107, $\gamma = 0.29$, and substantial equivalence of the bcc and fcc structures at freezing. In fact, due to the variational character of these calculations, we believe that the Gaussian *Ansatz* may be valuable to obtain in a simple manner reasonable estimates of freezing properties.

For the purpose of comparison we have also performed LDA band-structure calculations for the electron crystal and compared the resulting total energy with that of the liquid, using a very accurate fit[21] to the QMC correlation energy of the electron liquid. Not surprisingly we find that LDA fails substantially here, in that it places the transition from the polarized liquid to the bcc crystal at an r_s as low as 22.

In the foregoing we have presented a density-functional theory of freezing for quantum systems, based on the structural properties of the liquid phase, in which the quantum nature of particles is fully taken into account. We should mention that very recently an outline appeared of an alternative approach to the freezing of bosonic liquids.[22] Such an approach exploits the path-integral formalism—rather than band-structure calculations—to evaluate the relevant free-energy difference between solid and liquid. Both approaches are based on a second-order approximation to the nonideal free-energy functional. Here we have been concerned, for the purpose of illustration, with a system of many fermions. However, our scheme is immediately applicable to bosons as well. The statistics, in fact, enters the formulas above only through the specification of the occupation numbers of the single-particle Bloch orbitals of Eq. (7). The finite-temperature situation is not much more complicated than the zero-temperature case, if reliable response functions are available. The extremum condition for the grand potential Ω yields equations[3] that read essentially identical to Eqs. (4)-(7) above, provided that the density is constructed using finite-temperature occupation numbers, which must be used also to construct ideal kinetic energies and ideal entropies. From these one readily calculates the difference of grand potential between the two phases, $\Delta\Omega$, which is zero on the freezing (melting) curve. Applications of the present scheme to (i) bosons and (ii) suitable extensions of the scheme to include[23] terms beyond the quadratic ones in the expansion of Eq. (2) will be investigated elsewhere.

We are happy to acknowledge useful discussions, at various stages of the present work, with J. L. Barrat, M. Rovere, and M. P. Tosi. We also thank D. M. Ceperley for supplying his tabulations of the static structure of the electron liquid, and S. Baroni for making available to us an energy-band computer code. This work was supported in part by the Ministero della Pubblica Istruzione.

---

[1] P. Honenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[2] N. David Mermin, Phys. Rev. **137**, A1441 (1964).

[3] W. Kohn and L. J. Sham, Phys. Rev. **140**, 1133 (1965); see also, W. Kohn and P. Vashishta, in *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundquist and N. H. March (Plenum, New York, 1983), p. 79.

[4] We stress that in the second-order theory it is essential not to expand F_0. One would otherwise obtain an instability theory.

[5] T. V. Ramakrishnan and M. Yussouf, Phys. Rev. B **19**, 2775 (1979).

[6] A. D. J. Haymet and D. W. Oxtoby, J. Chem. Phys. **74**, 2559 (1981).

[7] A. D. J. Haymet, J. Chem Phys. **78**, 4641 (1983).

[8] J. L. Barrat, J. Phys. C **20**, 1031 (1987).

[9] B. B. Laird, J. D. McCoy, and A. D. J. Haymet, J. Chem. Phys. **87**, 5449 (1987).

[10] A. D. J. Haymet, Phys. Rev. Lett. **52**, 1013 (1984); M. Rovere and M. P. Tosi, J. Phys. C **18**, 3445 (1985); J. L. Barrat, Europhys. Lett. **3**, 523 (1987); J. L. Barrat, G. Pastore, and J. P. Hansen, Mol. Phys. **63**, 747 (1988); H. Iyetomi and S. Ichimaru, Phys. Rev. B **38**, 6761 (1988).

[11] J. L. Barrat, M. Baus, and J. P. Hansen, Phys. Rev. Lett. **56**, 1063 (1987); R. McRae and A. D. J. Haymet, J. Chem. Phys. **88**, 1114 (1988).

[12] K. Ding, D. Chandler, S. J. Smithline, and A. D. J. Haymet, Phys. Rev. Lett. **59**, 1698 (1987).

[13] See, for instance, K. S. Singwi and M. P. Tosi, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1981), Vol. 36.

[14] E. P. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).

[15] C. Care and N. H. March, Adv. Phys. **24**, 101 (1975).

[16] The parameter r_s gives a measure of the ratio of average potential to average kinetic energy.

[17] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 567 (1980); see also, D. Ceperley, Phys. Rev. B **18**, 3126 (1978).

[18] K. S. Singwi, M. P. Tosi, R. H. Land, and A. Sjölander, Phys. Rev. **176**, 589 (1968).

[19] To extrapolate $G(q)$ at values of r_s different from those reported in Fig. 1 we have used (see Refs. 2 and 3) rational approximants.

[20] L. L. Foldy, Phys. Rev. B **3**, 3472 (1971).

[21] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[22] J. D. McCoy, S. W. Rick, and A. D. J. Haymet, J. Chem. Phys. **90**, 4622 (1989).

[23] W. Curtin and W. Ashcroft, Phys. Rev. A **32**, 2909 (1985); Phys. Rev. Lett. **59**, 2385 (1987); M. Baus and J. L. Colot, Mol. Phys. **55**, 653 (1985); F. Igloi and J. Hafner, J. Phys. C **19**, 5799 (1986).