

Theory of freezing for quantum liquids

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 SA139

(<http://iopscience.iop.org/0953-8984/2/S/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:16

Please note that [terms and conditions apply](#).

Theory of freezing for quantum liquids

S Moroni and G Senatore

Dipartimento di Fisica 'A Volta', Università di Pavia, Pavia, Italy

Received 16 July 1990

Abstract. The density functional theory of freezing has been recently extended to treat quantum liquids. Here, we consider three approximations of the weighted-density type for the freezing of jellium at $T = 0$. The agreement with a simulation of the predicted freezing parameters varies from satisfactory to very good, depending on the approximation.

1. Introduction

The modern theory of freezing [1] relies crucially on the use of density functional theory (DFT). Using information on the structural and thermodynamic properties of the uniform liquid, the method leads to predictions for various properties of the coexisting periodic solid. One of the advantages of DFT is that one can treat both classical and quantum systems on the same footing, in terms of the Helmholtz free energy functional $F[n]$, $F[n] = F_0[n] + F_{\text{ex}}[n]$. Approximate theories readily arise from the approximation of the excess free energy $F_{\text{ex}}[n]$, whereas the classical or quantum nature of the problem—and therefore the statistics—appears explicitly [2, 3] only in the construction of the non-interacting particle free energy $F_0[n]$.

The recent development of a quantum density functional theory of freezing has followed two complementary routes. In one case [4], the mapping of quantum particles onto classical polymeric chains is exploited, employing the path-integral formalism. This approach, which has been used to study ^4He , by its very nature seems to be preferable for systems at not too low temperature. Also, it does not appear suitable to the treatment of Fermi systems. In the other case [5, 6], the Hohenberg-Kohn-Sham (HKS) formalism is invoked, to map the problem onto a band structure calculation. This approach can naturally cope with both Bose and Fermi systems. Contrary to the path-integral formalism, however, it is best suited for zero or small temperatures. Zero-temperature applications have been presented so far, for jellium [5] and Bose hard spheres [6].

An additional reason for which DFT is crucial to the theory of freezing is that it provides a systematic way to approximate $F_{\text{ex}}[n]$, using liquid information. Two routes have been followed thus far. In one of them [7], the excess free energy of the modulated phase is functionally expanded around the homogeneous liquid, usually up to second order in the density difference. In the other [8–10], one tries a mapping of the excess free energy density of the modulated system onto the excess free energy density of a homogeneous liquid with a suitably chosen weighted density.

In this paper, we consider the freezing of jellium at $T = 0$, using three different approximations of the weighted-density type within the HKS formalism. We briefly review the approximations, give the results of the various calculations and discuss them in relation to previous calculations. A more extended discussion will be given elsewhere [3].

2. Weighted-density approximations for jellium

We consider here three approximate forms of F_{ex} for jellium—a model system of electrons in a uniform neutralizing background with density n_0 . These approximations are suitable modifications of known schemes [8–10] to deal with a charged system.

The weighted-density approximation [9] (WDA) and the modified WDA [8] (MWDA) read respectively

$$F_{\text{ex}}[n] = \int d\mathbf{r} n(\mathbf{r}) \epsilon_{\text{xc}}(\bar{n}(\mathbf{r})) \quad (1)$$

and

$$F_{\text{ex}}[n] = N \epsilon_{\text{xc}}(\hat{n}) \quad (2)$$

with

$$\bar{n}(\mathbf{r}) = n_s + \int d\mathbf{r}' n_{\text{Q}}(\mathbf{r}') w(\mathbf{r} - \mathbf{r}', \bar{n}(\mathbf{r})) \quad (3)$$

and

$$\hat{n} = n_s + \frac{1}{N} \int \int d\mathbf{r} d\mathbf{r}' n_{\text{Q}}(\mathbf{r}) n_{\text{Q}}(\mathbf{r}') \tilde{w}(\mathbf{r} - \mathbf{r}', \hat{n}). \quad (4)$$

Above, $n_{\text{Q}}(\mathbf{r}) = n(\mathbf{r}) - n_0$, n_s is the average value of $n(\mathbf{r})$, which equals n_0 when charge neutrality is imposed ($\int d\mathbf{r} n_{\text{Q}}(\mathbf{r}) = 0$), and $N = \int d\mathbf{r} n(\mathbf{r})$. Also, $\epsilon_{\text{xc}}(n)$ is the exchange and correlation energy per particle in a jellium with uniform density n . The weight functions appearing in (3) and (4) are determined through the homogeneous limit condition

$$\lim_{n(\mathbf{r}) \rightarrow n_0} \left[\frac{\delta^2 F_{\text{ex}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \right] = -[\chi^{-1}(\mathbf{r} - \mathbf{r}', n_0) - \chi_0^{-1}(\mathbf{r} - \mathbf{r}', n_0)] \equiv -K(\mathbf{r} - \mathbf{r}', n_0) \quad (5)$$

with F_{ex} respectively from (1) and (2). Here, χ and χ_0 are the static linear response functions of the interacting and non-interacting uniform liquid. At variance with the case of uncharged particles, the weight functions above do not satisfy a normalization condition. In fact they contain a long-range Coulomb tail.

The generalized effective liquid approximation [10] (GELA), on the other hand, is obtained from

$$F_{\text{ex}} = N \epsilon_{\text{xc}}(n_0) - \int \int d\mathbf{r} d\mathbf{r}' n_{\text{Q}}(\mathbf{r}') \int_0^1 d\lambda (1 - \lambda) K(\mathbf{r} - \mathbf{r}', \hat{n}[n_0 + \lambda n_{\text{Q}}]) \quad (6)$$

where the effective density functional $\hat{n}[n]$ is determined by the additional condition of (2), and the kernel $K(\mathbf{r} - \mathbf{r}', n)$ is defined as in (5). In writing (6) explicit use has been made of charge neutrality.

3. Results and discussion

In the HKS formalism, the non-interacting particle free energy is treated exactly [2, 3, 5]. This requires the solution of one-particle Schrödinger equations—the Kohn–Sham (KS) equations—in a self-consistent potential whose explicit form is fixed by the excess free energy functional $F_{\text{ex}}[n]$. We have performed such band structure calculations for jellium at $T = 0$ for the three approximations listed above. We have considered only the coexistence between spin polarized liquid and BCC solid, and we have approximated the kernel $K(r, n)$ using quantum Monte Carlo (QMC) information [11] as previously discussed [5]. Comparison of the calculated total energy with that of the liquid, using an accurate fit [12] to the QMC data for $\epsilon_{\text{xc}}(n)$, locates the freezing transition.

Table 1. Freezing parameters of jellium at $T = 0$. Acronyms are as in the text. r_s^* denotes the Wigner sphere radius in units of Bohr radii; γ is the Lindemann ratio (root-mean-square deviation divided by the nearest-neighbour distance), and \hat{n} is the effective liquid density, whenever applicable.

	WDA	MWDA	GELA	SOT ^a	QMC ^b
r_s^*	71	70	100	102	100±20
γ	0.25	0.23	0.32	0.34	0.30±0.02
\hat{n}/n_0		1.35	1.07		

^a From [5].

^b From [11].

The results of the present calculations are summarized in table 1, together with the results of the second-order theory (SOT) [5] and of QMC. It is clearly seen that, of the various DFT approaches, the GELA appears to provide the best description of freezing in jellium. In fact, it yields freezing parameters which are in excellent agreement with those (virtually exact) estimated by QMC simulations. Though the results of the second-order theory were already very good, the GELA is able to improve the quality of the Lindemann ratio, which now agrees with QMC within the statistical error bar. This improvement is obtained at the cost of the additional effort needed to determine the functional dependence of \hat{n} , along a linear path joining the constant density of the uniform liquid to the modulated density of the periodic solid.

Evidently, the results obtained from the WDA and MWDA are about equivalent and, in particular, both less satisfactory than for the GELA. The freezing r_s is somewhat lower than the lower value given by QMC, considering the error bar. However, there is a considerable improvement upon LDA which yields $r_s^* = 22$. The Lindemann ratio is also underestimated. It should be noted that calculations with the MWDA for a totally different system (Bose hard spheres) give results [6] of slightly better quality than in the present case. However, this is obtained by invoking an *ad hoc* scaling of the kernel $K(r, n)$ to enforce the compressibility sum rule. In comparison with the freezing of classical liquids [1], in the quantum case, the comparatively minor knowledge of the static response functions makes it more difficult to separate the issue of the accuracy of the theory from the issue of the accuracy of the necessary input.

An interesting problem in the density functional theory of freezing is the importance of non-linear response functions in a systematic expansion of the excess free energy of the solid phase around the uniform liquid. Weighted-density theories, in

fact, correspond to an infinite-order resummation of the non-linear response functions, in an approximate fashion. Comparison with the SOT of the WDA and MWDA, on the one hand, and of the GELA, on the other, seems to yield opposite conclusions. However, one should keep in mind the approximate nature of the resummation. It is worth stressing, in this respect, the extremely delicate balance of energy terms in the freezing of jellium. Thus, the present implementation of the GELA—which directly approximates an energy difference—may well be more accurate than that of the WDA and the MWDA, which deal with the full F_{ex} . On the other hand, both the present implementation of the GELA and the classical one [10] contain a somewhat limited set of non-linear response functions. In conclusion, we believe that the issue of the accuracy of these effective liquid approximations deserves further investigations.

Acknowledgments

This work has been supported in part by the Ministero della Pubblica Istruzione and by the Consiglio Nazionale delle Ricerche of Italy.

References

- [1] Baus M 1990 *J. Phys.: Condens. Matter* **2** 2111
- [2] Senatore G and Pastore G 1990 *High Pressure Equation of State: Theory and Applications* CXIII Varenna School (Varenna, 1989) (Amsterdam: North-Holland)
- [3] Moroni S and Senatore G 1990 in preparation
- [4] McCoy J D , Rick S W and Haymet A D J 1989 *J. Chem. Phys.* **90** 4622
- [5] Senatore G and Pastore G 1990 *Phys. Rev. Lett.* **64** 303
- [6] Denton A R , Nielaba P , Runge K J and Ashcroft N W 1990 *Phys. Rev. Lett.* **64** 1529
- [7] Ramakrishnan T V and Yussouff M 1979 *Phys. Rev. B* **19** 2775
Haymet A D J and Oxtoby D W 1981 *J. Chem. Phys.* **74** 2559
- [8] Curtin W and Ashcroft W 1985 *Phys. Rev. A* **32** 2909
- [9] Denton A R and Ashcroft N W 1989 *Phys. Rev. A* **39** 4701
- [10] Lutsko J F and Baus M 1990 *Phys. Rev. Lett.* **64** 761
- [11] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 567
Ceperley D 1978 *Phys. Rev. B* **18** 3126
- [12] Vosko S H, Wilk L and Nusair M 1980 *Can. J. Phys.* **58** 1200