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## LETTER TO THE EDITOR

# Density functional theory of freezing with a self-consistent effective liquid

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**Abstract.** The effective liquid, used in a recent density functional theory of freezing to describe the direct correlations of the solid approximately, is given a self-consistent definition that allows us to make contact with the so-called weighted density approximation used by other authors. The uniform limit is recovered without approximation.

In traditional equilibrium statistical mechanics the thermodynamic properties are usually related directly to the system's Hamiltonian via the partition function. During the past decade, an alternative approach, known as the density functional theory (DFT) (see Evans 1979), has been widely used, for example to study non-uniform equilibrium phases and/or interfaces. In this approach the passage from the Hamiltonian to the thermodynamic properties is taken in two steps. Firstly, the thermodynamic properties are expressed in terms of the direct correlation functions (DCF), viewed as functionals of the non-uniform one-particle density  $\rho(\mathbf{r})$ . Secondly, the DCF are related to the ordinary correlation functions and to the Hamiltonian via some integral equation method. In practice, each step will involve specific approximations. In recent years, various forms of approximate DFT have been formulated that apparently bear little relation one to another (see Baus 1987). It is the purpose of this Letter to indicate the formal relations between some of these theories. For concreteness, we will use freezing terminology where the non-uniform state represents the 'solid' and the uniform state the 'liquid', although any other situation where one tries to describe approximately a non-uniform state in terms of a known uniform one could do as well.

The total (Helmholtz) free energy,  $F$ , of the solid can be written as the sum of three terms,  $F = F_{\text{id}} + F_{\text{ext}} + F_{\text{ex}}$ —the ideal gas term,  $F_{\text{id}}$ , the contribution of the external field (which fixes the boundary conditions for  $\rho(\mathbf{r})$ ),  $F_{\text{ext}}$ , and the excess term,  $F_{\text{ex}}$ , originating from the particle interactions. In the DFT these quantities are viewed as functionals of  $\rho(\mathbf{r})$ , e.g.  $F = F[\rho]$ . Whereas  $F_{\text{id}}[\rho]$  and  $F_{\text{ext}}[\rho]$  are known explicitly,  $-\beta F_{\text{ex}}[\rho] \equiv c_0[\rho]$  (with  $\beta = 1/k_{\text{B}}T$  the inverse temperature) is known only to be a generating functional of the various DCF,  $c_n[\rho]$ , which can be obtained by successive functional differentiation,  $c_{n+1} = \delta c_n / \delta \rho(\mathbf{r})$  (see Evans 1979).

Integrating the general result

$$\frac{\partial}{\partial \lambda} c_n(\mathbf{r}_1, \dots, \mathbf{r}_n; [\lambda \rho]) = \int d\mathbf{r}_{n+1} c_{n+1}(\mathbf{r}_1, \dots, \mathbf{r}_{n+1}; [\lambda \rho]) \rho(\mathbf{r}_{n+1}) \quad (1)$$

with respect to the 'charging' parameter  $\lambda$  and observing that  $c_n[0] \equiv 0$ , one obtains the exact relations

$$\beta F_{\text{ex}}[\rho] = - \int d\mathbf{r} \int_0^1 d\lambda c_1(\mathbf{r}; [\lambda \rho]) \rho(\mathbf{r}) \quad (2a)$$

$$\beta F_{\text{ex}}[\rho] = - \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' c_2(\mathbf{r}, \mathbf{r}'; [\lambda' \rho]) \rho(\mathbf{r}) \rho(\mathbf{r}') \quad (2b)$$

etc. Notice that in most of the original papers (see, e.g., Baus 1987) only relative excess free energies have been considered—in which case the charging process starts from some given reference state—but for the present discussion equations (2) are more convenient since they allow us to consider just one state at a time. Let us also introduce the dimensionless quantity,  $(\beta/\rho) f[\rho]$ , where  $f = F/V$  is the free energy per unit volume  $V$ ,  $f/\rho$  the free energy per particle and

$$\rho = \frac{1}{V} \int d\mathbf{r} \rho(\mathbf{r})$$

the average density. If, for later convenience, we rewrite (2a) as

$$F_{\text{ex}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi(\mathbf{r}; [\rho])$$

with, from (2),

$$\beta \psi(\mathbf{r}; [\rho]) = - \int_0^1 d\lambda c_1(\mathbf{r}; [\lambda \rho]) \quad (3a)$$

$$\beta \psi(\mathbf{r}; [\rho]) = - \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' c_2(\mathbf{r}, \mathbf{r}'; [\lambda' \rho]) \rho(\mathbf{r}') \quad (3b)$$

then  $\psi(\mathbf{r}; [\rho])$  is seen to be a *local* excess free energy per particle, in contrast to the true excess free energy per particle,  $f_{\text{ex}}[\rho]/\rho$ . For a uniform liquid (indicated by the superscript l) we have from (2) and (3)

$$\frac{\beta}{\rho} f_{\text{ex}}^l(\rho) \equiv \beta \psi^l(\rho) = - \int_0^1 d\lambda c_1^l(\lambda \rho) \quad (4a)$$

$$\frac{\beta}{\rho} f_{\text{ex}}^l(\rho) \equiv \beta \psi^l(\rho) = -\rho \int d\mathbf{r} \int_0^1 d\lambda \int_0^\lambda d\lambda' c_2^l(|\mathbf{r}|; \lambda' \rho) \quad (4b)$$

where the DCF are now translationally invariant functions, while the charging operations reduce to density integrations over the uniform density of the liquid,  $\rho^l(\mathbf{r}) \equiv \rho$ , the density functionals degenerating into ordinary functions.

The central idea behind some of the approximate DFT is to replace the unknown DCF of the solid by the better known DCF of the uniform liquid, but evaluated at some as yet undetermined density—the density of the liquid whose correlations 'effectively' describe those of the solid. The approximate theory will describe thus a solid with liquid-like

correlations or, alternatively, an effective liquid with a solid-like density. The resulting approximation,  $c_2(\mathbf{r}, \mathbf{r}'; [\lambda\rho]) \approx c_2^l(|\mathbf{r} - \mathbf{r}'|; \lambda\bar{\rho})$ , where  $\bar{\rho}$  is the density of the effective liquid, cannot hold as such because the translation-rotation invariance of the liquid is always partially broken in the solid, but it may be meaningful to use it in one of the integrated expressions (2) and (3). Introducing this approximation (superscript appr) in (2b) or (3b) we obtain

$$F_{\text{ex}}^{\text{appr}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi^{\text{appr}}(\mathbf{r}; [\rho]) \tag{5a}$$

$$\beta\psi^{\text{appr}}(\mathbf{r}; [\rho]) = - \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' c_2^l(|\mathbf{r} - \mathbf{r}'|; \lambda'\bar{\rho})\rho(\mathbf{r}') \tag{5b}$$

where the DCF of the liquid,  $c_2^l(|\mathbf{r}|; \bar{\rho})$ , is assumed to be known. To close the above approximation, equations (5), a defining relation for the effective density  $\bar{\rho}$  has still to be given. There is clearly more than one way to do this. In our earlier theory (Baus and Colot 1985) this relation was taken from an extraneous condition by scaling the structure factor of the effective liquid to the periodicity of the solid. In order to make contact with some of the other approximate DFT we now determine the effective liquid  $\bar{\rho}$  self-consistently. In a first version, closely related to the theory of Tarazona (1984, 1985) and of Curtin and Ashcroft (1985, 1986), we use a self-consistency relation for the local excess free energy per particle  $\psi^{\text{appr}}(\mathbf{r}; [\rho]) = \psi^l(\bar{\rho})$ . This relation can hold only if  $\bar{\rho}$  is itself a non-uniform (local) function,  $\bar{\rho} = \bar{\rho}(\mathbf{r})$ . On using (4b) and (5b), this self-consistency relation becomes

$$\bar{\rho} \int d\mathbf{r}'' \int_0^1 d\lambda \int_0^\lambda d\lambda' c_2^l(|\mathbf{r}''|; \lambda'\bar{\rho}) = \int d\mathbf{r}' \rho(\mathbf{r}') \int_0^1 d\lambda \int_0^\lambda d\lambda' c_2^l(|\mathbf{r} - \mathbf{r}'|; \lambda'\bar{\rho}) \tag{6a}$$

which can also be rewritten in terms of a 'weighted' density:

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\mathbf{r})) \tag{6b}$$

with a weighting function  $w$  given by (6a) as

$$w(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}) = \left( \int_0^1 d\lambda \int_0^\lambda d\lambda' c_2^l(|\mathbf{r} - \mathbf{r}'|; \lambda'\bar{\rho}) \right) \times \left( \int_0^1 d\lambda \int_0^\lambda d\lambda' \int d\mathbf{r}'' c_2^l(|\mathbf{r}''|; \lambda'\bar{\rho}) \right)^{-1} \tag{6c}$$

where it is understood that  $\bar{\rho} = \bar{\rho}(\mathbf{r})$ . Alternatively, one can use a strictly uniform effective density,  $\bar{\rho}$ , when the latter is defined from the same self-consistency relation but formulated in terms of the true excess free energy per particle,  $(\beta/\rho)f_{\text{ex}}^{\text{appr}}[\rho] = (\beta/\bar{\rho})f_{\text{ex}}^l(\bar{\rho})$ , which on using (4b) and (5) leads to

$$\bar{\rho} = \left( \int d\mathbf{r} \int d\mathbf{r}' w(|\mathbf{r} - \mathbf{r}'|; \bar{\rho})\rho(\mathbf{r})\rho(\mathbf{r}') \right) \left( \int d\mathbf{r}'' \rho(\mathbf{r}'') \right)^{-1} \tag{7}$$

where  $w(|\mathbf{r}|; \bar{\rho})$  is still given by (6c). Notice that both relations (i.e. equations (6b) and (7)) define  $\bar{\rho}(\mathbf{r})$  and  $\bar{\rho}$  only implicitly. They are relations for self-consistency between the solid and the effective liquid. In the uniform limit,  $\rho(\mathbf{r}) \rightarrow \rho$ , we have in both cases,  $\bar{\rho} \rightarrow \rho$ , so no approximation whatsoever is involved in this limit when the exact  $c_2^l$  is

used. It is thus not necessary to impose the uniform limit as a supplementary condition on  $w$  as was done in the theories of Tarazona (1985) and of Curtin and Ashcroft (1985). If the solution of (6b) can be obtained from a virial expansion, as assumed by Tarazona (1985), then we obtain in lowest-order from (6c)

$$w(|\mathbf{r}|; 0) = f(|\mathbf{r}|) \left( \int d\mathbf{r}' f(|\mathbf{r}'|) \right)^{-1} \quad (8)$$

where  $f(|\mathbf{r}|) = -1 + \exp -\beta V(|\mathbf{r}|)$  is the Mayer function. When (8) is used in (6b) or in (7) we recover exactly the results of, respectively, Tarazona (1984) and of Stoessel and Wolynes (1986), and both of these sets of results were found to be of value in studies of, for example, the freezing of hard spheres. Notice, finally, that in a recent study of the triplet correlations of a uniform liquid, Denton and Ashcroft (1989) have proposed a weighting function similar to (6c) but without the density integrals which, as seen from (2b), are nevertheless essential for reproducing the exact free energy of the liquid in the uniform limit.

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