

## Freezing of the classical one-component plasma: analyses of the non-perturbative density-functional theories

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

1992 J. Phys.: Condens. Matter 4 5493

(<http://iopscience.iop.org/0953-8984/4/25/005>)

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

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:10

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

# Freezing of the classical one-component plasma: analyses of the non-perturbative density-functional theories

M Hasegawa

Department of Mathematics, Faculty of Engineering, Iwate University, Morioka 020, Japan

Received 12 November 1991, in final form 6 March 1992

**Abstract.** Recently developed non-perturbative density-functional theories of freezing are applied to the classical one-component plasma (OCP). We consider the modified weighted-density approximation (MWDA) of Denton and Ashcroft and the generalized effective-liquid approximation (GELA) of Lutsko and Baus. It is shown that both the MWDA and the GELA completely fail to predict freezing of the classical OCP in contrast to their reasonable success for the quantum freezing of the electron jellium: the MWDA does not improve over the second-order theory (SOT) and the GELA is much worse. A semi-empirical analysis is made of how and to what extent the GELA must be modified for the classical OCP: in this analysis the SOT is used for the variational liquid-like solids and the Monte Carlo results are used for the stable (or metastable) BCC solids. It is found that the two effective liquids, which are assumed to be equivalent in the GELA, must differ by about 10% in density from each other at the freezing point.

## 1. Introduction

Since the pioneering work of Ramakrishnan and Yussouff [1], the density-functional theory (DFT) has been used as a useful tool in the study of the liquid–solid phase transition [2–5]. Even the simplest version of the theory, which involves a second-order density-functional expansion of the non-uniform solid free energy around a uniform liquid free energy, gives a reasonable prediction of the freezing properties of hard spheres [1, 6]. On the basis of this encouraging result, the theory has been extended to other systems interacting via softer potentials, but it gives increasingly worse results as the potential becomes softer [7] and completely fails for Coulombic systems [8, 9]. For these systems, the inclusion of the third-order term seems essential, as shown explicitly in the case of the classical one-component plasma (OCP) [10]. However, it is also found that the second- and third-order terms are comparable near the freezing of the OCP [10] and that the inclusion of the third-order term seemed to worsen the results for hard spheres [11]. These results suggest that the convergence of the usual perturbation series is not sufficient even at the third order. Recently, Lutsko and Baus [12] proposed a different type of perturbation theory that provides successful predictions for the freezing of soft spheres including the OCP. This theory is based on thermodynamic perturbation theory [13], which has been proved to give accurate descriptions of the structural and thermodynamic properties of fluids.

In recent years, several non-perturbative DFTs or so-called weighted-density-functional theories have also been proposed [14–19] to circumvent the convergence

problem of the usual perturbative approach. While these theories generally give good results for the freezing of hard spheres, they more or less fail to predict the freezing of soft-core systems such as those interacting via the Lennard-Jones, inverse-power and Yukawa potentials [20, 21]. Since all of these non-perturbative DFTs are based on *ad hoc* and therefore uncontrollable approximations, there is virtually no means of systematic improvement, although some attempts have been made to clarify the reason for the dispersed results of these theories [22, 23].

The present work is one such attempt for the OCP and we are primarily concerned with the generalized effective-liquid approximation (GELA) of Lutsko and Baus [19], which is viewed as the complete theory for the freezing of hard spheres. We also consider the modified weighted-density approximation (MWDA) of Denton and Ashcroft [17] for comparison. Recently, these theories have been extended to the electron jellium at  $T = 0$  and found to give reasonable results for the quantum freezing (Wigner crystallization) [24]. The formulations of the GELA and the MWDA for the classical OCP are similar to those for jellium and are easily obtained. We use these formulations to show how these theories can (actually, cannot) predict freezing of the OCP. Then, we make detailed analyses of how and to what extent the GELA must be modified for the OCP, which is the main purpose of this paper. To implement these analyses, we adopt a semi-empirical approach with the use of the second-order perturbation theory (SOT) for the variational liquid-like solids and the Monte Carlo (MC) results for the stable (or metastable) BCC solid phase. One should note that our aim is not to propose a new theory but to show the limitations and possible modifications of the existing theories.

The paper is organized as follows. In section 2, we summarize the relevant results of the DFT of the non-uniform OCP and present the formulations of the GELA and the MWDA, which have been originally formulated for non-Coulombic systems [17, 19] and extended to the electron jellium [24]. The results of applications are presented in section 3, where we show how these theories fail to predict freezing of the OCP and how the GELA must be modified. The final section is devoted to the summary and conclusions.

## 2. Density-functional theories of the non-uniform OCP

The OCP is a system consisting of point-like charged particles (which we call ions hereafter), with the electric charge  $Ze$ , embedded in a uniform neutralizing charge background. Let  $\rho_s(\mathbf{r})$  be the one-particle density of a non-uniform (solid) OCP in equilibrium at the inverse temperature  $\beta = 1/k_B T$ . Then, the total charge neutrality condition requires that the charge background density is equal to  $Ze\rho_s$ , where  $\rho_s$  is the spatial average of  $\rho_s(\mathbf{r})$ , i.e.,

$$\rho_s = \frac{1}{V} \int_V d\mathbf{r} \rho_s(\mathbf{r}) \quad (2.1)$$

$V$  being the volume of the system.

The quantity of interest in the following is the intrinsic (Helmholtz) free energy  $F$  of the system, which is the unique functional of  $\rho_s(\mathbf{r})$  according to the DFT [25]. For the OCP, it is convenient and common practice to write  $F$  as

$$F[\rho_s] = G[\rho_s] + E_{es}[\rho_s]. \quad (2.2)$$

Here,  $G$  is the so-called non-Coulombic part of  $F$  and  $E_{es}$  is the electrostatic energy given by

$$E_{es}[\rho_s] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \Delta\rho_s(\mathbf{r}) \Delta\rho_s(\mathbf{r}') v(|\mathbf{r} - \mathbf{r}'|) \quad (2.3)$$

where  $\Delta\rho_s(\mathbf{r}) = \rho_s(\mathbf{r}) - \rho_s$  and  $v(r) = (Ze)^2/r$ . The non-Coulombic part  $G$  consists of two terms,

$$G[\rho_s] = G_{id}[\rho_s] + G_{ex}[\rho_s] \quad (2.4)$$

where  $G_{id}$  is the ideal-gas contribution and  $G_{ex}$  the excess term due to the inter-particle interaction. The explicit expression for  $G_{id}$  is known and given by [25]

$$\beta G_{id}[\rho_s] = \int d\mathbf{r} \rho_s(\mathbf{r}) \{\ln[\Lambda^3 \rho_s(\mathbf{r})] - 1\} \quad (2.5)$$

where  $\Lambda = (2\pi\hbar^2/mk_B T)^{1/2}$  is the thermal de Broglie wavelength,  $m$  being the particle mass. Therefore, the final goal in the density-functional formalism is to devise an approximation scheme for calculating  $G_{ex}$ .

### 2.1. Second-order perturbation theory (SOT)

The simplest approach to this goal is the functional expansion of  $G_{ex}$  in the density difference  $\delta\rho_s(\mathbf{r}) = \rho_s(\mathbf{r}) - \rho_r$ , where  $\rho_r$  is the density of a uniform (liquid) reference OCP. Although  $\rho_r$  can be chosen arbitrarily, the simplest and most convenient way may be to put  $\rho_r = \rho_s$ , where  $\rho_s$  is given by equation (2.1). Then, to second-order in  $\Delta\rho_s(\mathbf{r}) = \rho_s(\mathbf{r}) - \rho_s$ , as in the original work [1],  $\beta g_{ex}[\rho_s] = \beta G_{ex}[\rho_s]/N$  ( $N = \rho_s V$ ) is given by

$$\beta g_{ex}[\rho_s] = \beta g_{ex}(\rho_s) - \frac{1}{2N} \int d\mathbf{r} \int d\mathbf{r}' C_{NC}(|\mathbf{r} - \mathbf{r}'|; \rho_s) \Delta\rho_s(\mathbf{r}) \Delta\rho_s(\mathbf{r}') \quad (2.6)$$

where  $g_{ex}(\rho_s)$  is the excess free energy per particle of the uniform OCP with density  $\rho_s$  and  $C_{NC}$  is the non-Coulombic part of the direct correlation function (DCF) defined by

$$C_{NC}(|\mathbf{r} - \mathbf{r}'|; \rho_s) = -\{\delta^2 \beta G_{ex}[\rho_s] / \delta\rho_s(\mathbf{r}) \delta\rho_s(\mathbf{r}')\}_{\rho_s(\mathbf{r})=\rho_s}. \quad (2.7)$$

The total excess free energy per particle,  $f_{ex}[\rho_s] = g_{ex}[\rho_s] + f_{es}[\rho_s]$  with  $f_{es}[\rho_s] = E_{es}[\rho_s]/N$ , is then given by

$$\beta f_{ex}[\rho_s] = \beta f_{ex}(\rho_s) - \frac{1}{2N} \int d\mathbf{r} \int d\mathbf{r}' C(|\mathbf{r} - \mathbf{r}'|; \rho_s) \Delta\rho_s(\mathbf{r}) \Delta\rho_s(\mathbf{r}') \quad (2.8)$$

where  $C(r; \rho_s)$  is the DCF and related to its non-Coulombic part  $C_{NC}(r; \rho_s)$  by

$$C_{NC}(r; \rho_s) = C(r; \rho_s) + \beta v(r). \quad (2.9)$$

Note that, for a uniform OCP,  $f_{es}$  vanishes and so  $f_{ex} = g_{ex}$ .

## 2.2. Generalized effective-liquid approximation (GELA)

Moroni and Senatore [24] formulated a modified version of the GELA for jellium, which is appropriate to treat the Wigner crystallization that takes place at extremely low density. For the classical OCP, however, the original formulation of Lutsko and Baus [19] may be followed.

For the OCP, it is convenient to start from the definition of  $C_{\text{NC}}$ , the non-Coulombic part of the DCF:

$$C_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\rho_s]) = -\delta^2 \beta G_{\text{ex}}[\rho_s] / \delta \rho_s(\mathbf{r}) \delta \rho_s(\mathbf{r}'). \quad (2.10)$$

Equation (2.10) can be converted into the integral form by parametrizing the density as  $\rho_\lambda(\mathbf{r}) = \lambda \rho_s(\mathbf{r})$ :

$$\beta G_{\text{ex}}[\rho_s] = - \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' \rho_s(\mathbf{r}) \rho_s(\mathbf{r}') C_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\lambda' \rho_s]). \quad (2.11)$$

The total excess free energy per particle is then given by

$$\beta f_{\text{ex}}[\rho_s] = \beta f_{\text{es}}[\rho_s] - \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' \rho_s(\mathbf{r}) \rho_s(\mathbf{r}') C_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\lambda' \rho_s]). \quad (2.12)$$

Then, we follow Lutsko and Baus [19] and consider the mapping of the unknown free energy itself onto that of an effective liquid with density  $\hat{\rho}_1$  (*thermodynamic mapping*):

$$\beta f_{\text{ex}}[\rho_s] = \beta f_{\text{ex}}(\hat{\rho}_1). \quad (2.13)$$

The density  $\hat{\rho}_1$  defined by this mapping is in general a functional of  $\rho_s(\mathbf{r})$ , i.e.  $\hat{\rho}_1 = \hat{\rho}_1[\rho_s]$ . Another mapping considered by them is based on the observation that only the unknown of equation (2.12) is the DCF of the non-uniform (solid) OCP, and it is defined by (*structural mapping*)

$$\int d\mathbf{r} \int d\mathbf{r}' \rho_s(\mathbf{r}) \rho_s(\mathbf{r}') C_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\rho_s]) = \int d\mathbf{r} \int d\mathbf{r}' \rho_s(\mathbf{r}) \rho_s(\mathbf{r}') C_{\text{NC}}(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}_2) \quad (2.14)$$

where  $C_{\text{NC}}(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}_2)$  is the non-Coulombic part of the DCF of another effective liquid with density  $\hat{\rho}_2$ , which is also a functional of  $\rho_s(\mathbf{r})$ :  $\hat{\rho}_2 = \hat{\rho}_2[\rho_s]$ . Then, combining equations (2.12)–(2.14), we have

$$\begin{aligned} \beta f_{\text{ex}}(\hat{\rho}_1) &= \beta f_{\text{es}}[\rho_s] - \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' \rho_s(\mathbf{r}) \rho_s(\mathbf{r}') \\ &\quad \times C_{\text{NC}}(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}_2[\lambda' \rho_s]) \\ &= - \frac{\rho_s}{V} \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' C_{\text{NC}}(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}_2[\lambda' \rho_s]) \\ &\quad - \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' \Delta \rho_s(\mathbf{r}) \Delta \rho_s(\mathbf{r}') C(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}_2[\lambda' \rho_s]). \end{aligned} \quad (2.15)$$

In the second step of equation (2.15), we have used the fact that  $\beta f_{\text{es}}[\rho_s]$  can be formally written as

$$\beta f_{\text{es}}[\rho_s] = \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' \Delta\rho_s(\mathbf{r}) \Delta\rho_s(\mathbf{r}') \beta v(|\mathbf{r} - \mathbf{r}'|). \quad (2.16)$$

For a later reference, we also note the identity

$$\int_0^1 d\lambda \int_0^\lambda d\lambda' h(\lambda') = \int_0^1 d\lambda (1 - \lambda) h(\lambda) \quad (2.17)$$

valid for any function  $h(\lambda)$ .

Up to this stage, we have done nothing except define two effective liquids with density  $\hat{\rho}_1$  and  $\hat{\rho}_2$  for a given  $\rho_s(\mathbf{r})$ . The basic assumption made in the GELA is that the above two effective liquids are identical [19], i.e.,

$$\hat{\rho}_1[\rho_s] = \hat{\rho}_2[\rho_s] = \hat{\rho}[\rho_s]. \quad (2.18)$$

With this assumption, equation (2.15) becomes an implicit equation for  $\hat{\rho}[\rho_s]$ , which can be solved to give the solid excess free energy (given by either side of equation (2.15)). This completes the formal translation of the GELA originally developed for a non-Coulombic system into that for the OCP.

The method of solving equation (2.15) with the assumption (2.18) has been given by Lutsko and Baus [19]. The starting point of this method is to change  $\rho_s(\mathbf{r})$  to  $\lambda\rho_s(\mathbf{r})$  in equation (2.15), which results in

$$\begin{aligned} \lambda\beta f_{\text{ex}}(\rho[\lambda\rho_s]) &= -\frac{\rho_s}{V} \int d\mathbf{r} \int d\mathbf{r}' \int_0^\lambda d\alpha \int_0^\alpha d\alpha' C_{\text{NC}}(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}[\alpha'\rho_s]) \\ &\quad - \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \int_0^\lambda d\alpha \int_0^\alpha d\alpha' \Delta\rho_s(\mathbf{r}) \Delta\rho_s(\mathbf{r}') C(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}[\alpha'\rho_s]). \end{aligned} \quad (2.19)$$

Then, we expand  $\hat{\rho}[\lambda\rho_s]$  as

$$\hat{\rho}[\lambda\rho_s] = \lambda\hat{\rho}\{1 + a_1(\lambda - 1) + a_2(\lambda - 1)^2 + \dots\} \quad (2.20)$$

and substitute the expansion into equation (2.19). The successive differentiations of both sides of the resulting equation with respect to  $\lambda$  yield a sequence of equations which, when  $\lambda$  is set equal to 1, can serve to determine  $\hat{\rho} = \hat{\rho}[\rho_s]$  and  $\{a_n\} = \{a_n[\rho_s]\}$  in equation (2.20). A few of these equations are given by

$$\begin{aligned} \beta f_{\text{ex}}(\hat{\rho}) &= (\rho_s/\hat{\rho})\beta f_{\text{ex}}(\hat{\rho}) - \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' \Delta\rho_s(\mathbf{r}) \Delta\rho_s(\mathbf{r}') \\ &\quad \times C(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}[\lambda'\rho_s]) \end{aligned} \quad (2.21a)$$

$$\begin{aligned} \beta f_{\text{ex}}(\hat{\rho}) + (1 + a_1)\hat{\rho}\beta f'_{\text{ex}}(\hat{\rho}) &= -(\rho_s/\hat{\rho}) \int_0^1 d\lambda \tilde{C}_{\text{NC}}(0; \hat{\rho}[\lambda\rho_s]) \\ &\quad - \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \Delta\rho_s(\mathbf{r}) \Delta\rho_s(\mathbf{r}') C(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}[\lambda\rho_s]) \end{aligned} \quad (2.21b)$$

$$\begin{aligned} 2(1 + 2a_1 + a_2)\hat{\rho}\beta f'_{\text{ex}}(\hat{\rho}) + (1 + a_1)^2\hat{\rho}^2\beta f''_{\text{ex}}(\hat{\rho}) &= -\rho_s \tilde{C}_{\text{NC}}(0; \hat{\rho}) \\ &\quad - \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \Delta\rho_s(\mathbf{r}) \Delta\rho_s(\mathbf{r}') C(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}) \end{aligned} \quad (2.21c)$$

where  $f'_{\text{ex}}(\hat{\rho}) = \partial f_{\text{ex}}(\hat{\rho})/\partial \hat{\rho}$ ,  $f''_{\text{ex}}(\hat{\rho}) = \partial^2 f_{\text{ex}}(\hat{\rho})/\partial \hat{\rho}^2$ , and  $\tilde{C}_{\text{NC}}(0; \hat{\rho})$  is the long-wavelength limit of the Fourier transform of  $C_{\text{NC}}(\mathbf{r}; \hat{\rho})$ :

$$\tilde{C}_{\text{NC}}(\mathbf{q}; \hat{\rho}) = \int d\mathbf{r} C_{\text{NC}}(\mathbf{r}; \hat{\rho}) \exp(i\mathbf{q} \cdot \mathbf{r}). \quad (2.22)$$

In equation (2.21a), which is nothing but equation (2.15) assuming (2.18), we have used the result (see equation (2.16) of Lutsko and Baus [19])

$$-\frac{\rho_s}{V} \int d\mathbf{r} \int d\mathbf{r}' \int_0^1 d\lambda \int_0^\lambda d\lambda' C_{\text{NC}}(|\mathbf{r}-\mathbf{r}'|; \hat{\rho}[\lambda'\rho_s]) = -\rho_s \int d\mathbf{r} \int_0^1 d\lambda \int_0^\lambda d\lambda' \times C_{\text{NC}}(\mathbf{r}; \lambda'\hat{\rho}) = (\rho_s/\hat{\rho})\beta f_{\text{ex}}(\hat{\rho}). \quad (2.23)$$

In the first step of this equation we have used that  $\hat{\rho}[\lambda\rho_s] = 0$  for  $\lambda = 0$ ,  $\hat{\rho}[\lambda\rho_s] = \hat{\rho}$  for  $\lambda = 1$  and the integration over the coupling constant is path-independent in the case of a uniform density.

### 2.3. Modified weighted-density approximation (MWDA)

The MWDA of Denton and Ashcroft, [17] was rederived by Laird and Kroll [21] in a different manner. This derivation is physically more transparent than the original one of Denton and Ashcroft and can be easily extended to a Coulombic system. Moroni and Senatore [24] actually made such an extension to derive the MWDA for jellium. The correspondence of this result with that for the classical OCP is immediate, once the quantum direct correlation function  $K(\mathbf{r}; \rho)$  is replaced by  $\beta^{-1}C(\mathbf{r}; \rho)$  and the exchange-correlation energy  $\epsilon_{\text{xc}}(\rho)$  by  $f_{\text{ex}}(\rho)$ . Nevertheless, it may be useful for completeness and for later references to repeat its derivation for the OCP.

One starts from the integral form of the definition of  $C_{\text{NC}}^{(1)}$ , the non-Coulombic part of the one-body DCF [21]:

$$\beta G_{\text{ex}}[\rho_s] = - \int d\mathbf{r} \int_0^1 d\lambda \rho_s(\mathbf{r}) C_{\text{NC}}^{(1)}(\mathbf{r}; [\lambda\rho_s]). \quad (2.24)$$

Similarly, converting the relation  $\delta C_{\text{NC}}^{(1)}(\mathbf{r}; [\rho_s])/\delta \rho_s(\mathbf{r}') = C_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\rho_s])$  into an integral form, one has

$$C_{\text{NC}}^{(1)}(\mathbf{r}; [\lambda\rho_s]) = C_{\text{NC}}^{(1)}(\lambda\hat{\rho}) + \int d\mathbf{r}' \lambda \int_0^1 d\lambda' [\rho_s(\mathbf{r}') - \hat{\rho}] C_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\lambda\rho_{\lambda'}]) \quad (2.25)$$

where the integration path is parametrized as

$$\rho_{\lambda'}(\mathbf{r}) = \hat{\rho} + \lambda'[\rho_s(\mathbf{r}) - \hat{\rho}] \quad (2.26)$$

$\hat{\rho}$  being the density of a uniform liquid specified later. Then, substitution of equation (2.25) into (2.24) yields

$$\beta G_{\text{ex}}[\rho_s] = N\beta f_{\text{ex}}(\hat{\rho}) - \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_s(\mathbf{r}) [\rho_s(\mathbf{r}') - \hat{\rho}] \bar{C}_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\rho_s]) \quad (2.27)$$

with

$$\bar{C}_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\rho_s]) = 2 \int_0^1 d\lambda \lambda \int_0^1 d\lambda' C_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\lambda\rho_{\lambda'}]). \quad (2.28)$$

At this point, the unknown functional  $\bar{C}_{\text{NC}}$  is approximated by an as-yet-unspecified homogeneous two-point function  $X$ :

$$\bar{C}_{\text{NC}}(\mathbf{r}, \mathbf{r}'; [\rho_s]) \simeq X(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}). \quad (2.29)$$

Then, one requires that the resulting approximate excess free energy functional, which is denoted as  $F_{\text{ex}}^{\text{MWDA}}[\rho_s]$ , satisfies the condition (thermodynamic mapping)

$$F_{\text{ex}}^{\text{MWDA}}[\rho_s] = N f_{\text{ex}}(\hat{\rho}). \quad (2.30)$$

This condition implies that the sum of the second term on the right-hand side (RHS) of equation (2.27) and the electrostatic energy  $\beta E_{\text{es}}[\rho_s]$  vanishes, which yields

$$\hat{\rho} = \rho_s + \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \Delta \rho_s(\mathbf{r}) \Delta \rho_s(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}) \quad (2.31)$$

with

$$w(\mathbf{r}; \hat{\rho}) = [1/\bar{X}(0; \hat{\rho})] \{X(\mathbf{r}; \hat{\rho}) - \beta v(\mathbf{r})\} \quad (2.32)$$

where  $\bar{X}(0; \hat{\rho})$  is the long-wavelength limit of the Fourier transform of  $X(\mathbf{r}; \hat{\rho})$ .

Finally, as in the original derivation [17], one requires that the approximate free energy functional  $F_{\text{ex}}^{\text{MWDA}}[\rho_s]$  produces the DCF exactly in the limit of uniform density, i.e.,

$$\{\beta F_{\text{ex}}^{\text{MWDA}}[\rho_s] / \delta \rho_s(\mathbf{r}) \delta \rho_s(\mathbf{r}')\} |_{\rho_s(\mathbf{r})=\rho} = -C(|\mathbf{r} - \mathbf{r}'|; \rho) \quad (2.33)$$

for any  $\rho$ . A unique specification of the weight function  $w$  in equation (2.31) follows from this condition [17, 24]: with  $\rho = \hat{\rho}$  in equation (2.33), one has

$$w(\mathbf{r}; \hat{\rho}) = -[1/2\beta f'_{\text{ex}}(\hat{\rho})] \{C(\mathbf{r}; \hat{\rho}) + (\hat{\rho}/V)\beta f''_{\text{ex}}(\hat{\rho})\}. \quad (2.34)$$

Here we note the compressibility sum rule for the OCP:

$$\hat{\rho} \bar{C}_{\text{NC}}(0; \hat{\rho}) = 1 - \frac{1}{\hat{\rho} k_{\text{B}} T \chi_{\text{T}}} = -2\hat{\rho} \beta f'_{\text{ex}}(\hat{\rho}) - \hat{\rho}^2 \beta f''_{\text{ex}}(\hat{\rho}) \quad (2.35)$$

where  $\chi_{\text{T}}$  is the isothermal compressibility. Using this sum rule, it is easy to show that the result of equation (2.34) corresponds to the choice

$$X(\mathbf{r}; \hat{\rho}) = C_{\text{NC}}(\mathbf{r}; \hat{\rho}) + (\hat{\rho}/V)\beta f''_{\text{ex}}(\hat{\rho}) \quad (2.36)$$

for the two-point function introduced in equation (2.29).

We note that equation (2.29) is now the basic assumption in the MWDA for Coulombic systems and could be crucial in determining the quality of the MWDA. The corresponding assumption for a non-Coulombic system leads to a normalized weight function [21], which was the basic assumption in the original derivation of the MWDA [17]: for a Coulombic system, the weight function  $w$  is not normalized (see equation (2.32) or (2.34)) and the original derivation cannot be followed.

Now, substitution of equation (2.34) into (2.31) yields

$$2(\hat{\rho} - \rho_s)\beta f'_{\text{ex}}(\hat{\rho}) = -\frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \Delta \rho_s(\mathbf{r}) \Delta \rho_s(\mathbf{r}') C(|\mathbf{r} - \mathbf{r}'|; \hat{\rho}). \quad (2.37)$$



Given  $\rho_s(\mathbf{r})$ , equation (2.37) can be easily solved for  $\hat{\rho}$  and the solid excess free energy is obtained from equation (2.30).

The requirement (2.33) implies that the MWDA exactly reproduces the SOT result in the limit of uniform density, where  $\Delta\hat{\rho} = \hat{\rho} - \rho_s$  clearly vanishes. It is easy to show that equation (2.37) is in fact consistent with this implication. To show this, we consider a situation where the density is nearly uniform and so  $\Delta\hat{\rho}$  is small. In such a situation, from equation (2.37) we have

$$\hat{\rho} - \rho_s \simeq \beta \Delta f_{\text{ex}}^{\text{SOT}} / \beta f'_{\text{ex}}(\rho_s) \quad (2.38)$$

where  $\beta \Delta f_{\text{ex}}^{\text{SOT}}$  is the second-order term of the perturbation series and given by the second term (including minus sign) on the RHS of equation (2.8). Using equation (2.38), the solid free energy  $\beta f_{\text{ex}}[\rho_s] = \beta f_{\text{ex}}(\hat{\rho})$  is obtained as

$$\beta f_{\text{ex}}(\hat{\rho}) \simeq \beta f_{\text{ex}}(\rho_s) + \beta f'_{\text{ex}}(\rho_s)(\hat{\rho} - \rho_s) \simeq \beta f_{\text{ex}}(\rho_s) + \beta \Delta f_{\text{ex}}^{\text{SOT}}. \quad (2.39)$$

Equation (2.39) holds exactly in the limit of uniform density and is nothing but the SOT result given by equation (2.8). The perturbation series does not seem to converge rapidly near freezing [10], and we may expect some difference between the MWDA and the SOT.

We can also show the relation between the MWDA and the GELA by rewriting equation (2.37) as

$$\begin{aligned} 2\hat{\rho}\beta f'_{\text{ex}}(\hat{\rho}) + (\rho_s/\hat{\rho})\rho^2\beta f''_{\text{ex}}(\hat{\rho}) \\ = -(\rho_s/\hat{\rho})\hat{\rho}\tilde{C}_{\text{NC}}(0;\hat{\rho}) - \frac{1}{N} \int d\mathbf{r} \int d\mathbf{r}' \Delta\rho_s(\mathbf{r})\Delta\rho_s(\mathbf{r}')C(|\mathbf{r}-\mathbf{r}'|;\hat{\rho}) \end{aligned} \quad (2.40)$$

where we have used the compressibility sum rule (2.35). The MWDA equation (2.40) results from the GELA if we disregard equations (2.21a) and (2.21b) and impose additional constraints,  $a_1 = (\rho_s/\hat{\rho})^{1/2} - 1$  and  $a_2 = -2a_1$ , in equation (2.21c). This correspondence between the MWDA and the GELA for the OCP is the same as that for a non-Coulombic system [19], but it does not necessarily mean that these theories produce similar results for the freezing of the OCP as in the case of hard-sphere freezing [19].

### 3. Applications: analysis of the GELA

#### 3.1. Prescriptions for the liquid OCP and crystal density

The knowledge of the free energy and structural functions of the uniform liquid is a prerequisite in the theory of freezing. For the OCP, a very accurate expression for the free energy is available from the MC simulations [26]:

$$\beta f_{\text{ex}}(\rho) = a\Gamma + 4(b\Gamma^{1/4} - c/\Gamma^{1/4}) + d \ln \Gamma - [a + 4(b - c) + 0.4363] \quad 1 < \Gamma < 160 \quad (3.1)$$

where  $\Gamma$  is the plasma parameter defined by  $\Gamma = \beta(Ze)^2/R_s$ ,  $R_s$  being the ionic sphere radius defined by  $(4\pi/3)R_s^3 = 1/\rho$ ,  $a = -0.897744$ ,  $b = 0.95043$ ,  $c =$

0.18956 and  $d = -0.81487$ . With this result, together with the MC result for the BCC solid free energy (see equation (3.14)), the melting occurs at  $\Gamma \simeq 178$  [26]. Slightly different and probably more accurate values of  $a$ ,  $b$ ,  $c$  and  $d$  in equation (3.1), which predict melting at  $\Gamma \simeq 180$ , have been obtained by Ogata and Ichimaru [27]. But we did not use this result for consistency with the prescription for the DCF of the OCP, which is given below. Equation (3.1) may be safely used beyond  $\Gamma = 160$ , probably up to  $\Gamma \simeq 180$ . For  $\Gamma < 1$ , we used the expression

$$\beta f_{\text{ex}}(\rho) = -0.6244\Gamma^{3/2} + 0.2126\Gamma^2 - 0.0245\Gamma^{5/2} \quad \Gamma < 1. \quad (3.2)$$

The coefficients in this expansion were determined such that  $\beta f_{\text{ex}}$  and its first and second derivatives are continuous at  $\Gamma = 1$ . The excess internal energy  $\beta u_{\text{ex}}(\rho)$  obtained from equation (3.2) is in good agreement with the MC result for  $\Gamma < 1$  [26].

The DCF of the liquid OCP was calculated in the modified hypernetted-chain (MHNC) approximation of Rosenfeld and Ashcroft [28], in which the hard-sphere bridge function in the Percus–Yevick approximation was fitted to the compressibility obtained from equations (3.1) and (3.2) [29]. The DCFs calculated in this way are in good agreement with the MC results. The DCFs at all values of  $\Gamma$  ( $\Gamma < 180$ ) are involved in the applications of the GELA (see equations (3.9a)–(3.9c)). To avoid the difficulty of repeating time-consuming computations for solving the MHNC integral equation, we used the interpolation scheme with the use of the DCFs tabulated at the interval of  $\Delta\Gamma = 5$ . This scheme was proved to be very accurate because of the scaling property of the OCP (i.e.,  $C(r; \rho)$  is nearly proportional to  $\Gamma$  for a given  $X = r/R_s$ ).

In this work we used a sum of the Gaussians peaked at each site of a periodic lattice for describing the solid density  $\rho_s(\mathbf{r})$  [30]:

$$\rho_s(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_i \exp[-\alpha(\mathbf{r} - \mathbf{R}_i)^2] \quad (3.3a)$$

$$\rho_s(\mathbf{r}) = \rho_s \sum_j \exp\left(-\frac{G_j^2}{4\alpha}\right) \exp(i\mathbf{G}_j \cdot \mathbf{r}) \quad (3.3b)$$

where the  $\{\mathbf{R}_i\}$  denote the Bravais-lattice vectors for a chosen crystal lattice and  $\{\mathbf{G}_j\}$  the corresponding reciprocal lattice vectors (RLV). With the use of the above  $\rho_s(\mathbf{r})$ , the variational principle for the free energy  $F$  reduces to a minimization of  $F$  with respect to the Gaussian width parameter  $\alpha$ . Another popular method is a general Fourier decomposition of  $\rho_s(\mathbf{r})$ , in which the amplitude of each (non-symmetry-related) Fourier component is treated as an independent parameter. This method has the ability to explore more realistic crystal density, but we avoided the use of this method because of the inconvenience in our analysis. The Gaussian and Fourier methods have been compared in the study of the freezing transition of the hard-sphere and Lennard-Jones systems and were found to give essentially the same results for the phase diagram [31].

For  $\rho_s(\mathbf{r})$  given by equation (3.3), we can easily obtain the expression for the ideal-gas contribution  $\beta g_{\text{id}} = \beta G_{\text{id}}/N$  [16, 19], which we conveniently write as

$$\beta g_{\text{id}}[\rho_s] = \beta g_{\text{id}}(\rho_s) + \beta \Delta g_{\text{id}}[\rho_s]. \quad (3.4)$$

Here,  $\beta g_{id}(\rho_s)$  is the ideal-gas free energy of the uniform liquid,

$$\beta g_{id}(\rho_s) = \ln(\Lambda^3 \rho_s) - 1 = 3 \ln \Gamma_s - 1 + \ln \left( \frac{3}{4} \pi^{1/2} \right) + \frac{3}{2} \ln(k_B T)_{Ryd} \quad (3.5)$$

where  $\Gamma_s$  is the plasma parameter corresponding to  $\rho_s$  and  $(k_B T)_{Ryd}$  is the energy  $k_B T$  in units of the atomic Rydberg. The deviation from the uniform part is given by [19]

$$\beta \Delta g_{id}[\rho_s] = \frac{3}{2} \ln \left( \frac{\alpha R_s^2}{\pi} \right) - \ln \left( \frac{3}{4\pi} \right) - \frac{3}{2} + \frac{\alpha}{\pi} \int d\mathbf{r} \exp(-\alpha r^2) \ln \left\{ \sum_j \exp[-\alpha(R_j^2 - 2\mathbf{r} \cdot \mathbf{R}_j)] \right\}. \quad (3.6)$$

This expression was used for  $\alpha R_s^2 > 1$ . We performed numerical calculations to evaluate the last term on the RHS of (3.6) and found that this term is negligibly small for  $\alpha R_s^2 > 20$  [16]. For  $\alpha R_s^2 < 1$ , we used an approximate result [19]

$$\beta \Delta g_{id}[\rho_s] = \frac{1}{2} N_1 \exp(-G_1^2/2\alpha) \quad (3.7)$$

where  $N_1$  is the number of the nearest neighbours in the reciprocal space and  $G_1$  is the smallest RLV.

With the prescriptions for the uniform liquid OCP and crystal density  $\rho_s(\mathbf{r})$ , the freezing properties can be easily obtained in the approximations discussed in the previous section. We find it convenient to work in reciprocal space using equation (3.3b) and to make use of the scaling properties of the OCP, i.e.,  $\beta f_{ex}(\rho_s) = \tilde{f}_{ex}(\Gamma_s)$  and  $\rho_s \tilde{C}(G_j, \rho_s) = \tilde{D}(Y_j, \Gamma_s)$  with  $Y_j = G_j R_s$ . Here and hereafter,  $R_s$  and  $\Gamma_s$  refer to the ionic-sphere radius and plasma parameter corresponding to  $\rho_s$ .

The excess free energy of the solid,  $\beta f_{ex}[\rho_s] = \tilde{f}_{ex}(\Gamma_s; \alpha R_s^2)$ , in the SOT (equation (2.8)) is then written as

$$\tilde{f}_{ex}(\Gamma_s; \alpha R_s^2) = f_{ex}(\Gamma_s) - \frac{1}{2} \sum_j' \exp \left( -\frac{Y_j^2}{2\alpha R_s^2} \right) \tilde{D}(Y_j; \Gamma_s) \quad (3.8)$$

where the prime on the summation indicates the exclusion of the term with  $Y_j = 0$  ( $G_j = 0$ ).

The GELA equations (2.21a)–(2.21c) become

$$\tilde{f}_{ex}(\hat{\Gamma}) = (\Gamma_s/\hat{\Gamma})^3 \tilde{f}_{ex}(\hat{\Gamma}) - \sum_j' \exp \left( -\frac{Y_j^2}{2\alpha R_s^2} \right) \int_0^1 d\lambda (1-\lambda) [\Gamma_s/\hat{\Gamma}(\lambda)]^3 \times \tilde{D}(\hat{Y}_j(\lambda); \hat{\Gamma}(\lambda)) \quad (3.9a)$$

$$\tilde{f}_{ex}(\hat{\Gamma}) + \frac{1}{3}(1+a_1)\hat{\Gamma} f'_{ex}(\hat{\Gamma}) = -(\Gamma_s/\hat{\Gamma})^3 \int_0^1 d\lambda \tilde{D}_{NC}(0; \hat{\Gamma}(\lambda)) - \sum_j' \exp \left( -\frac{Y_j^2}{2\alpha R_s^2} \right) \times \int_0^1 d\lambda [\Gamma_s/\hat{\Gamma}(\lambda)]^3 \tilde{D}(\hat{Y}_j(\lambda); \hat{\Gamma}(\lambda)) \quad (3.9b)$$

$$\frac{2}{3}(1+2a_1+a_2)\hat{\Gamma} \tilde{f}'_{ex}(\hat{\Gamma}) + \frac{1}{9}(1+a_1)^2 [-2\hat{\Gamma} \tilde{f}'_{ex}(\hat{\Gamma}) + \hat{\Gamma}^2 \tilde{f}''_{ex}(\hat{\Gamma})] = -(\Gamma_s/\hat{\Gamma})^3 \left\{ \tilde{D}_{NC}(0; \hat{\Gamma}) + \sum_j' \exp \left( -\frac{Y_j^2}{2\alpha R_s^2} \right) \tilde{D}(\hat{Y}_j; \hat{\Gamma}) \right\}. \quad (3.9c)$$

In these equations,  $\tilde{f}'_{\text{ex}}(\hat{\Gamma})$  and  $\tilde{f}''_{\text{ex}}(\hat{\Gamma})$  now represent the derivatives with respect to  $\hat{\Gamma}$ ,  $\hat{Y}_j(\lambda) = G_j \hat{R}_s(\lambda) = Y_j[\Gamma_s/\hat{\Gamma}(\lambda)]$ , and  $\hat{R}_s(\lambda)$  and  $\hat{\Gamma}(\lambda)$  are the ionic-sphere radius and plasma parameter, respectively, corresponding to  $\hat{\rho}(\lambda) = \rho[\lambda\rho_s]$  (equation (2.20)). In equation (3.9a) we used the identity (2.17). We retained up to the term with  $a_2$  in the expansion of equation (2.20) (third-order GELA [19]) and used the variable  $\nu = \lambda^{1/3}$  rather than  $\lambda$  in the numerical integrations over the coupling constant in equations (3.9a) and (3.9b), which is more efficient since  $\tilde{D}(\hat{Y}_j(\lambda); \hat{\Gamma}(\lambda))$  is nearly proportional to  $\nu$ .

The MWDA equation can be obtained from equation (3.9c) by imposing the constraints  $a_1 = (\rho_s/\hat{\rho})^{1/2} - 1 = (\Gamma_s/\hat{\Gamma})^{3/2} - 1$  and  $a_2 = -2a_1$ , as discussed at the end of the previous section.

### 3.2. Results in the SOT, GELA and MWDA

Figure 1 shows the results of the free-energy difference  $\Delta\tilde{f}$  calculated for the BCC crystal in the three approximation schemes:  $\Delta\tilde{f}$  is defined by  $\Delta\tilde{f} = \beta\Delta f[\rho_s] = \beta f[\rho_s] - \beta f(\rho_s)$ , where  $f = g_{\text{id}} + f_{\text{ex}}$ , and given by

$$\Delta\tilde{f}(\Gamma_s; \alpha R_s^2) = \Delta\tilde{g}_{\text{id}}(\alpha R_s^2) + \Delta\tilde{f}_{\text{ex}}(\Gamma_s; \alpha R_s^2) \quad (3.10)$$

where  $\Delta\tilde{g}_{\text{id}}(\alpha R_s^2) = \beta\Delta g_{\text{id}}[\rho_s]$  (equation (3.4)) and  $\Delta\tilde{f}_{\text{ex}}(\Gamma_s; \alpha R_s^2) = \tilde{f}_{\text{ex}}(\Gamma_s; \alpha R_s^2) - \tilde{f}_{\text{ex}}(\Gamma_s)$  with  $\tilde{f}_{\text{ex}}(\Gamma_s; \alpha R_s^2) = \tilde{f}_{\text{ex}}(\hat{\Gamma})$  in the GELA and the MWDA. Note that no volume (or density) change on freezing is considered in the case of the OCP.

As we have already mentioned in section 1, all the theories considered in this work completely fail to predict freezing transition of the OCP:  $\Delta\tilde{f}$  has no local minimum as the function of  $\alpha R_s^2$ , showing no tendency to freeze into even a metastable solid. Furthermore, of the three theories, the GELA is the worst and the SOT the best, which is quite in contrast to the case of hard spheres. In their SOT, with the use of the Fourier method, Rovere and Tosi [8] proposed to ignore the density-wave contributions with  $G_2$  (the second-smallest RLV of the BCC lattice), which shows strong rigidity against freezing into the BCC lattice. Similar and physically acceptable results are also obtained in our Gaussian method if we ignore that Fourier component of  $\rho_s(\mathbf{r})$  in equation (3.8), and such a procedure, though difficult to confirm by direct calculation, could be interpreted as simulating higher-order terms. A similar analysis was made by Iyetomi and Ichimaru [10] in their third-order perturbation theory, which itself predict freezing at  $\Gamma \simeq 140$ : they showed that their theory can predict freezing at  $\Gamma \simeq 180$  if one retains only 22% of the density-wave contributions with  $G_2$  in the second-order term. These analyses suggest that the convergence of the perturbation series is not sufficient even including the third-order term and, in fact, the second- and third-order terms are comparable at freezing [10].

The stability of the solid phase in the GELA unphysically lowers as  $\Gamma_s$  increases, which is another serious aspect of the failure. The failure of the GELA can be understood in terms of equation (3.9a): the second term (including minus sign) on the RHS of this equation is positive and very small (even for large  $\alpha R_s^2$ ) and the resulting  $\hat{\Gamma}$  is only slightly smaller than  $\Gamma_s$ , producing a solid excess free energy  $\tilde{f}_{\text{ex}}(\Gamma_s; \alpha R_s^2) = \tilde{f}_{\text{ex}}(\hat{\Gamma})$  slightly smaller in magnitude than the liquid free energy  $\tilde{f}_{\text{ex}}(\Gamma_s)$ . As the result, the free-energy difference  $\Delta\tilde{f}$  is essentially determined by the ideal-gas contribution  $\Delta\tilde{g}_{\text{id}}$ , which is independent of  $\Gamma_s$  and increases with  $\alpha R_s^2$

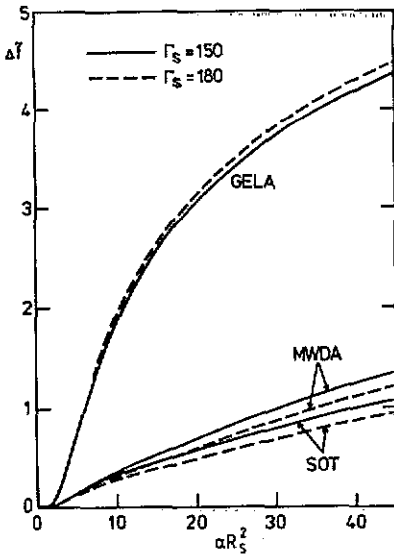


Figure 1. Comparisons of the free-energy difference  $\Delta\bar{f}$  (equation (3.10)) calculated in the SOT, GELA and MWDA at  $\Gamma_s = 150$  and  $\Gamma_s = 180$ .

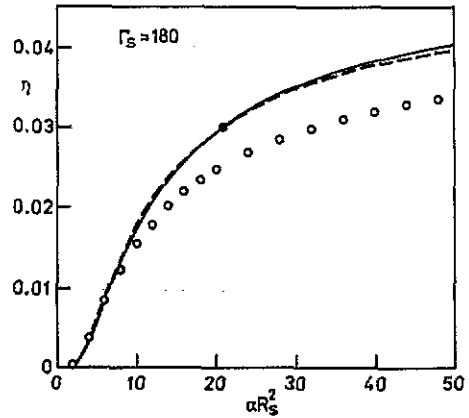


Figure 2. The Gaussian width parameter dependence of  $\eta$  at  $\Gamma_s = 180$ , which is defined by equation (3.12) and specifies the relation between the two effective liquids in the modified GELA: open circles, obtained from the SOT; filled circle, obtained from the MC result for the solid OCP; full (broken) curve, fitted to the SOT value of  $\eta$  at  $\alpha R_s^2 = 6$  ( $\alpha R_s^2 = 4$ ) and to the MC value (filled circle) using the parametrized function given by equation (3.15).

(see equation (3.6)). These unfavourable features of the GELA are not specific to the present prescriptions for the liquid DCF or  $\rho_s(r)$  but must be ascribed to the basic assumption of this theory.

The results for  $\Delta\bar{f}$  in the MWDA and in the SOT are close to each other in the range of small  $\alpha R_s^2$ , which is not accidental but a general attribute of the MWDA as discussed in the previous section (see equation (2.39)). The deviation of the MWDA result for  $\Delta\bar{f}$  from the SOT result increases with  $\alpha R_s^2$ , but this deviation is not in such a direction as to be an improvement over the SOT. This result suggests that higher-order terms are not properly incorporated, at least in principle, in the MWDA in spite of its reasonable success for the freezing of hard-spheres. This unfavourable feature of the MWDA may also be traced back to the basic requirement (equation (2.29)) of this theory.

### 3.3. Analysis of the GELA

The failures of the GELA and MWDA for the OCP suggest that the basic assumptions (or requirements) of these theories must be abandoned. In a circumstance in which it is difficult to establish a new and more reasonable assumption from purely theoretical considerations, an immediate task may be empirical. The GELA is easier to tackle than the MWDA and we are concerned with the former in the following analysis.

The only assumption of the GELA is that the two effective liquids onto which the

solid is mapped are identical (equation (2.18)). In our variational approach with the use of equation (3.3), the SOT may be a good approximation for liquid-like solids, i.e. the ones with small width parameters  $\alpha$ , for which we may expect a rapid convergence of the perturbation series. We determined plasma parameters  $\hat{\Gamma}_1$  and  $\hat{\Gamma}_2$  of the two effective liquids with density  $\hat{\rho}_1$  and  $\hat{\rho}_2$ , respectively, by setting both sides of equation (2.15) equal to the solid excess free energy calculated in the SOT (equation (3.8)). In the calculations of the second term on the RHS of equation (2.15) (or (3.9a) with  $\hat{\Gamma} = \hat{\Gamma}_2$ ), we used the approximation

$$\hat{\rho}_2(\lambda) = \lambda \hat{\rho}_2 \quad \text{or} \quad \hat{\Gamma}_2(\lambda) = \lambda^{1/3} \hat{\Gamma}_2 \quad (3.11)$$

which corresponds to the so-called first-order GELA [19] and was proved to give accurate results for liquid-like solids with small  $\alpha R_s^2$ . We actually confirmed that we gain very little in using the full expansion (2.20) for the OCP and so equation (3.11) can be used as a good approximation, especially for small  $\alpha R_s^2$ .

The values of  $\hat{\Gamma}_1$  and  $\hat{\Gamma}_2$  determined in this way are larger and smaller, respectively, than  $\Gamma_s$  and their deviations from  $\Gamma_s$  increase with  $\alpha R_s^2$ . To establish the relationship between  $\hat{\Gamma}_1$  and  $\hat{\Gamma}_2$ , both being functions of  $\alpha R_s^2$ , we used the quantity defined by

$$\eta(\alpha R_s^2) = (\hat{\Gamma}_1 - \hat{\Gamma}_2)/\hat{\Gamma}_1 = 1 - \hat{\Gamma}_2/\hat{\Gamma}_1. \quad (3.12)$$

The values of  $\eta$  obtained from the SOT are shown in figure 2 (open circles). If we use this relation between  $\hat{\Gamma}_1$  and  $\hat{\Gamma}_2$ , together with the approximation (3.11), in equation (2.15), we recover the result of the SOT shown in figure 1. We also note that  $\eta = 0$  for the GELA.

In the absence of any theory to estimate  $\eta$  for large  $\alpha R_s^2$ , we used the MC results for the solid free energy. To make a connection between our variational approach and the MC simulations, we used the Lindemann ratio  $\gamma$ , which is defined as the mean-square displacement divided by the nearest-neighbour distance. For the parametrized  $\rho_s(\mathbf{r})$  given by equation (3.3),  $\gamma$  is given by

$$\gamma^2 = \frac{1}{2} (3/\pi)^{2/3} / \alpha R_s^2 \quad (3.13)$$

for the BCC lattice, which is the stable structure of the solid OCP. The MC results for  $\gamma$  have been given by Pollock and Hansen [32] and we used these results to obtain corresponding values of  $\alpha R_s^2$ . For the value of  $\alpha R_s^2$  determined in this way at each  $\Gamma_s$  we determined  $\hat{\Gamma}_1$  and  $\hat{\Gamma}_2$  by setting both sides of equation (2.15) plus the ideal-gas free energy  $\beta g_{\text{id}}[\rho_s]$  (equation (3.4)) equal to the MC free energy  $\beta f^{\text{MC}}(\rho_s)$  of the BCC solid [26, 32]:

$$\beta f^{\text{MC}}(\rho_s) = \frac{1}{2} \alpha_{\text{BCC}} \Gamma_s + \frac{9}{2} \ln \Gamma_s - 1.8856 - 1613/\Gamma_s^2 + \frac{3}{2} \ln(k_B T)_{\text{Ryd}} \quad (3.14)$$

where  $\alpha_{\text{BCC}}$  is the Madelung constant of the BCC lattice,  $\alpha_{\text{BCC}} = -1.79186$ . In the calculations of the second term on the RHS of equation (2.15), we also used the approximation (3.11). The results of these calculations are summarized in table 1. The values of  $\eta$  determined in this way are about 20% larger than those determined by the SOT (see figure 2).

**Table 1.** Parameters of the BCC solid OCP and of the effective liquids in the modified GELA:  $\gamma$ , the MC Lindemann ratio [32];  $\alpha R_s^2$ , the corresponding Gaussian width parameter (equation (3.13));  $\hat{\Gamma}_1$  and  $\hat{\Gamma}_2$ , plasma parameters of the effective liquids onto which solid OCP is mapped (see the text);  $\eta$ , defined by equation (3.12);  $A$  and  $B$ , the parameters in equation (3.15) fitted to the MC value of  $\eta$  in this table and to the SOT value at  $\alpha R_s^2 = 6$  (the values in the parentheses are fitted to the SOT value at  $\alpha R_s^2 = 4$ ).

$\Gamma_s$	$\gamma$	$\alpha R_s^2$	$\hat{\Gamma}_1$	$\hat{\Gamma}_2$	$\eta$	$A$	$B$
150	0.1673	17.32	152.69	148.06	0.0303	0.0560	10.61
160	0.1620	18.48	162.85	157.92	0.0303	0.0538	10.62
170	0.1571	19.65	173.00	167.78	0.0302	0.0519	10.64
180	0.1526	20.82	183.15	177.65	0.0300	0.0501	10.66
						(0.0487)	(10.05)
200	0.1449	23.09	203.42	197.38	0.0297	0.0472	10.72

To establish the relation between  $\hat{\Gamma}_1$  and  $\hat{\Gamma}_2$  that can be used in the whole range of  $\alpha R_s^2$ , we used a parametrized function of the form

$$\eta(\alpha R_s^2) = A \exp(-B/\alpha R_s^2). \quad (3.15)$$

The parameters  $A$  and  $B$  in this equation were fitted to the MC value at the corresponding  $\alpha R_s^2$  (see table 1) and to the SOT value at a small  $\alpha R_s^2$ , say  $\alpha R_s^2 = 6$ . The results of this fitting for  $\Gamma_s = 180$  are shown in figure 2 (full and broken curves). The use of equation (3.15) is based on the observation that the SOT results for  $\eta$  can be fitted to this equation with high accuracy.

With these results for  $\eta(\alpha R_s^2)$ , we can solve equation (2.15) to obtain  $\hat{\Gamma}_1$  (or  $\hat{\Gamma}_2$ ) without using the assumption (2.18). If any purely theoretical prescription could be given to calculate such an  $\eta(\alpha R_s^2)$ , the theory would be called a modified GELA: for simplicity, we use this terminology hereafter. We used the approximation (3.11) to solve equation (2.15) for the consistency with the procedure used to determine  $\hat{\Gamma}_1$  and  $\hat{\Gamma}_2$ . The free energy difference  $\Delta \tilde{f}$  (equation (3.10)) calculated in this modified GELA has now a local minimum near the value of  $\alpha R_s^2$  fitted to the MC Lindemann ratio, showing the tendency to freeze into the BCC solid (see figure 3). The freezing occurs at  $\Gamma_s \simeq 180$  in agreement with the MC simulations [26, 27], although the Gaussian width or Lindemann ratio at freezing slightly deviates from the prescribed (and expected) value, shown by vertical arrows in figure 3. We note that, with our fitting procedure, our calculations exactly reproduce the MC solid free energy at the value of  $\alpha R_s^2$  fitted to the MC Lindemann ratio, but the calculated  $\Delta \tilde{f}$  does not necessarily have a (local) minimum at that value of  $\alpha R_s^2$ , as it does not for large  $\Gamma_s$  (see figure 3). The freezing properties such as the position of the local minimum of  $\Delta \tilde{f}$  or the Lindemann ratio calculated in our modified GELA are very sensitive to the interpolated (or extrapolated)  $\eta(\alpha R_s^2)$ . In fact, the use of slightly different values of  $A$  and  $B$  in equation (3.15) produces a substantial difference in the freezing properties as demonstrated for  $\Gamma_s = 180$  in figure 3. These results suggest that it is very difficult to establish, from purely theoretical considerations, a relation between the two effective liquids in the modified GELA.

We have considered only the BCC structure in this work because our analyses are not sufficiently advanced to allow discussion of the relative stability of various crystal structures.

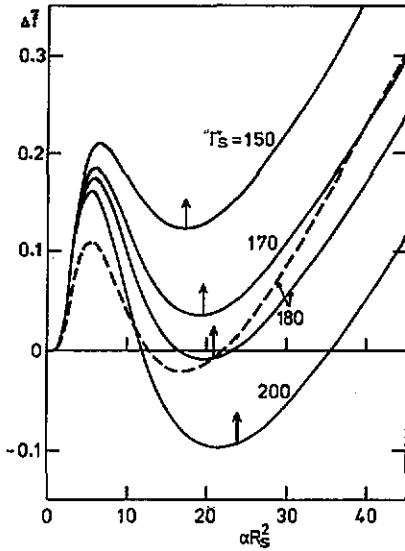


Figure 3. The free-energy difference  $\Delta \bar{f}$  (equation (3.10)) calculated in the modified GELA. Full curves: obtained using fitted  $\eta(\alpha R_s^2)$  (equation (3.15)), whose parameters  $A$  and  $B$  are given in table 1; broken curve: the result for  $\Gamma_s = 180$  obtained by using slightly different  $\eta(\alpha R_s^2)$  specified by the values of  $A$  and  $B$  in the parentheses in table 1. Note that each curve (full and broken) for  $\Gamma_s = 180$  corresponds to that in figure 2. The vertical arrow on each curve shows the position (the value of  $\alpha R_s^2$ ) at which the solid free energy is fitted to the MC result (see table 1).

#### 4. Summary and conclusions

We have studied the freezing of the OCP using the recently developed MWDA and GELA, which have been proved to be successful in predicting the freezing of hard spheres. We showed that these theories completely fail to predict freezing of the OCP into the BCC solid phase, which could have been anticipated from their failures for the soft-sphere systems [20, 21]. The present study has been primarily concerned with the analysis of these failures and with possible modifications. The results of our analysis are summarized as in the following.

(i) While the MWDA exactly reproduces the SOT result for the free energy in the limit of uniform density, it does not improve over the SOT for non-uniform densities in the case of the OCP. This result suggests that higher-order terms are not properly taken into account in the MWDA and its reasonable success for the freezing of hard spheres must be viewed as a sort of accident [23].

(ii) The formal relation between the GELA and the MWDA for the OCP is the same as that for non-Coulombic systems [19], but these theories give quite different results for the stability of the solid OCP, with much worse results in the GELA (figure 1).

(iii) It is clear that the basic assumptions in the GELA and the MWDA are responsible for the failure of these theories and must be subject to modification. The modification of the GELA is easier to implement and we have made a semi-empirical analysis of this theory using the SOT and MC results for the solid OCP. This analysis has shown that the two effective liquids, which are assumed to be identical in the GELA, must differ from each other by about 3% in the coupling constant (10% in the density) near the freezing in a successful theory (modified GELA). The analysis also suggests that it is very difficult to develop such a successful theory from purely theoretical considerations.



## Acknowledgment

Part of this work was carried out under the Visiting Researcher's Program of the Institute for Materials Research, Tohoku University, through No. 911046.

## References

- [1] Ramakrishnan T V and Yussouff M 1979 *Phys. Rev. B* **19** 2775
- [2] Haymet A D J 1987 *Ann. Rev. Phys. Chem.* **38** 89
- [3] Baus M 1990 *J. Phys.: Condens. Matter* **2** 2111
- [4] Singh Y 1991 *Phys. Rep.* **207** 351
- [5] Evans R *Inhomogeneous Fluids* ed H Henderson (New York: Dekker) at press
- [6] Haymet A D J and Oxtoby D W 1981 *J. Chem. Phys.* **74** 2559
- [7] Barrat J L, Hansen J P, Pastore G and Waisman E M 1987 *J. Chem. Phys.* **86** 6360
- [8] Rovere M and Tosi M P 1985 *J. Phys. C: Solid State Phys.* **18** 3445
- [9] Barrat J L 1987 *Europhys. Lett.* **3** 523
- [10] Iyetomi H and Ichimaru S 1988 *Phys. Rev. B* **38** 6761; 1992 *Phys. Rev. B* **45** 437
- [11] Curtin W A 1988 *J. Chem. Phys.* **88** 7050
- [12] Lutsko J F and Baus M 1991 *J. Phys.: Condens. Matter* **3** 6547
- [13] Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* 2nd edn (London: Academic) p 155
- [14] Tarazona P 1984 *Mol. Phys.* **52** 81; 1985 *Phys. Rev. A* **31** 2672
- [15] Curtin W A and Ashcroft N W 1985 *Phys. Rev. A* **32** 2909; 1986 *Phys. Rev. Lett.* **56** 2775
- [16] Baus M and Colot J L 1985 *Mol. Phys.* **55** 653
- [17] Denton A R and Ashcroft N W 1989 *Phys. Rev. A* **39** 4701
- [18] Baus M 1989 *J. Phys.: Condens. Matter* **1** 3131
- [19] Lutsko J F and Baus M 1990 *Phys. Rev. A* **41** 5547
- [20] de Kuijper A, Vos W L, Barrat J L, Hansen J P and Schouten J A 1990 *J. Chem. Phys.* **93** 5187
- [21] Laird B B and Kroll D M 1990 *Phys. Rev. A* **42** 4810
- [22] Lutsko J F 1991 *Phys. Rev. A* **43** 4124
- [23] Rosenfeld Y 1991 *Phys. Rev. A* **43** 5424
- [24] Moroni S and Senatore G 1990 *J. Phys.: Condens. Matter* **2** SA139; 1991 *Phys. Rev. B* **44** 9864
- [25] See, for example, Evans R 1979 *Adv. Phys.* **28** 143
- [26] Slattery W L, Doolen G D and DeWitt H E 1980 *Phys. Rev. A* **21** 2087; 1982 *Phys. Rev. A* **26** 2255  
 Note that the expression for the free energy  $\beta f(\rho)$  given in these papers does not contain the term  $(\frac{3}{2}) \ln(k_B T)_{\text{Ryd}}$ , part of the ideal-gas contribution (see equation (3.5) in the text).
- [27] Ogata S and Ichimaru S 1987 *Phys. Rev. A* **36** 5451
- [28] Rosenfeld Y and Ashcroft N W 1979 *Phys. Rev. A* **20** 1208
- [29] Hasegawa M and Watabe M 1985 *J. Phys. C: Solid State Phys.* **18** 2081
- [30] Jacobs R L 1983 *J. Phys. C: Solid State Phys.* **16** 273
- [31] Laird B B, McCoy J D and Haymet A D J 1987 *J. Chem. Phys.* **87** 5449
- [32] Pollock E L and Hansen J P 1973 *Phys. Rev. A* **8** 3110