Density functional theory for the freezing of soft–core fluids

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We present a simple density functional theory for the solid phases of systems of particles interacting via soft–core potentials. In particular, we apply the theory to particles interacting via repulsive point Yukawa and Gaussian pair potentials. We find qualitative agreement with the established phase diagrams for these systems. The theory is able to account for the bcc–fcc solid transitions of both systems and the re–entrant melting that the Gaussian system exhibits.

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I. INTRODUCTION

When an ensemble of particles is at a sufficiently high density, the fluid will often freeze to form a crystalline solid. This freezing is driven by the repulsion that invariably exists between particles when at close separations. The question that naturally arises is: how much repulsion is needed for freezing and what crystal structures are formed? The answer is that even particles interacting via repulsive pair potentials are formed? The answer is that even particles interacting via repulsive pair potentials may be able to freeze [1, 2, 3]. The particular crystal structure that is formed depends upon the form of the particle interactions and especially on the ‘softness’ of the decay of $v(r)$ as $r \to \infty$ [4]. Furthermore, there can be solid–solid transitions, with different crystal structures being stable in different portions of the phase diagram.

In this paper we present a simple density functional theory (DFT) [5] for determining the location of the melting and solid–solid phase boundaries for soft–core particles.

For the purposes of this paper, we define ‘soft–core’ particles as those with purely repulsive pair potentials $v(r)$, for which the integral over all space of $v(r)$ is finite, i.e. $\int dr v(r) < \infty$. Alternatively, one can define soft–core potentials as those for which the Fourier transform $\hat{v}(k)$ of the pair potential exists. Commonly encountered (model) potentials in the theory of liquids such as the Coulomb potential, the hard–sphere potential or the Lennard–Jones potential [6] do not fall into this category. However, a wide class of fluids can be modelled by particles interacting via potentials that do fall into the soft–core category. One common example is the Yukawa core model (YCM):

$$v(r) = \frac{\epsilon \exp(-\lambda r)}{\lambda r},$$

where $\lambda > 0$ and $\epsilon > 0$. Such a potential is used to model the effective interaction between charged point particles, where the Coulomb interaction between the particles is screened by a background medium. The effects of the screening are incorporated in the parameter $\lambda$ [7, 8]. Examples of systems where the particle interactions may be modelled by a Yukawa pair potential range from charged colloidal solutions [8–10] to dusty plasmas [11–14].

Another soft–core potential is the Gaussian core model (GCM):

$$v(r) = \epsilon \exp(-\lambda^2 r^2).$$

The freezing behaviour of a fluid composed of particles interacting via such a potential aroused much interest due to the novel re–entrant melting behaviour: for certain temperatures, on increasing the fluid density, the fluid freezes. However, on further increasing the density, the crystal re–melts [1]. On the other hand, the high density phase of the GCM is the fluid state [1, 15, 16, 17, 18, 19]. A Gaussian potential is used to model the effective interaction between the centres of mass of polymers, star–polymers and dendrimers in solution [4, 20]. In this case $\lambda^{-1} \approx R$, the radius of gyration of the polymers.

The DFT theory for freezing presented here is a simple qualitatively accurate theory which, for the cases we have tested, gives the correct topology of the phase diagram, including the existence of solid–solid phase transitions – i.e. the theory incorporates in a simple way much of the physics of the soft phases of soft core fluids. Furthermore, we believe the present theory is of general interest to the classical DFT community, since many DFT theories are unable to describe solid–solid coexistence. For example, in Refs. [21, 22] the authors applied DFTs that are very successful for hard–spheres to fluids composed of particles interacting via Yukawa and inverse power pair potentials and found them not to predict the bcc phase.

This paper is laid out as follows: In Sec. II we describe the DFT theory. In Sec. III we apply the theory to the GCM and then in Sec. IV to the YCM. Finally, in Sec. V we discuss our results and draw some conclusions.

II. THE DFT THEORY

Given an expression for the Helmholtz free energy of a system, one can obtain all other thermodynamic quanti-
ties. It can be shown that the Helmholtz free energy $F$ is a unique functional of the one body density profile of the system, $\rho(r)$. We can divide the Helmholtz free energy into two parts:

$$F[\rho] = F_{id}[\rho] + F_{ex}[\rho]. \quad (3)$$

The first term is the ideal gas contribution:

$$F_{id}[\rho] = k_B T \int dr \rho(r) [\ln(\rho(r)\Lambda^3) - 1], \quad (4)$$

where $T$ is the temperature, $k_B$ is Boltzmann’s constant and $\Lambda$ is the thermal de–Broglie wavelength. The excess part is given formally by:

$$F_{ex}[\rho] = \frac{1}{2} \int dr \int dr' v(r, r')\rho(r)\rho(r') \int_0^1 \text{d}g(r, r'; a) \quad (5)$$

where $g(r, r'; a)$ is the inhomogeneous radial distribution function corresponding to a system of particles interacting via the pair potential $v(r, r')$, i.e. Eq. (4) is formally derived by ‘turning–on’ the interactions between the particles (via the parameter $0 \leq a \leq 1$) and integrating $g(r, r'; a)$ as $a$ is increased from 0 to 1 keeping $\rho(r)$ fixed.

Together with the assumption that $\rho(r)$ takes the form in Eq. (4) we make the further assumption that $F_{ex}$ takes the form:

$$F_{ex} = \frac{1}{2} \sum_{i \neq j} \int dr \int dr' v(r - r') G(r - R_i)G(r' - R_j). \quad (8)$$

This constitutes an RPA like approximation for $\int_0^1 \text{d}a g(r, r'; a)$ in Eq. (4), with the ‘self–energy’ term in the summation over lattice vectors, $R_i = R_j$, being subtracted. When $\alpha$ is sufficiently large so that there is negligible overlap between the density peaks on neighbouring lattice sites, our assumption is equivalent to:

$$\int_0^1 \text{d}a g(r, r'; a) = \begin{cases} 0 & |r - r'| < l \\ 1 & |r - r'| > l, \end{cases} \quad (9)$$

where the length $l \sim b_1/2$ and $b_1$ is the distance between nearest neighbour lattice sites. This approximation therefore constitutes quite a drastic simplification of the function $\int_0^1 \text{d}a g(r, r'; a)$, which neglects much of the information about correlations in the system that this function contains.

Eq. (8) is very appealing because it takes the form of a double convolution and can therefore be written in the form:

$$F_{ex}(\rho, \alpha) = \frac{1}{2} \sum_{i \neq j} \frac{1}{(2\pi)^3} \int \text{d}k \exp(ik \cdot R_{ij}) \hat{\psi}(k)\hat{G}(k)\hat{G}(k) \quad (10)$$

where $R_{ij} = R_j - R_i$ and $\hat{G}(k)$ is the Fourier transform of $G(r)$. Since $G(r)$ is a Gaussian function, then so is $\hat{G}(k)$.

The ideal gas contribution to the Helmholtz free energy also takes a simple form if we assume $\rho(r)$ is given by Eq. (4) and we further assume that $\alpha$ takes values sufficiently large that the overlap between the Gaussian density peaks on neighbouring lattice sites is negligible. Then the ideal gas part of the Helmholtz free energy, Eq. (4), is simply (see e.g. [21])

$$F_{id}(T, N, \alpha) = N k_B T \left[ \frac{3}{2} \ln \left( \frac{\Lambda^2 \alpha}{\pi} \right) - \frac{5}{2} \right]. \quad (11)$$

Givien a pair potential $v(r)$, for which the Fourier transform $\hat{\psi}(k)$ exists, Eqs. (10) and (11) together provide an expression for the free energy $F$ which is a function of temperature, the average density $\rho$, the parameter $\alpha$ and the set of lattice vectors $\{R_i\}$. For a given state point $(T, \rho)$ and lattice structure, we assume that the parameter $\alpha$ is determined by the minimisation condition $(\partial F/\partial \alpha)_{\alpha=\alpha_{\text{min}}} = 0$ and we assume that the Helmholtz free energy $F = F(\alpha_{\text{min}})$. We can therefore calculate the Helmholtz free energy for a number of candidate crystal structures and then the equilibrium crystal structure is that with the lowest free energy. In order to determine the melting phase boundary we could compare this minimal value of $F = F/V$ with that calculated from
the theory applied to the liquid state and then perform
the common tangent construction between these free en-
gergies (which is equivalent to equating chemical poten-
tials and pressures in the coexisting phases \(1\)). In the
liquid state, where \(\rho(r) = \rho\), the ideal gas contribu-
tion to the Helmholtz free energy \(\mathcal{F}_{id}\) becomes
\[
\mathcal{F}_{id}(\rho) = Nk_B T \ln(\rho \Lambda^3) - 1,
\]
and the excess contribution, obtained from Eqs. \(5\) and \(1\), is:
\[
\mathcal{F}^{ex}_{\text{ex}}(\rho) = 2\pi N \rho \int_1^\infty dr r^2 v(r).
\]

The latter constitutes a very crude approximation for the
liquid state free energy. Given that our aim here is to
construct a theory which is above all simple, but which
is still able to provide a qualitative description of the
solid phases of soft–core particles, we choose to employ
a Lindemann criterion \(26\) to calculate the solid melt-
ing curves, rather than compare our solid free energy
with that of the liquid. The Lindemann criterion sim-
ply states that when the root–mean–square displacement,
\(\sigma \equiv \langle (r^2) - \langle r \rangle^2 \rangle^{1/2}\), of a particle about its equilibrium
position is roughly 10% of the nearest neighbour distance
\(b_1\), the crystal will melt. For the Gaussian density
profile, Eq. \(\sigma = \sqrt{3}/2\alpha\) and we determine approximate
melting boundaries from the locus defined by \(\sigma/b_1 = 0.1\).

One can improve upon Eq. \(\sigma \equiv \sqrt{3}/2\alpha\) as an approximation for
the density profile in the crystal: in order to incorporate
the effects of anisotropy in the density peaks around each
lattice site one can assume the density profile is of the
following form:
\[
\rho(r) = \sum_{i=1}^{N} \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha(r-R_i)^2} [1 + \tau \alpha^2 f(r-R_i)],
\]
where the function \(f(r) = x^4 + y^4 + z^4 - 3r^4/5\) is the
leading term for the unit cell anisotropy in cubic lattices
\(27, 28\) and \(\tau\) is an anisotropy parameter. One then
minimises the free energy with respect to \(\tau\), as well as \(\alpha\).
We attempted such an approach for the GCM, but we
found it made no significant change to the phase diagram
that we obtained from the simple choice \(\alpha\).

III. APPLICATION TO THE GCM

In the GCM, the interparticle pair potentials are given
by Eq. \(1\). The Fourier transform of this Gaussian po-
tential is also a Gaussian and so the excess Helmholtz
free energy given by Eq. \(10\) takes the particularly simple
form:
\[
\mathcal{F}^{GCM}_{\text{ex}} = \sum_{i \neq j} \frac{\epsilon \gamma^{3/2}}{2\Lambda^4} \exp(-\gamma R_{ij}^2),
\]
where \(\gamma = (1/\lambda^2 + 2/\alpha)^{-1}\) and \(R_{ij} = |R_{ij}|\). Using Eqs.
\(11\) and \(15\) as our approximation for the Helmholtz free
energy of the crystal, we calculate the phase diagram for
the GCM. The results are displayed in Fig. \(1\). Recently,
Prestipino et al. \(19\) made an accurate determination of the
GCM phase diagram using Monte Carlo simulations, so
we are able to compare with these essentially exact
results (see also Ref. \(18\)). We find, as did Prestipino et al. \(19\),
that at low temperatures, on increasing the den-
sity, the fluid first freezes to form a face–centred–cubic
(fcc) crystal, and then on further increasing the density
there is a transition from the fcc to a body–centred–cubic
(bcc) crystal \(25\) – see Fig. \(1\). Performing the common
tangent construction between the bcc and fcc free en-
ergies, we find that the two–phase region between the two
crystals is very narrow, the difference between the
coexisting densities \(\Delta \rho = 3 \times 10^{-4}\) – see also the inset
to Fig. 9 of Ref. \(18\). Since we are mostly interested in
providing a simple theory which accounts for the topol-
ology of the phase diagram, we determined the density at
which the Helmholtz free energy of the bcc equals that
of the fcc structure for a given temperature \(31\). The
resulting line is plotted in Fig. \(1\). The present theory also
accounts for the most striking feature of the GCM phase
diagram: the re–entrant melting of the bcc phase – i.e. for
a given (low) temperature, on increasing the fluid den-
sity it freezes, but on further increasing the density the
crystal remelts. The high density phase of the GCM is a
fluid. This means there is also a maximum temperature for
which there is crystal. The present theory predicts this
maximum to be at a temperature \(k_B T/\epsilon \approx 0.012\),
whereas it is actually at \(k_B T/\epsilon \approx 0.009\) \(19\). In general,
the present theory over estimates the region of stability
for the solid phases.

We also determine an approximate melting boundary
by calculating the locus in the phase diagram where the bcc free energy equals the liquid state free energy \[23\], where the liquid Helmholtz free energy is calculated using the crude approximation, Eq. \[13\], which for the GCM becomes:

\[
\mathcal{F}_{ex}^{GCM,liq} = \frac{1}{2} N \rho \pi^{3/2} \epsilon^{\lambda} - \frac{3}{2} \left[ \frac{2M}{\sqrt{\pi}} \exp(-\lambda^2 l^2) + \text{erfc}(\lambda l) \right],
\]

where \(\text{erfc}(x) = 1 - 2\pi^{-1/2} \int_x^\infty dt \exp(-t^2)\) is the complementary error function. Whilst we know \(l \approx b_1/2\), there is no constraint on a particular value. We choose the value \(l \approx 0.58(2/\rho)^{1/3}\) (recall that for the bcc crystal \(b_1 = (\sqrt{3}/2)(2/\rho)^{1/3}\)). This value of \(l\) is chosen so that the maximum temperature that freezing occurs is predicted to be roughly at the same temperature as that from the results of Prestipino et al. \[19\]. Note, on the scale of Fig. 2, using this approach there is no difference between the predicted locations of the bcc–liquid melting boundary and the fcc–liquid melting boundary. Given the crude nature of the theory for the liquid, the results are surprisingly good – see Fig. 2.

The main feature of the GCM phase diagram that is not accounted for by the present theory, and which can be seen in the results of Prestipino et al. \[19\] (see also Fig. 1), is that the transition line between the fcc and bcc phases is not the (almost) straight line predicted by the present theory. Instead, on following the fcc–bcc boundary as the temperature is increased, the boundary obtained in simulation curves over to lower densities and in fact reaches a maximum and then bends down to lower temperatures and densities, such that there is a small window in the phase diagram where for temperatures around \(k_B T/\epsilon \approx 0.0035\), on increasing the density, the fluid first freezes to form the bcc, then the fcc and then the bcc phase again, before finally re-melting \[19\].

This bending over of the fcc–bcc boundary was ascribed to anharmonic effects in the crystal \[19\]. In an attempt to incorporate this effect we assumed the density took the form given in Eq. \[14\]. Within the present theory anharmonic effects do indeed become more significant in the high temperature part of the fcc portion of the phase diagram. However, they do not become significant enough to result in the fcc–bcc boundary curving over, as in the results of Prestipino et al. \[19\]. Assuming \[14\] leaves the phase diagram unchanged when plotted on the scale given in Fig. 1.

For the results presented in Fig. 1 we summed over 40 shells of lattice vectors (including any more does not change the value calculated for the free energy). However, it is interesting to note that if one includes only the first two shells – i.e. nearest neighbour and next nearest neighbour contributions only, then the results are qualitatively unchanged \[22\]. This is not too surprising, given the short ranged nature of the GCM pair potential.

### IV. APPLICATION TO THE YCM

The Fourier transform of the YCM pair potential, Eq. \[11\], is \(\tilde{v}(k) = 4\pi\epsilon\lambda^{-1}(\lambda^2 + k^2)^{-1}\). Using this, together with Eq. \[10\], we obtain the following expression for the YCM excess Helmholtz free energy:

\[
\mathcal{F}_{ex}^{YCM} = \sum_{i\neq j} \frac{\epsilon \lambda^{1/2}\alpha}{4\lambda R_{ij}} \left[ e^{-\lambda R_{ij}} \text{erfc} \left( \frac{\lambda}{\sqrt{2}\alpha} - R_{ij} \sqrt{\frac{\alpha}{2}} \right) - e^{\lambda R_{ij}} \text{erfc} \left( \frac{\lambda}{\sqrt{2}\alpha} + R_{ij} \sqrt{\frac{\alpha}{2}} \right) \right].
\]

This approximation, together with Eq. \[11\], is our expression for the Helmholtz free energy of the solid phases of the YCM. For a given state point \((\rho, T)\) and set of lattice vectors \(\{R_i\}\), we minimise the free energy with respect to the parameter \(\alpha\). We estimate the melting boundaries using the Lindemann criterion – i.e. the locus defined by \(\sigma/b_1 = 0.1\). In Fig. 3 we display the resulting phase diagram. For the YCM, the crude estimate for the liquid state excess Helmholtz free energy, Eq. \[13\], does not give physically acceptable results. For some choices of \(l\) in \[13\] it (incorrectly) predicts that the YCM exhibits re-entrant melting. We therefore employ only the Lindemann criterion for determining melting boundaries in this section.

The low density portion of the YCM phase diagram is qualitatively similar to that of the GCM – i.e. for sufficiently low temperatures, on increasing the density the fluid first freezes to form an fcc crystal, then, at higher densities, there is a transition to the bcc. The biggest difference between the YCM and the GCM phase diagram is that there is no re-entrant melting in the YCM. This is because the divergence of the YCM pair potential as \(r \to 0\) means that the particles behave more and more like hard spheres as the density is increased, where the
that a divergence in the pair potential at temperatures. For the GCM this is not the case. Note that in the YCM phase diagram that we obtain together with that of Hamaguchi et al. [34], plotted in terms of the variables $\Gamma = \beta \psi / \lambda a$ of Hamaguchi et al. [34] (see also Refs. [33, 34, 35, 36, 37, 38, 39, 40, 41]), plotted in terms of the variables $\Gamma = \beta \epsilon / \lambda a$ and $\kappa = \lambda a$, where $a = (3/4\pi \rho)^{1/3}$. These are commonly considered variables when using the Yukawa potential [11] to model the interactions in plasma systems. We see that the present simple theory is able to account qualitatively for the YCM phase diagram.

V. DISCUSSION AND CONCLUSIONS

We have constructed a simple DFT for the solid phases of soft-core particles. The theory is able to account for the transition from a fcc to a bcc solid and also able to determine whether the system exhibits re-entrant melting, as is the case for the GCM, or not, as in the case for the YCM (when a Lindemann criterion is used to determine the melting boundaries). This makes the DFT useful, since many DFTs are not able to describe solid–solid coexistence in soft core fluids [21, 22]. There are some DFT theories able to describe solid–solid transitions in other (hard–core) model fluids – see for example Refs. [1, 42, 43]. In fact, the present theory bears some similarities in its structure to that of Likos et al. [1, 42]. This can be traced to the use of the Gibbs–Bogoliubov inequality to construct their theory. When one applies this inequality, one obtains the following equation (Eq. (4.18) in Ref. [1]):

$$\mathcal{F}[\rho] \leq \mathcal{F}_0[\rho] + \frac{1}{2} \int dr \int dr' g_0(r, r') \rho(r) \rho(r') v(r - r'),$$

(18)

where $g_0$ and $\mathcal{F}_0$ are the pair distribution function and the Helmholtz free energy respectively of the reference system; Likos et al. [1, 42] used a hard–sphere fluid as the reference system. If we compare Eq. (18) with Eq. (6) we can see that depending on our approximations for $g_0(r, r')$ in (18) and $\int_0^1 \delta g(r, r'; \alpha)$ in (6), one can end up with theories that have a similar structure.

One also sees similar features when we compare our expression for the GCM Helmholtz free energy, Eqs. (11) and (12), with that obtained by Lang et al. [1, 18] using the Gibbs–Bogoliubov inequality together with the Einstein model as their reference system. Their resulting Helmholtz free energy is almost exactly the same as that in the present theory (the free energies differ only by $k_B T$ per particle, with that of Lang et al. being lower). In the theory of Lang et al. [1, 18] the Einstein model spring constant is the variational parameter for minimising the free energy, whereas in the present theory it is the parameter $\alpha$ in Eq. (9). However, formally these parameters play exactly the same role. Use of the Gibbs–Bogoliubov inequality therefore seems to lead to theories with a structure similar to the theory presented here. When taking our present approach, i.e. using the Lindemann criterion to determine the melting boundaries, the difference of $N k_B T$ between the Helmholtz free energy of the present theory and that of Lang et al. [18] makes no difference since this term is independent of $\alpha$. However, it would matter if we were to compare our result

![FIG. 3: Phase diagram of the YCM. The solid line is the bcc melting boundary and the dashed line is the fcc melting boundary, both determined using the Lindemann criterion – see the text. The dot–dashed line is the locus of points where the Helmholtz free energies of the bcc and fcc phases are equal.](image)

![FIG. 4: Same as Fig. 3 except here the results are plotted in terms of the variables $\kappa$ and $\Gamma$. The symbols joined by solid lines are the simulation results of Hamaguchi et al. [34].](image)
for the solid free energy with that obtained for the liquid from some other theory, more accurate than that from Eq. (13).

Some soft core fluids exhibit freezing to states with multiple occupancies of each lattice site [1, 14]. In order to apply the present theory to such systems, some modification of the theory is required. Firstly, one must assume a generalisation of Eq. (6) for the density profile of the crystal:

$$\rho(r) = \eta \sum_{i=1}^{N} \left( \frac{\alpha}{\pi} \right)^{3/2} e^{-\alpha(r-R_i)^2}, \quad (19)$$

where $\eta$ is the average lattice site occupancy. $\eta$ should be treated as a parameter to minimise the Helmholtz free energy, in the same way as with the parameter $\alpha$. In this case, there would be two minimisation conditions to be satisfied: $(\partial F/\partial \alpha)_{\alpha=\alpha_{\text{min}}, \eta=\eta_{\text{min}}} = 0$ and $(\partial F/\partial \eta)_{\eta=\eta_{\text{min}}} = 0$. One would then assume that the Helmholtz free energy $F = F(\alpha_{\text{min}}, \eta_{\text{min}})$. This would also be the scheme to apply if one intended to study the effect of lattice defects in the present YCM and GCM systems. However, in these cases one would expect $\eta \approx 1$. For systems exhibiting multiple occupancies of each lattice site, we expect one would also have to make a different approximation for the function $\int_0^\infty \rho_{\text{eq}}(r, r'; \alpha) \, dr$ in Eq. (3). We would propose the following generalisation of Eq. (3):

$$\mathcal{F}_{\text{ex}}[\rho] = -\frac{\eta}{2} \sum_{j=1}^{N} \sum_{i=1}^{N} (\eta - \delta_{ij}) \int dr \int dr' v(r, r') G(r - R_i) G(r' - R_j) \quad (20)$$

From a more general point of view, the present theory seems to provide a good qualitative description of the solid phases of soft-core systems. The Yukawa potential, $\phi$, is used to model the effective interaction between charged colloidal particles [12, 23, 33, 46]. For example, the phase diagram of polystyrene particles suspended in a potassium chloride solution can be mapped on to that of the YCM [14]. The present theory should also be relevant to soft matter systems, for example polymeric micelles [7, 8, 9, 10], star polymers [33] and dendrimers [46]. Given an effective pair potential $v(r)$ between such objects [11], one could use the present theory to calculate an approximate phase diagram.

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regions of the phase diagram where the system is a fluid. However, one must be aware that as $\alpha \to 0$, Eq. (11) gives a spurious divergence $\to -\infty$ in the free energy.

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