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Density Functional Theory for Quantum Freezing: The Wigner Crystallization in A2d Electron System

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Abstract – The density functional theory (DFT) is based on an exact correspondence between equilibrium one-particle densities and external potentials [10]. If we denote by n(r) the one-particle density of the system, the system can be characterized by an appropriate thermodynamic potential which attains its minimum [11] value for the correct (equilibrium) density n0(r). For the study of crystallization, the relevant thermodynamic potentials are the grand potential Ω and the intrinsic Helmholtz free energy F, the latter being a unique functional of the one–particle density.

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If μ is the chemical potential of the system at some temperature T and v(**r**) is an arbitrary external potential, the quantity:

$$\widetilde{\Omega}[n,u] = F[n] - \int d\mathbf{r} n(\mathbf{r}) u(\mathbf{r}),$$

where u(**r**)= μ- v(**r**), is a minimum for given u(**r**) at the equilibrium density n_0(**r**). The quantity

$$\Omega(u) = \widetilde{\Omega}[n_0, u],$$

is then the grand potential of the system. The equilibrium condition is given by

$$\frac{\delta F[n]}{\delta n(\mathbf{r})}_{n_{o(\mathbf{r})}} = \mathrm{u}(\mathbf{r}).$$

For vanishing external potential and fixed particle number N, the intrinsic free energy F[n] is a minimum at the equilibrium density. Quite generally, F[n] is separated into contribution from the non-interacting system under a suitable external potential that makes n(**r**) the equilibrium density. i.e.,

$$F[n] = F_{id}[n] + F_{ex}[n],$$

where F_{id} [n] is the contribution of the non-interacting system and $F_{ex}[n]$ represents the excess contributions to $F[n]$. To study the DFT of quantum freezing, we follow the Hohenberg-Kohn-Sham formalism [10-12] as we are interested in T=0K freezing. In this case, F[n] is simply the intrinsic ground–state energy E[n]. The ideal part $F_{id}[n]$ reduces to the kinetic energy of non-interacting particles $T_O[n]$ and $F_{ex}[n]$ is the excess energy $E_{ex}[n]$.

For practical implementation of the Hohenberg-Kohn-Sham formalism, an essential ingredient is the linear–response function χ(**r**, n) of the fluid, or its Fourier transform $\tilde{x}(q;n)$ where q is the wave vector magnitude and n is the average density. In particular, the quantum direct correlation function, i.e., the difference between the inverse linear-response functions of the interacting and non-interacting systems given as $\tilde{K}(q,n) = \tilde{x}^{-1}(q;n) - \tilde{x}_o^{-1}(q;n)$, is a quantity of main interest. Therefore, the DFT predictions are expected to be sensitive [14] to the choice made for $\tilde{x}(q;n)$.

Quantum Density Functional Theory of Freezing

Writing

$$E[n] = T_O[n] + E_{ex}[n]$$

and using equations (3.1) and (3.2), we see that a necessary condition for equilibrium is

$$\left[\frac{\delta T_0[n]}{\delta n(\mathbf{r})}+\frac{\delta E_{ex}[n]}{\delta n(\mathbf{r})}\right]_{n_0(\mathbf{r})}=\mu-v(\mathbf{r}).$$

This is formally equivalent to the condition of equilibrium for non-interacting particles under the influence of an effective external potential

$$v_{eff}(\mathbf{r})=\frac{\delta E_{ex}[n]}{\delta n(\mathbf{r})}+v(\mathbf{r}).$$

Evidently, the effective potential is itself a functional of the one-particle density, through the dependence of $E_{ex}[n]$ on $n(\mathbf{r})$. Therefore, we are confronted with a self-consistent calculation which in practice is implemented as follows:

We make an initial guess for density profile, which yields an initial form for the effective potential. Then the one-particle Schrödinger equations (the so-called Kohn–Sham equations)

$$\left[-\frac{\hbar^2}{2m}\nabla^2+v_{eff}(\mathbf{r})\right]\psi_i(\mathbf{r})=\varepsilon_i\psi(\mathbf{r}),$$

are solved, yielding the eigenfunctions $\psi_i(\mathbf{r})$ and the associated energy ε_i. One then construct from the knowledge of $\psi_i(\mathbf{r})$ a new particle density as

$$n(\mathbf{r})=\sum_i n_i|\psi_i(\mathbf{r})|^2$$

where n_i are the occupation numbers suitable for the given statistics (Bose or Fermi). The new density serves for the construction of the new effective potential, and the cycle is continued until a self-consistent solution has been found. Once the self–consistent orbitals and the corresponding eigenvalues ε_i and density $n_0(\mathbf{r})$ are known, the ideal kinetic energy T_0 is given by

$$T_O=\sum_i n_i\int dr\,\psi_i^*(\mathbf{r})(-\frac{\hbar^2}{2m}\nabla^2)\psi_i(\mathbf{r})$$

$$\sum_i n_i\varepsilon_i-\int dr\,n_o(\mathbf{r})v_{eff}(\mathbf{r}).$$

Up to this point, the formalism given above is exact, provided the *v* representability holds [15]. However, in real practical situations the excess energy functional $E_{ex}[n]$ is not known exactly and one has to resort to approximations. One usual and physically motivated approximation is the so-called second order theory (SOT) [8], developed originally for the freezing of classical liquids by Ramakrishnan and Yussouf [16].

Second Order Theory of Quantum Freezing

In this approximation, we expand functionally the unknown excess energy functional $E_{ex}[n]$ about a uniform fluid of density n_l, keeping terms up to second-order only,

$$E_{ex}[n]=E_{ex}(n_l)+\int dr\left.\frac{\delta E_{ex}[n]}{\delta n(\mathbf{r})}\right|_{n_l}\delta n(\mathbf{r})+\frac{1}{2}\iint dr dr'\left.\frac{\delta^2 E_{ex}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n_l}\delta n(\mathbf{r})\delta n(\mathbf{r}'),$$

with $\delta n(\mathbf{r})=n(\mathbf{r})-n_l$ and $E_{ex}(n_l)$ the excess intrinsic energy of the uniform liquid, a function of n_l. Due to the translational and rotational invariance of the liquid, the first functional derivative on the right–hand side of equation (3.6) is just a position-independent constant, equal to excess chemical potential of the homogeneous liquid. The second functional derivative is a function of $|\mathbf{r}-\mathbf{r}'|$ only; of course both depend on n_l. We define

$$\left.\frac{\delta^2 E_{ex}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right|_{n_l}\equiv -K(|\mathbf{r}-\mathbf{r}'|;n_l).$$

The function $K(\mathbf{r};n)$ is the excess part of the linear static inverse response function of the homogeneous liquid, and can also be expressed as [8]

$$K(\mathbf{r};n)=\chi^{-1}(\mathbf{r};n)-\chi_o^{-1}(\mathbf{r};n),$$

where $\chi^{-1}(\mathbf{r};n)$ and $\chi_0^{-1}(\mathbf{r};n)$ are the functional inverses of the density-density static linear-response functions of the interacting and non-interacting liquid, respectively. The function $K(\mathbf{r};n_l)$ is formally the quantum analog of the classical Ornstein-Zernicke direct correlation function.

Now we set v=0 (i.e., the external potential) in the quadratic approximation for the excess part of the energy functional. The effective potential which enters in the Kohn-

Sham calculation is periodic with Fourier components given by

$$v_{eff}(\mathbf{Q})=\delta n_{\mathbf{Q}}[-\tilde{\chi}^{-1}(\mathbf{Q};n_l)+\tilde{\chi}_o^{-1}(\mathbf{Q};n_l)],$$

where $\mathbf{Q}$ is a reciprocal–lattice vector (RLV) of the given lattice and $\delta n_{\mathbf{Q}}$ is the Fourier component of the periodic function $\delta n(\mathbf{r})\equiv n(\mathbf{r})-n_l$, and $\tilde{\chi}^{-1}(q;n_l)$ is the Fourier transform of the function $\chi^{-1}(\mathbf{r};n_l)$. For the Bose systems at T=0K, the kinetic energy of non-interacting particles vanishes in the uniform limit. Thus, the difference between the grand potential of the solid and the liquid is

$$\Delta\Omega[n]=T_O[n]-\frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'K(|\mathbf{r}-\mathbf{r}'|;n_l)\delta n(\mathbf{r})\delta n(\mathbf{r}')$$

$$= T_O[n] - \frac{V}{2}\tilde{K}(0;n_l)(n_s - n_l)^2 - \frac{V}{2}\sum_{Q\neq 0}|n_Q|^2\tilde{K}(Q;n_l).$$

In equation (3.10), V is the volume of the system, n_s is the average density of the solid, $\tilde{K}(q;n)$ denotes the Fourier transform of $K(\mathbf{r};n)$ at wave vector q , and n_Q is the Fourier component of the periodic density at RLV Q. We change μ and minimize ΔΩ[n] with respect to n(**r**), and freezing occurs when min{ΔΩ[n]} vanishes. For min{ΔΩ[n] }>0(<0) the liquid (solid) is stable.

For a system composed of particles carrying a charge *e* and interacting via the coulomb potential $v_c(r)=e^2/r$, the presence of a uniform, rigid, neutralizing background of opposite charge guarantees the stability of the system. The presence of background imposes the constraint that the freezing transition now takes place at the constant density (isochoric freezing). The relevant thermodynamic potential is now the total energy E[n]; the phase with the lowest E[n] is the thermodynamically stable one. It is customary for such systems to separate the excess energy into Hartree contribution and exchange-correlation contribution, i.e.,

$$E_{ex}[n] = \frac{e^2}{2}\iint d\mathbf{r}d\mathbf{r}'\frac{\delta n(\mathbf{r})\delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[n],$$

where $\delta n(\mathbf{r}) = n(\mathbf{r}) - \bar{n}$ and $\bar{n}$ is the average electron density. If we now define

$$\frac{\delta^2 E_{xc}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \equiv -K_{xc}(|\mathbf{r}-\mathbf{r}'|;n_l)$$

then equation (3.7) and (3.11) imply

$$K(|\mathbf{r}-\mathbf{r}'|;n_l) = -v_c(|\mathbf{r}-\mathbf{r}'| + K_{xc}(|\mathbf{r}-\mathbf{r}'|;n_l).$$

In the Fourier space, one writes the Fourier transform $\tilde{K}_{xc}(q;n)$ of $K_{xc}(\mathbf{r};n)$ as $\tilde{K}_{xc}(q;n) = v_c(q)G(q;n)$, where $v_c(q)$ is the Fourier transform of coulomb potential with $v_c(q)=4\pi e^2/q^2$ in three dimensions and $2\pi e^2/q$ in two dimensions, and G(q; n) is the so-called local-field correction factor [9]. Thus, from (3.13), we finally have

$$-\tilde{K}(q;n) = v_c(q)[1-G(q;n)].$$

Due to the long range nature of the coulomb potential, the functional expansion of the energy of inhomogeneous phase can now be performed only about a liquid whose density n_l is equal to the average density $\bar{n} \equiv n_s$ of the solid. Using equations (3.6), (3.7), (3.13) and (3.14), we obtain the difference between the energy of the solid and the liquid phase as

$$\Delta E[n] = T_O[n] - \frac{d}{d+2}N\varepsilon_F + \frac{V}{2}\sum_{Q\neq 0}|n_Q|^2 v_c(\mathbf{Q})[1-G(\mathbf{Q};n_s)].$$

Equation (3.15) above is valid for fermions in *d* dimensions with ε_F being the Fermi energy of non-interacting particles in the liquid phase. For the system of bosons, the second term on the R. H. S is simply zero. It is evident from equation (3.15) that the computation of ΔE[n] requires the knowledge of the local-field correction factor G(Q; n_s) of the uniform liquid at density n_s. It has been found in literature [8] that the transition point depends crucially on the choice of G(Q; n_s). This point is detailed in the following section.

Liquid–state Input, Quantum Direct Correlation Function, and Effective Interactions

The Fourier transform of the direct correlation function is related to the experimentally measured static structure factor S(q) by a simple algebraic relation [17] by virtue of fluctuation-dissipation theorem for classical liquids. Whereas for quantum system, the theorem relates dynamical quantities, and the relation between static quantities is not simple [8]. As a result, various approximations for the static linear response function $\tilde{\chi}(q)$ have been developed. A widely used scheme to relate the local-field factor G (q) with the structure factor S(q) has been introduced by Singwi, Tosi, Land and Sjolander (STLS) [18]. An important feature of the STLS scheme is that in the limit of large –q, the local field factor G(q) approaches the unity and this implies that $-\tilde{K}(q;n_l)$ approaches zero in that limit. In this respect, the STLS scheme for systems of charged particles has the same features as the Feynman approximation. However, it has been shown exactly that in the large q limit, G(q) goes like q^2 in three dimensions [19]; moreover it can easily be shown that it scales like q in two dimensions [20]. For fermions in three dimensions, the large q local–field factor is given by [19, 21]

$$G(q;n_l) = \frac{2(\langle KE\rangle - \langle KE\rangle_o)q^2}{3m\omega_{pl}^2} + \frac{2}{3}[1-g(0)] + \frac{16(\langle (KE)^2\rangle - \langle (KE)^2\rangle_o)}{5\hbar^2\omega_{pl}^2} - \frac{16\langle KE\rangle^2 - \langle KE\rangle_o^2}{9\hbar^2\omega_{pl}^2} + O(q^{-2}). \quad (3.16)$$

where $\langle\ldots\ldots\rangle_o$ denotes a non-interacting average, and the coefficient of q^2 term- the difference in the kinetic energy per particle between the interacting and non-interacting system is a positive quantity. Using equations (3.14) and (3.16), we finally obtain $-n_l\tilde{K}(\infty;n_l) = -\frac{2}{3}(\langle KE\rangle - \langle KE\rangle_o)$.

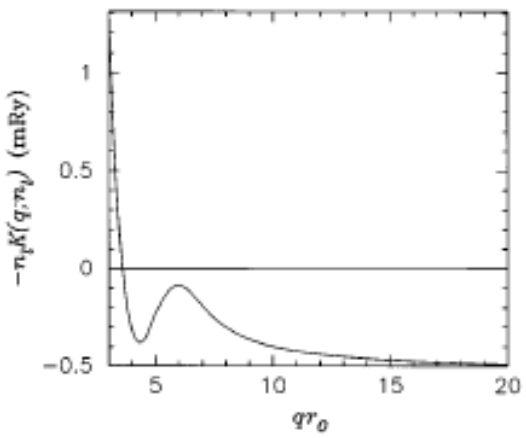

Fig. 1: The function-$-n_l\tilde{K}(q;n_l)$ (in mRy) of spin - polarized charged fermions, as obtained from simulations, at $r_s = 100$.

In figure (1), we show the QMC direct correlation function [22] for a fully polarized 3D electron system at r_s=100. It is clearly seen that at large values of q the function $-\tilde{K}(q;n_l)$ tends to a negative constant. In the system of point charged particles, by virtue of the virial theorem, this constant may be expressed most simply as

$$-n_l\tilde{K}(\infty;n_l)=\frac{2}{3}\frac{d(r_sE)}{dr_s}, \qquad (3.18)$$

with $E=\varepsilon_C(r_s)$ the correlation energy per particle.

In two dimensions, the situation is quite similar. Using the asymptotic behavior of the static linear-response function, it has been shown that the local-field factor scales linearly with q, as $q\to\infty$, namely,

$$G(q;n_l)=\frac{(\langle KE\rangle-\langle KE\rangle_O)}{2\pi e^2 n_l}q+1-g(0)+o(q^{-1}), \qquad (3.19)$$

where g(0) is the static pair-correlation function at contact. From equations (3.14) and (3.19), we obtain

$$-n_l\tilde{K}(\infty;n_l)=-(\langle KE\rangle-\langle KE\rangle_O). \qquad (3.20)$$

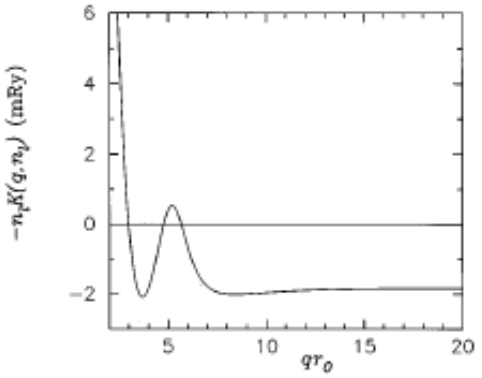

Fig. 2: The function$-n_l\tilde{K}(q;n_l)$ (in mRy) of spin-polarized charged fermions in 2D, as obtained from simulations at $r_s = 40$.

In figure (2), we show the direct correlation function of fully polarized electrons in two dimensions, near freezing, i.e., at r_s=40, as obtained from QMC simulations [22]. Again the saturation of $\tilde{K}(q,n_l)$ to a constant- which may be conveniently expressed as

$$-n_l\tilde{K}(\infty;n_l)=-(\langle KE\rangle-\langle KE\rangle_O)=\frac{d(r_s\varepsilon_c)}{dr_s}, \qquad (3.21)$$

with $\varepsilon_c(r_s)$ as the correlation energy per particle. We note that the large-q behavior of $-n_l\tilde{K}(q.n_l)$ for all the systems considered above is given by

$$-n_l\tilde{K}(q,n_l)=-\frac{2}{d}(\langle KE\rangle-\langle KE\rangle_O)+O(q^{-d+1})+o(q^{-2}), \qquad (3.22)$$

and evidently for the non-interacting Bose systems $\langle KE\rangle_O=0$. In fact one may easily show that equation (3.22) above is valid for any quantum liquid interacting with pair potentials, both in three and two dimensions, provided the second term on the R.H.S is only retained for columbic systems ($1/r$ interaction) in two dimensions.

Application of SOT in Two Dimensions

In two dimensions, the energy difference (between the solid and liquid phases) functional $\Delta E[n]$ is given as [23]

$$\Delta E[n]=T_o[n]-\frac{1}{2}N\varepsilon_F+\frac{V}{2}\sum_{Q\neq 0}|n_Q|^2 v_c(Q)[1-G(Q;n_s)]$$

where **Q** is a reciprocal-lattice vector of the given lattice, n_Q is the Fourier transform of n(**r**), $v_c(Q)=\frac{2\pi e^2}{Q}$, is the 2D Fourier transform of the coulomb potential, and $G(Q;n_s)$ is the local-field correction factor. At equilibrium density profile $n_o(\mathbf{r})$, which is to be obtained from the self-consistent solution of the Kohn-Sham equations, $\Delta E[n]$ gives the desired

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energy differences between the solid and the liquid phases.

In actual practice, the Kohn-Sham equations are solved in the Fourier space. Exploiting the periodicity of the effective potential $V_{eff}(\mathbf{r})$, in the Fourier space the Kohn-Sham equation transform as:

$$\left(\frac{\hbar^2(k-Q)^2}{2m} - \varepsilon\right) C_{k-Q} + \sum_{Q'} v_{eff}(Q'-Q)\, C'_{k-Q} = 0,$$

where

$$v_{eff}(Q) = \delta n_Q v_c(Q)(1 - G(Q)).$$

The Kohn-Sham orbitals $\psi_k(\mathbf{r})$ and the one-particle density are now given as

$$\psi_k(r) = \sum_Q C_{k-Q}\, e^{i(k-Q).r}$$

$$n(r) = \sum_{k(occ.),i} |\psi_k(r)|^2,$$

where *i* is the band index and the summation runs over the occupied orbitals. Apparently, the solution of Kohn-Sham equations amounts to a self-consistent band structure calculations. The numerical computation proceeds as follows: an initial guess is made for the density n_Q, which in turn yields $v_{eff}(\mathbf{Q})$. The local field-correction factor G(Q) is taken from the accurate QMC simulations by Moroni et al [22]. Equation (3.26) is then solved for the Kohn-Sham orbitals and their corresponding eigenvalues by the matrix diagonalization technique. The KS orbitals thus obtained are used in equation (3.27) to construct a new density and hence, a new effective potential. The cycle is repeated till a self-consistent n_Q is obtained, which is then used in equation (3.23) to obtain ΔE[n].

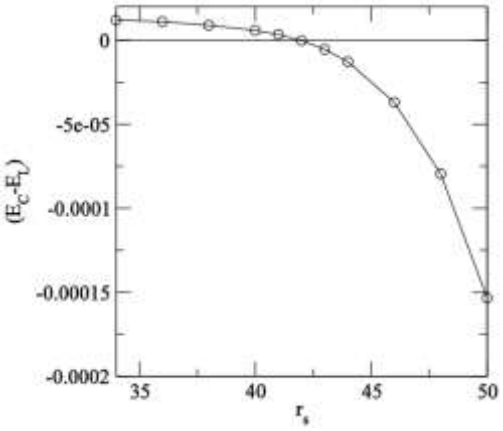

Fig. 3: Plot of difference between triangular crystal energy and polarized liquid energy as a function of r_s. The solid squares are the calculated points and the line is just a guide for the eye.

In our calculation, we have used a plane wave basis set and we have systematically checked the convergence with respect to the plane-wave cutoff and the number of k-points in the Brillouin zone. The ground-state energy difference between triangular-solid and polarized liquid is plotted in figure (3) as a function of r_s parameter. As it can be seen, at $r_s = 40,$ (where the QMC G(q) is available [22]) the solid is still unstable, though its energy is only 6 micro Rydbergs higher than that of polarized liquid. On the ground that the explicit dependence of G(q; r_s) on r_s should be very weak, we have neglected it altogether to perform the calculations of ΔE[n] at other (higher) values of r_s. In this way, we find that there occurs a phase transition from the liquid phase to the triangular electron crystal at r_s=42. Thereafter, the crystal state remains the stable phase. The critical density for the onset of Wigner crystallization agrees nicely (within error bars) with the QMC prediction of Tanatar and Ceperley [7] $r_s = 37 \pm 5$ and is within two error bars from a more recent QMC prediction [24]. We may thus conclude that the SOT is capable of predicting freezing in two dimensions with a very good accuracy.

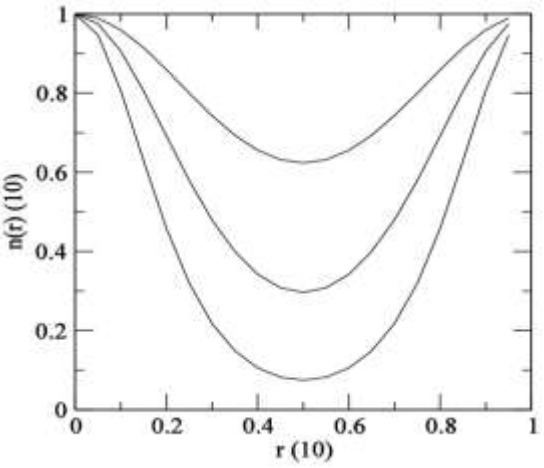

Fig. 4: Self-consistent density n(r)/n(0) along the (10) direction for r_s=38, 42 and 46. Curves from bottom to top are in the order of decreasing r_s. Here, r has been scaled with the lattice parameter.

In figures (4) and (5) we have plotted the self-consistent ground-state density n(**r**) (divided by n(0)) along the (10) and (11) directions by taking r_s as 36, 42 and 46. It is apparent that the extent of density modulation increases with the increasing r_s. Particularly, the density becomes nearly zero in the region between lattice sites for r_s>46. One may also note the overlap between the density profiles of the neighboring sites in the (11) direction of the triangular crystal. Thus, we see from the behavior of n(**r**) that the extent of localization increases with

r_s increasing past the critical r_s for Wigner crystallization.

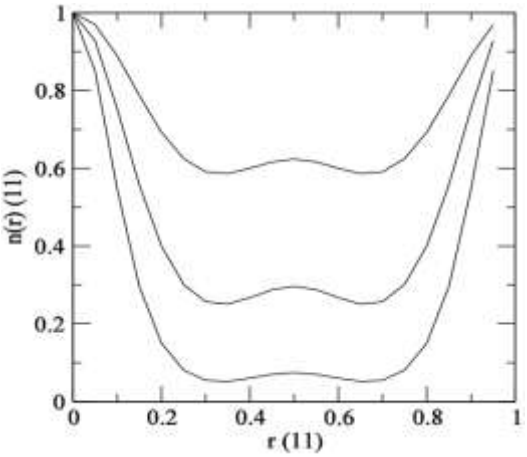

Fig 5: Self-consistent density n(r)/n(0) along the (11) direction for r_s=38, 42 and 46. Curves from bottom to top are in the order of decreasing r_s. Here, r has been scaled with the lattice parameter.

CONCLUSIONS

In conclusion, we find that the Second Order Theory based implementation of the density functional theory provides an excellent description of the liquid-Wigner crystal phase transition. The predicted critical density of crystallization is found to be in very good agreement with the quantum Monte Carlo simulation results [7] and the recent transport experiments [6]. However, we must mention that the results are very much sensitive to the quality of the liquid state input. In two dimensions, we have used for the liquid-state input the accurate quantum Monte Carlo simulation data.

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