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"The thermodynamics of small inhomogeneous systems"

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submitted by   Professor Leslie V Woodcock PhD

Scientific Simulation Services

Department of Chemistry

UMIST Faraday Building

Manchester M60 1QD

Declaration:

I certify that there were no subject inventions to declare during the performance
of this grant.   Leslie V Woodcock: 20th September 2004

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M117 Faraday Building
UMIST
Manchester M60 1QD
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14. ABSTRACT

This report results from a contract tasking Scientific Simulation Services as follows: The contractor will conduct a comprehensive review of the studies of thermodynamics of small systems, including under non-negligible gravity, and its application to processing. The contractor will develop a computer program that starts with input of the material's thermodynamic equations of state in the thermodynamic limit, and predicts the state and profiles of the inhomogeneous small system in a gravitational field. The contractor will predict the properties of a fluidized system of nano-particles and its phase and state behavior under gravity. The contractor will test that prediction against a granular dynamics computer simulation of the steady-state properties of a system of nano-particles under gravity.

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Summary

A computer simulation program based upon local density functional approximation for predicting the surface crystallization of a thermodynamically small system under gravity has been developed and is here tested.

Using the model of the classical soft-sphere fluid, the state parameters for such systems are identified. A generalized phase diagram based upon the scaling variables has been obtained; systems with the same reduced-state parameters exhibit identical profiles of thermodynamic properties such as density, pressure and intrinsic chemical potential, measured in the direction of the applied field.

The point thermodynamic approximation of Rowlinson and the local density approximation (LDA) of the density functional formalism, are compared with our computer simulation results and found to be remarkably accurate.
A configurational temperature is defined and shown to agree with the corresponding kinetic temperature for small inhomogeneous systems at equilibrium.

The test findings may have resulted in the discovery of interfacial mesolayers, not seen in the thermodynamic limit large system description. The structural profiles at the crystal-fluid interface are indicative of a meso-layer, between the two thermodynamically stable phases (large system limit) of lower density crystal, not previously observed.

1. Background: literature survey [1] and software [2]

A computer program has been written and developed that predicts the steady-state behavior of assemblies of fluidized colloidal particles under gravity. The program begins with the theoretical tenets of a developing field, i.e. the thermodynamics of small systems, to predict how a small inhomogeneous thermodynamic system, of known thermodynamic-limit properties, equilibrates under a gravitational field.

The question to be addressed is "can this equilibrated state be predicted from the known thermodynamic properties of the same system in the thermodynamic limit"?

This project has obtained the law of corresponding states between the inhomogeneous thermodynamic system, and a steady-state quasi-thermodynamic inhomogeneous granular system of fluidized nanoparticles.

The science of the thermodynamics of small systems has not been properly recognized as the science underlying and underpinning the now booming research industry into nano-materials and their self-assembly. The first objective and deliverable [1] was a comprehensive literature search and review of the studies of thermodynamics of small systems (i.e. under non-negligible gravity) and its application hitherto, to processing.

A computer program has been developed and submitted [2] that starts with the input of the thermodynamic equations of state of a material in the thermodynamic limit, and predicts the state and profiles of the inhomogeneous small system in a gravitational field. The objectives of this program are (i) to predict the properties of a fluidised system of nano-particles and its phase and state behavior under gravity, and (ii) to test that prediction against a granular dynamics computer simulation of the steady-state properties of a system of nano-particles under gravity.

2. Introduction to final report

Thermodynamics of macroscopic systems is treated using principles of statistical mechanics but these are valid for infinite systems and require modification to be able to describe thermodynamics of small, finite systems. Development of a thermodynamics of small systems began in the 1960s when Hill derived general equations applicable to non-macroscopic systems, which in the limiting case of an infinite system would reduce to "ordinary thermodynamics" [3]. Instead of deriving the fundamental relations between thermodynamic quantities in the various statistical mechanical ensembles for application to small systems, an alternative approach is to adopt a quasi-thermodynamic approximation and to use density functional theory. This leads to a variety of approximations of increasing complexity, as the accuracy of the theoretical predictions is increased.

The systems that we are interested in are small, not simply because of the number of molecules but because the system itself is characterized by a finite length scale. This characteristic length may be determined by an externally imposed field or in the case of an interface, it is of the order of the range of intermolecular forces [4,5]. The system becomes "smaller" as this characteristic length approaches the correlation length of the liquid. In this sense, all inhomogeneous systems in an external field are small to some extent with the "smallness" directly related to the inhomogeneity.

According to Rowlinson [4], the correlation length of a liquid is equal to the range of the intermolecular forces except at the critical point where it diverges to infinity. Under an external field, if the characteristic length is much greater than the correlation length of the fluid, then local thermodynamic functions can be defined, that are functions of other well-defined local variables. If there is more than one fluid phase, however, then effect of a weak external field may not be trivial.

In the present work, the concept of a local thermodynamics is tested for the classical soft-sphere fluid under gravity, by making use of the unique scaling properties. The fluid under gravity is an example of a small system with its "smallness" varying with the strength of the gravitational field. Such a system exhibits characteristic profiles of thermodynamic properties in the direction of the gravitational field. As in the case of a homogeneous system at equilibrium, the temperature and total chemical potential is uniform throughout the system but the gravitational field induces a pressure and density gradient in the direction of the field.

Here, the principle objective is to derive, and test by computer simulations, equations for the temperature, pressure and density profiles of such a system under the influence of gravity. The starting point for such theoretical predictions are the known thermodynamic properties of state in the thermodynamic limit. The soft-sphere fluid has known accurate equations of state for both the crystal and fluid phases. The thermodynamic chemical potential and freezing point parameters are also well known. The unique scaling properties of the soft-sphere fluid, moreover, mean that the state of the small inhomogeneous system, under gravity, cannot depend separately on the temperature and gravitational constant. The overall thermodynamic state description is therefore considerably simplified in this model case.

3.   Scaling and Reduced Units

The soft-sphere fluid with the potential of interaction, $\phi(r) = \varepsilon \left(\dfrac{\sigma}{r} \right)^{12}$, was chosen due to its unique scaling properties. As a result of the inverse power law, the state of the system and all the excess thermodynamic properties in that state are determined by a single hybrid parameter[4, 5], $\rho^4 \varepsilon / k\,\mathrm{T}$. The density, ρ and temperature, T cannot be varied independently. In contrast, for the Lennard-Jones system, two parameters e.g., temperature and density are required to completely determine the system state. The equation of state for the soft-sphere fluid and solid regimes is known within statistical accuracy [5] and is a function only of the hybrid parameter, $\rho^4 \varepsilon / k\,\mathrm{T}$.

We introduce gravitational units where the unit of mass is the mass of a soft-sphere

particle, m, the unit of distance is the diameter σ, the unit of energy is $mg\sigma$ and the unit

of time is $\left(\dfrac{\sigma}{g}\right)^{\frac{1}{2}}$. The soft-sphere potential energy, ε, is set equal to $mg\sigma$.

$$\varepsilon = mg\sigma \qquad\qquad\qquad \text{Equation 1}$$

So that the interparticle potential is

$$\phi(r) = \varepsilon(\sigma/r)^{12} = mg\sigma(\sigma/r)^{12} \qquad\qquad \text{Equation 2}$$

The reduced (number) density, pressure and temperature are as per the common

definition (distinguished by an asterisk):

$$\rho^* = \frac{N\sigma^3}{V}, \qquad T^* = \frac{k_B T}{mg\sigma}, \qquad P^* = \frac{P\sigma^3}{mg\sigma} \qquad\qquad \text{Equation 3}$$

We will also use the expression for density and pressure in soft-sphere reduced units. As

mentioned before, the soft-sphere system is unique in that the hybrid parameter [4, 5],

$\widetilde{\rho}_{ss}$ solely determines the state of the homogenous soft-sphere system in the

thermodynamic limit and it is defined as,

$$\widetilde{\rho}_{SS} = \frac{N\sigma^3}{V}\left(\frac{\varepsilon}{kT}\right)^{5/4} = \rho^*/(T^{*0.25}) \qquad\qquad \text{Equation 4}$$

The soft-sphere reduced pressure is defined as :

$$\widetilde{P}_{SS}(\widetilde{\rho}_{SS}) = \frac{PV}{NkT}\widetilde{\rho}_{ss} = (P^*)\left(\frac{1}{T^*}\right)^{\frac{5}{4}} \qquad\qquad \text{Equation 5}$$

The temperature in soft-sphere reduced units is the same as the definition in equation 3.

For brevity we will use ε instead of $mg\sigma$ keeping in mind that they are equal to each

other by definition.

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The main difference between the homogeneous soft-sphere system and the inhomogeneous soft-sphere system under gravity is that the number density is not constant and a single $\tilde{\rho}_{ss}$ cannot be defined in the latter. As will be shown in the subsequent sections, the soft-sphere scaling is still applicable in conjunction with the local density approximation. However, instead of a single parameter required to describe the homogeneous soft-sphere system, two parameters are required to completely describe the inhomogeneous system. In section 4, we identify these two state variables. Note from equation 3, that temperature and gravity cannot be varied independently, i.e., increasing g is equivalent to reducing T and vice-versa.

4.   MD Simulation tests

The molecular dynamics simulations were carried out at the desired temperature using the isokinetic constraint method [8] combined with the leap-frog verlet integration scheme [9]. Systems of 2400, 3600 or 4800 particles were first equilibrated at the desired $\tilde{\rho}_{SS}$ under periodic boundary conditions in all directions. A very large system of 16800 particles was also studied to obtain more detailed structural information on the structure of the inhomogeneous crystal-fluid interface. Gravitational force was then included in the simulation and the force in gravitational units, g*, is equal to -1.0 in the Z-direction. All the systems are periodic in the X-Y plane, and aperiodic in the Z-direction due to a structureless hard base, and condensation at the base could be observed due to the gravitational force. If a particle collides with the hard base, then its position is restored to

that before the collision while the Z-component of the new velocity is reversed. In the presence of gravity the number density is conserved without the need for a roof on the box.

The equilibration under gravity with an aperiodic base takes relatively longer (greater than 120000 cycles with time step $10^{-3}\sqrt{\dfrac{\sigma}{g}}$) compared to simulation of homogeneous systems with periodic boundary conditions. For the low temperature state, $T^* \sim 1.0$, the equilibration time is even longer as the system configuration does not change much due to the small velocities and small rate of momentum exchange. To speed up the equilibration time for systems in the low temperature states, the system was first equilibrated under gravity at a higher temperature and gradually brought down to the desired temperature. It might be important to reduce the temperature gradually and to let the system come to equilibrium at each of the intermediate temperatures. If the initial equilibration is done at a high temperature and then the system is quenched all of a sudden to the desired low temperature, this might effectively freeze the system at the equilibrium configuration of the high temperature simulation.

5.   Configurational temperature

There are many ways to find out whether the molecular dynamics simulation has reached equilibrium, the most obvious being that of thermal equilibrium where the temperature over the entire inhomogeneous system has to be equal within statistical accuracy. Configurational temperature presents another measure of determining whether the system

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has reached equilibrium because at equilibrium, the configurational temperature [8] and

kinetic temperature should be equal to each other upto $O\left(\dfrac{1}{N}\right)$. The configurational

temperature was calculated using the following equation [9] :

$$k_B T_{config} = \frac{\left\langle \sum\limits_{i=1}^{N} \mathbf{F}_i^2 \right\rangle}{\left\langle -\sum\limits_{i=1}^{N} \sum\limits_{j \neq i} \nabla_{r_{ij}} \bullet \mathbf{F}_{ij} \right\rangle}, \text{where,} \quad \mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij} = -\sum_{j \neq i} \frac{\partial \phi(r_{ij})}{\partial \mathbf{r}_{ij}}$$

For the soft-sphere potential, $\phi(r_{ij}) = \varepsilon(\sigma / r_{ij})^n$ and $n = 12$, the configurational

temperature is given by

$$k_B T_{config} = \frac{\left\langle \left[\sum\limits_{i=1}^{N} \sum\limits_{\substack{j=1 \\ j \neq i}}^{N} n.\frac{\vec{r}_{ij}}{r_{ij}^2}.\phi(r_{ij}) \right]^2 \right\rangle}{\left\langle (n^2 - n).\sum\limits_{i=1}^{N} \sum\limits_{\substack{j=1 \\ j \neq i}}^{N} \frac{\phi(r_{ij})}{r_{ij}^2} \right\rangle} \qquad \text{Equation 6}$$

For soft-sphere systems, under gravity, the Hamiltonian includes a gravitational potential

energy term, which depends only on the z-coordinate of the particles. Instead of $\phi(r_{ij})$,

substituting the total potential energy in a gravitational field,

$\phi^g(r_i) = \sum\limits_{\substack{j=1 \\ j \neq i}}^{N} \phi(r_{ij}) + (r_{zi} - r_0)$, into equation 6, we have the expression for configurational

temperature of soft-spheres under gravity in gravitational reduced units,

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$$k_B T_{config} = \frac{\left\langle \sum_{i=1}^{N} F_{xi}^2 + F_{yi}^2 + (F_{zi} - 1)^2 \right\rangle}{\left\langle (n^2 - n) . \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{\phi(r_{ij})}{r_{ij}^2} \right\rangle}$$

Equation 7

$$F_{xi} = \sum_{\substack{j=1 \\ j \neq i}}^{N} n. \frac{r_{xij}}{r_{ij}^2}. \phi(r_{ij}), F_{yi} = \sum_{\substack{j=1 \\ j \neq i}}^{N} n. \frac{r_{yij}}{r_{ij}^2}. \phi(r_{ij}) \text{ and } F_{zi} = \sum_{\substack{j=1 \\ j \neq i}}^{N} n. \frac{r_{zij}}{r_{ij}^2}. \phi(r_{ij})$$

The choice of the height of zero gravitational potential energy does not affect equation 7.
It is noted that a similar modification to take into account the 'g' contribution to the
Hamiltonian is not made for the calculation of the average Z-component of the pressure
tensor, P_{ZZ}, using the virial equation derived from the classical virial theorem [8].

The particles in the inhomogeneous system were segregated into horizontal layers of
width $1.0*\sigma$ based on the value of the z-coordinate as shown in figure 1.We define
configurational temperature of each layer, even though it is a non-local property. The
configurational temperature profile was also plotted in [12] and was found to give
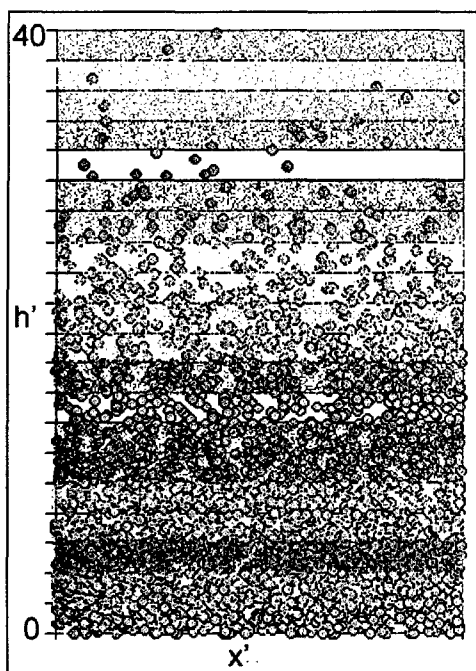meaningful results compared to the kinetic temperature profile.

Figure 1 Inhomogeneous system with a field applied in the Z-direction; the system is divided into horizontal layers as shown above and thermodynamic profiles are collected.

The configurational temperature for a horizontal layer within the system, was calculated from equation 7 but the summation over all particles in the system was replaced by the summation over all particles lying in the particular horizontal layer.
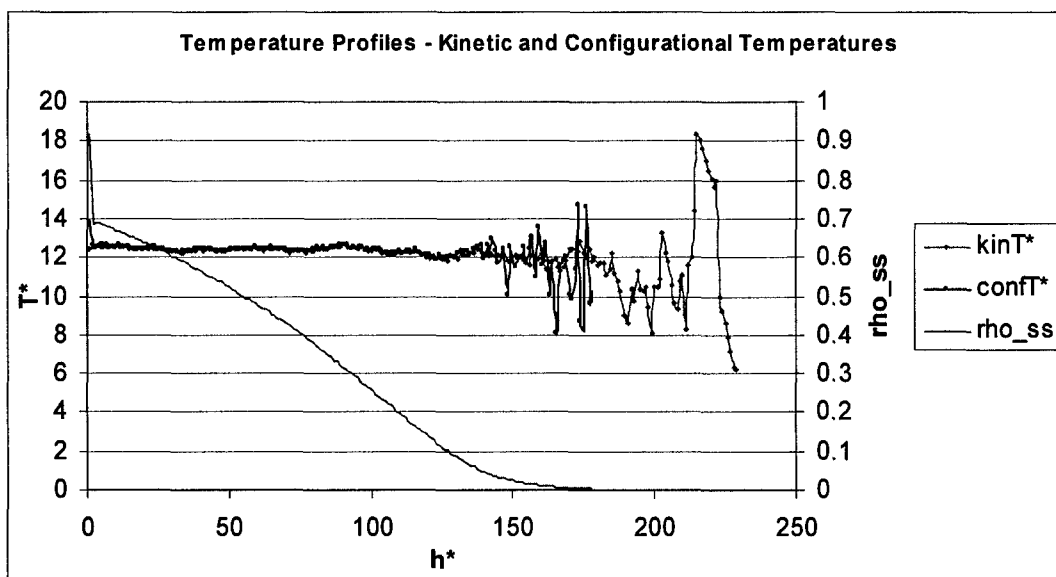

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Figure 2 Kinetic and configurational temperature profile for system under gravity with N=2400, base area of the simulation box, A* = 106.995and T* = 12.4.

Extremely high configurational temperatures obtained for the very low-density top layers, with packing fractions less than 0.2% and these have not been plotted for clarity. Configurational temperature is calculated from inter-particle interactions and as mentioned in [9], the configurational expression will differ from the kinetic temperature at low densities where the number of particle interactions per time-step is small. As can be seen from figure 2, in the bulk of the inhomogeneous system, the configurational temperature is found to be close to the kinetic temperature. The deviation from kinetic temperature at the layer next to the bottom wall may be attributed to the fact that the contribution of the structure-less wall to the Hamiltonian was not taken into account in equation 7.

6. System states and functionals under gravity

Two systems belong to the same state point if they have identical temperatures and pressure and density profiles. The parameters N/A^* and T*, were identified as the state variables that define the state of the soft-sphere fluid system under gravity and plots of simulation data in figures 3-5 confirm this. N is the total number of particles in the system, A^* is the base area of the simulation box in reduced units where gravity is applied normal to this area and T* is the temperature in reduced units of the system.

In figure 3, the two systems have the same value for the surface density parameter N/A* ~ 107(106.995 to be exact) but have different temperatures. The density profiles for system A(N_A = 2400) and B(N_B = 2400) differ as they belong to different states with different T*.
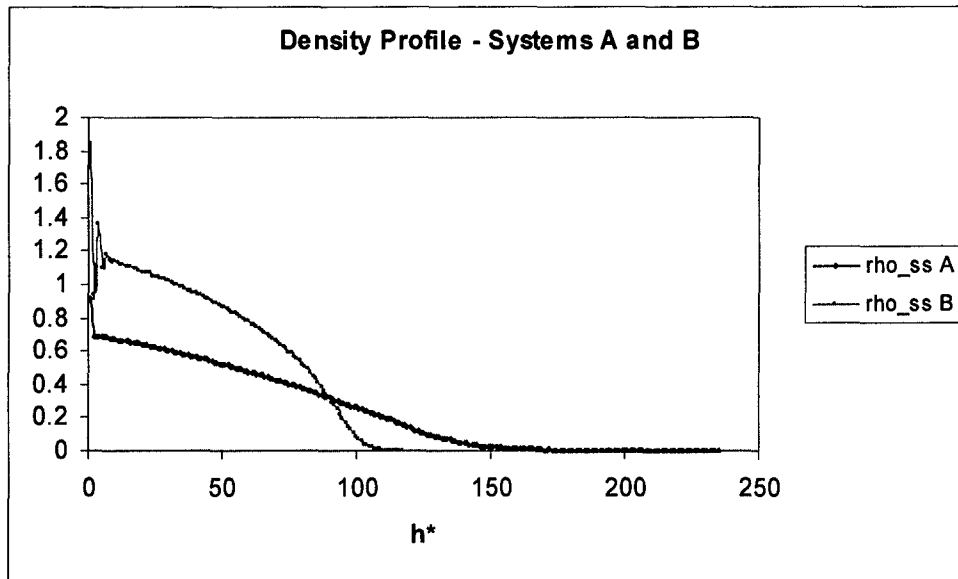

Figure 3 System A - N/A* = 106.995, T* = 12.4; System B – N/A* = 106.995, T* = 3.2

In figure 4 the two systems A(N_A = 2400) and C(N_C=4800) have the same value for the surface density parameter N/A*~107(106.995) and reduced temperature, T*. The two systems belong to the same state point with identical density profiles.
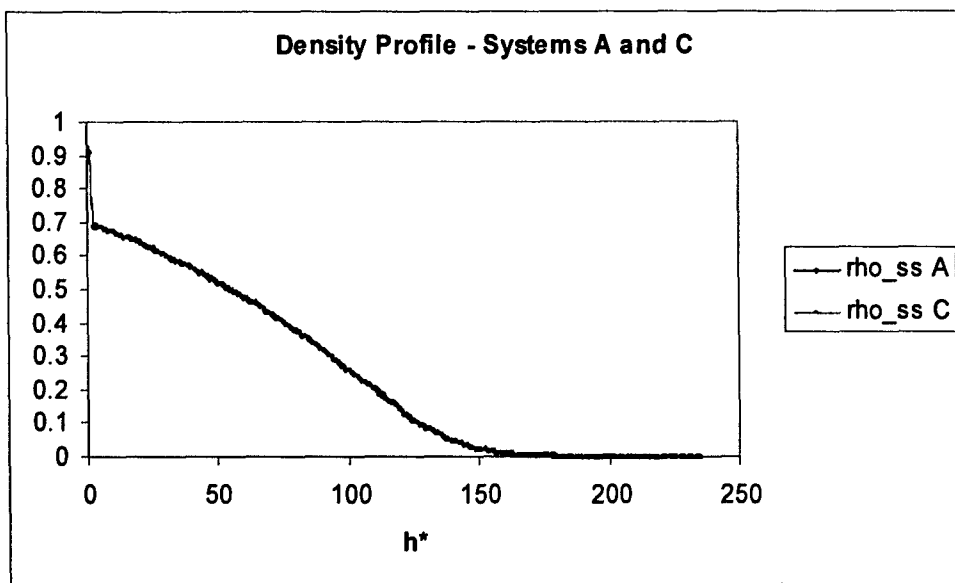
Figure 4 System A and C are at the state point N/A*= 106.995 and T*=12.4.

In figure 5, the two systems A(N_A = 2400) and D(N_D=1280) are at the same temperature, T* but have different values of the surface density parameter.
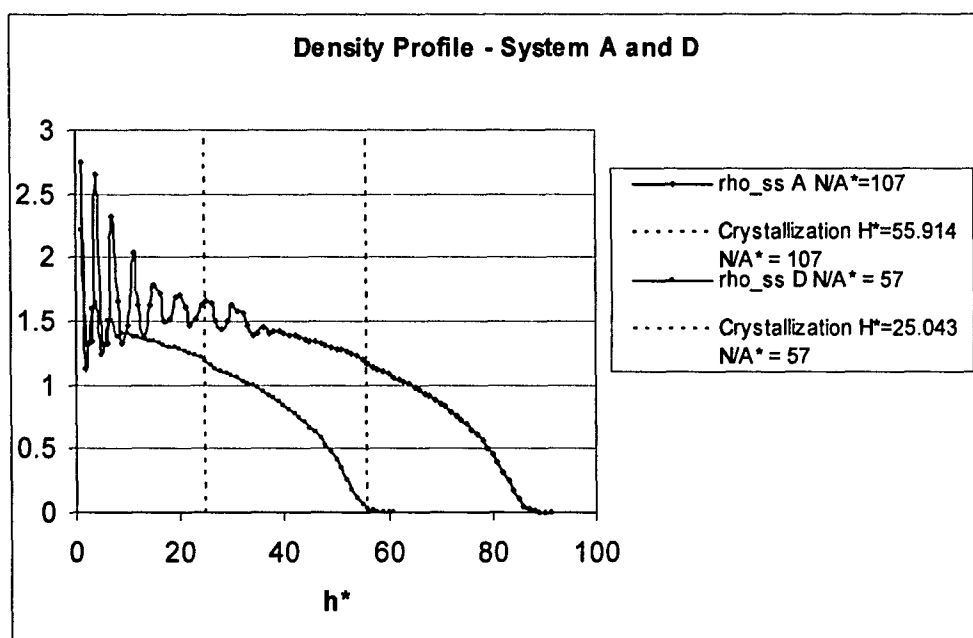

Figure 5 System A-N/A* ~ 107(106.995), T* = 1; System D-N/A* ~ 57(56.543), T* = 1

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From equations 12 and 13 in the next section, it is clear that density profiles of two

systems at the same T*, will exhibit the same *variation* of density with height. But for

different N/A* the density profiles differ by a constant offset in the height. Hence, a

system with a smaller N/A* can be considered as a sub-system of another system with a

larger N/A* at the same T*. The system can then be effectively considered to be

described by the single parameter, the reduced temperature, T*. This is confirmed in

figures 6-7 for two different values of T*. The density profile of systems with a smaller

N/A* is shifted by an offset so that, it overlaps with the density profile of another system

with a larger N/A* at the same T*.

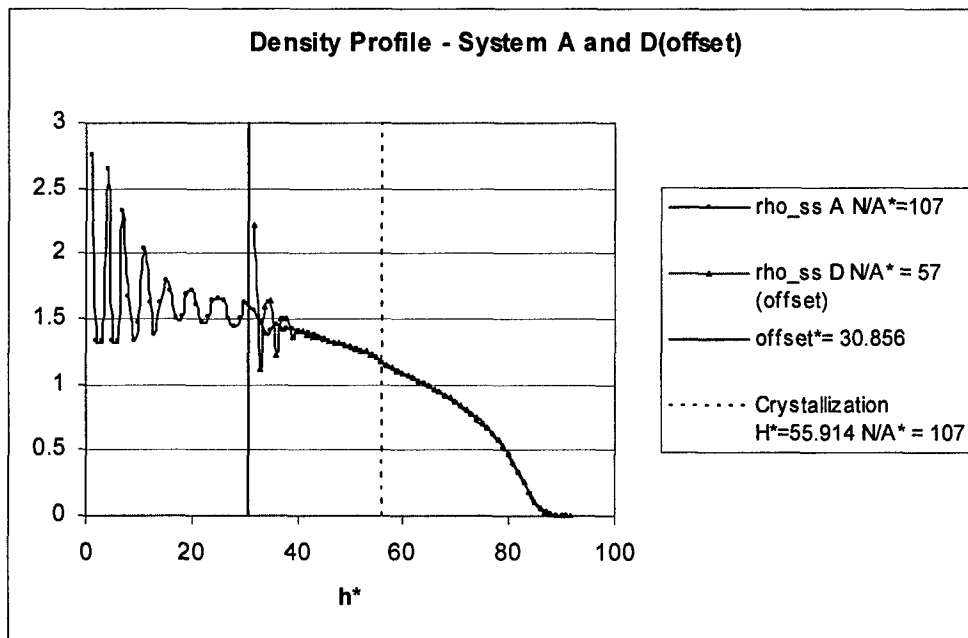
Figure 6 The two interfacial systems A and D at T*=1 can be considered as sub-systems of a single system characterized by T*: increasing N results in increasing the amount of crystal while the fluid density profile remains the same.
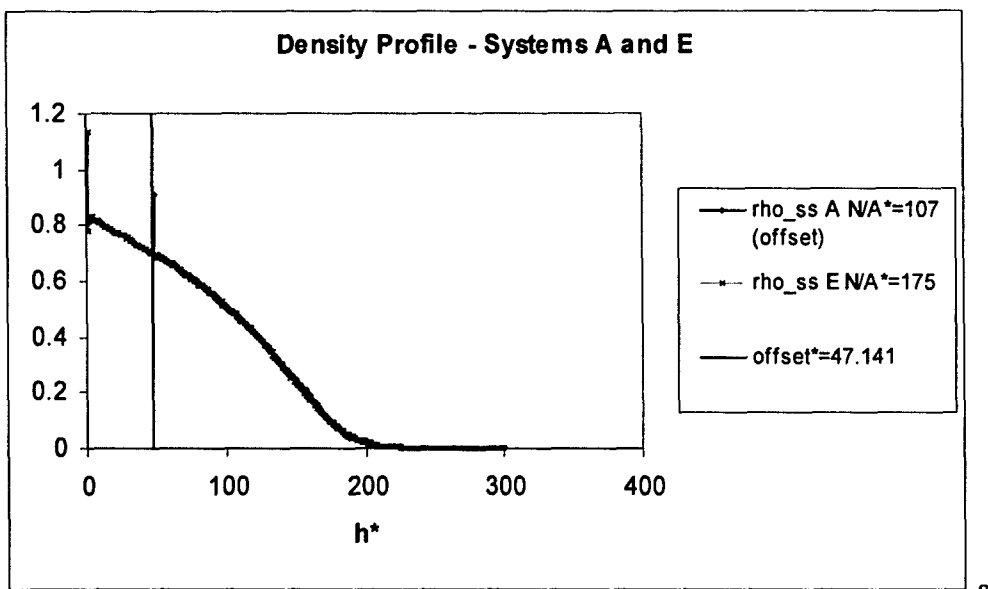
Figure 7 System A-N/A* = 107(106.995), T* = 12.4 and System E-N/A* = 175(174.994), T*=12.4; system A density profile is shifted by a constant offset of Δh* = 47.141 and overlaps with System E density profile.

It should be emphasized here that the these inhomogeneous systems can be described by just two state parameters (or one !) due to the fact that they are composed of soft-spheres and the properties of thermodynamically large, homogeneous soft-sphere systems are applicable on a local scale as long as density varies over a distance larger than the correlation length. The profiles above were generated by dividing the system into horizontal layers of width 1.0*σ.

7.   Thermodynamic profiles for the inhomogeneous fluid system

At equilibrium, the soft-sphere system under gravity satisfies the condition of thermal, mechanical and chemical equilibrium. In this section, the condition of mechanical equilibrium is used to derive expressions for the thermodynamic profiles of this system.

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The main assumption in the derivation below is that the length scale of the inhomogeneity due to the external field is much larger than the correlation length of the fluid, so that a local definition of pressure, density and temperature is valid.

Consider a horizontal layer of particles of thickness Δh at height h such that Δh is small enough to assume a constant density $\rho(h)$ over the layer. In this case, the point thermodynamic approximation of Rowlinson/ local density approximation is valid and the thermodynamic state of this layer is equivalent to that of the corresponding homogenous, thermodynamically infinite, soft-sphere system with soft-sphere reduced density equal to $\tilde{\rho}_{ss} = \rho(h)\sigma^3 \left(\dfrac{\varepsilon}{kT} \right)^{\frac{1}{4}}$, where T is the temperature of the inhomogeneous system under study.

The condition of mechanical equilibrium under an external field can be written as [2]:

$$\nabla \cdot P(\vec{r}) + \rho(\vec{r})\nabla v(\vec{r}) = 0$$

where, $v(\vec{r})$ is the potential due to the external field at the point $\vec{r}$, e.g, due to the gravitational field and the field of force generated by the walls of the containing vessel. The force equation for the pressure in a gravitational field is given by ,

$$dP(h) = -\rho(h)mgdh \qquad\qquad \text{Equation 8}$$

$P(h)$ is the pressure and $\rho(h)$ is the number density at height, h, in the simulation box. m is the mass of a single particle and g is the gravitational acceleration. At static equilibrium and except near wall-fluid or solid-fluid interfaces, the pressure at any height h is isotropic and the diagonal elements in the pressure tensor, P_{XX}, P_{YY} and P_{ZZ} are equal in value and the off-diagonal elements are zero.

Converting equation 8 to reduced units, and with $\varepsilon = mg\sigma$,

$$\frac{d\tilde{P}_{SS}}{\tilde{\rho}_{SS}} = -\frac{dh*}{T*} \qquad \text{Equation 9}$$

The well-known soft-sphere equation of state, $f_{liquid/solid}(\tilde{\rho}_{SS})$, gives the relation between density and pressure, in the liquid/solid phases

$$\tilde{P}_{SS} = f_{liquid/solid}(\tilde{\rho}_{SS}) \qquad \text{Equation 10}$$

The expressions for the liquid and solid branches (shown below) and the virial coefficients B_i and C_i on the right-hand-side are given in equations [4, 5].

$$f_{liquid}(\tilde{\rho}_{SS}) = \sum_{i=1}^{6} B_i (\tilde{\rho}_{ss})^i$$

$$f_{solid}(\tilde{\rho}_{SS}) = 7\tilde{\rho}_{SS} + 0.5 C_{latt}\tilde{\rho}_{SS}^{5} - 4C_1\tilde{\rho}_{SS}^{-3} - 8C_2\tilde{\rho}_{SS}^{-7}$$

The differential equation 9 can be expressed purely in terms of the soft-sphere reduced densities as,

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$$\frac{f'_{liquid\,/\,solid}(\widetilde{\rho}_{SS})d\widetilde{\rho}_{SS}}{\widetilde{\rho}_{SS}} = -\frac{dh*}{T*}$$

Equation 11

Integrating equation 11 using the fluid soft-sphere equation of state [5], i.e.,

$f_{liquid\,/\,solid}(\widetilde{\rho}_{ss}) = f_{liquid}(\widetilde{\rho}_{ss})$, we get the expression for the density profile in the fluid

region of the inhomogeneous system,

$$-\frac{(h*-h_{0,l}^{*})}{T*} = B_1 \ln \widetilde{\rho}_{SS} + 2B_2 \widetilde{\rho}_{SS} + \frac{3}{2}B_3 \widetilde{\rho}_{SS}^{\;2} + \frac{4}{3}B_4 \widetilde{\rho}_{SS}^{\;3} + \frac{5}{4}B_5 \widetilde{\rho}_{SS}^{\;4} + \frac{6}{5}B_6 \widetilde{\rho}_{SS}^{\;5} - \mu_{0,l}^{*}$$

Equation 12

where ,

$$\mu_{0,l}^{*} = B_1 \ln \widetilde{\rho}_{SS0,l} + 2B_2 \widetilde{\rho}_{SS0,l} + \frac{3}{2}B_3 \widetilde{\rho}_{SS0,l}^{\;2} + \frac{4}{3}B_4 \widetilde{\rho}_{SS0,l}^{\;3} + \frac{5}{4}B_5 \widetilde{\rho}_{SS0,l}^{\;4} + \frac{6}{5}B_6 \widetilde{\rho}_{SS0,l}^{\;5}$$

Equation 13

The subscript '*l*' in equations 12 and 13 refers to the liquid state. $\mu_{0,l}^{*}$ is the integration

constant. $\widetilde{\rho}_{SS0,l}$ is the soft-sphere reduced density at height $h_{0,l}^{*}$. The value of $\widetilde{\rho}_{SS0,l}$ at

$h_{0,l}^{*}$ is the boundary condition for the solution of differential equation 11 and has to be

known *a priori* in order to obtain the density profile.

$\widetilde{\rho}_{SS0,l}$ at the base of the box, $h_{0,l}^{*} = 0$ can be obtained from the knowledge that the

pressure at the base is equal to the total weight of the particles in the box divided by the

area. Using equations 4-5 to convert to reduced units, we have equation 14, which can be

solved for the unknown, $\widetilde{\rho}_{SS0,l}(h^{\bullet}_{0,l} = 0)$:

$$\left(\frac{N}{A*}\right)\left(\frac{1}{T*}\right)^{\frac{5}{4}} = \widetilde{P}_{SS0,l} = \sum_{i=1}^{6} B_i (\widetilde{\rho}_{SS0,l})^i \qquad \text{Equation 14}$$

For an inhomogeneous fluid system, equations 12 to 14 were able to predict the density

accurately compared to the simulation results, as shown in figure 8. The pressure profile

also follows from the derivation above and is compared with the simulation profile in

figure 9.

Figure 8 Comparison of Simulation density profile with the predicted profile for system A at N/A* = 106.995 and T*=12.4; for clarity, simulation density of every 5th layer is plotted.

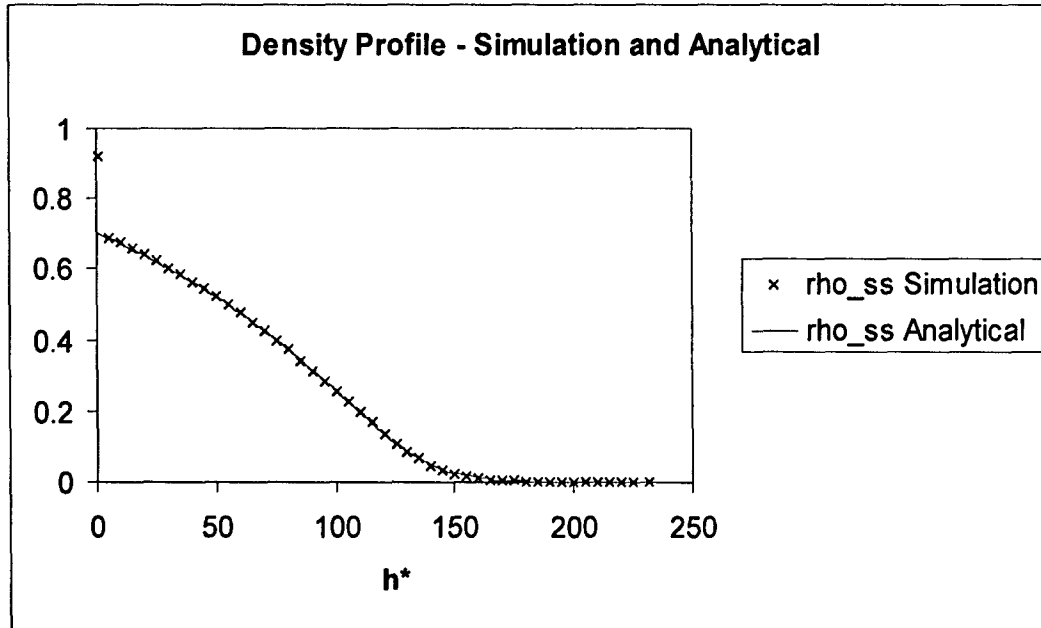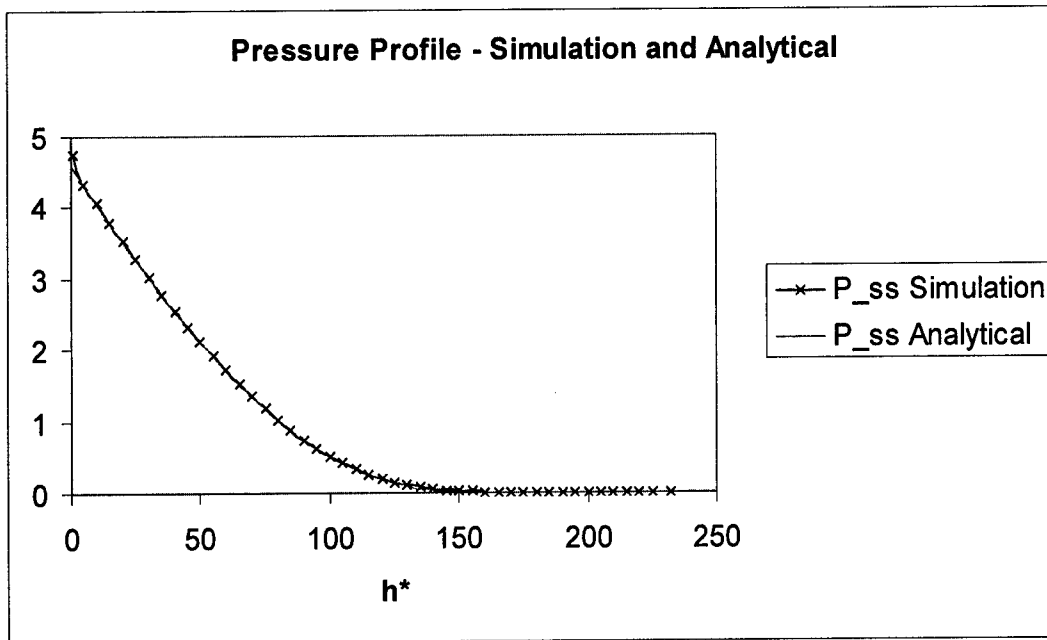**Figure 9** Comparison of Simulation density profile with the predicted profile for system A at N/A* = 106.995 and T*=12.4. For clarity, simulation density of every 5th layer is plotted.

8.   Thermodynamic profiles for inhomogeneous interface
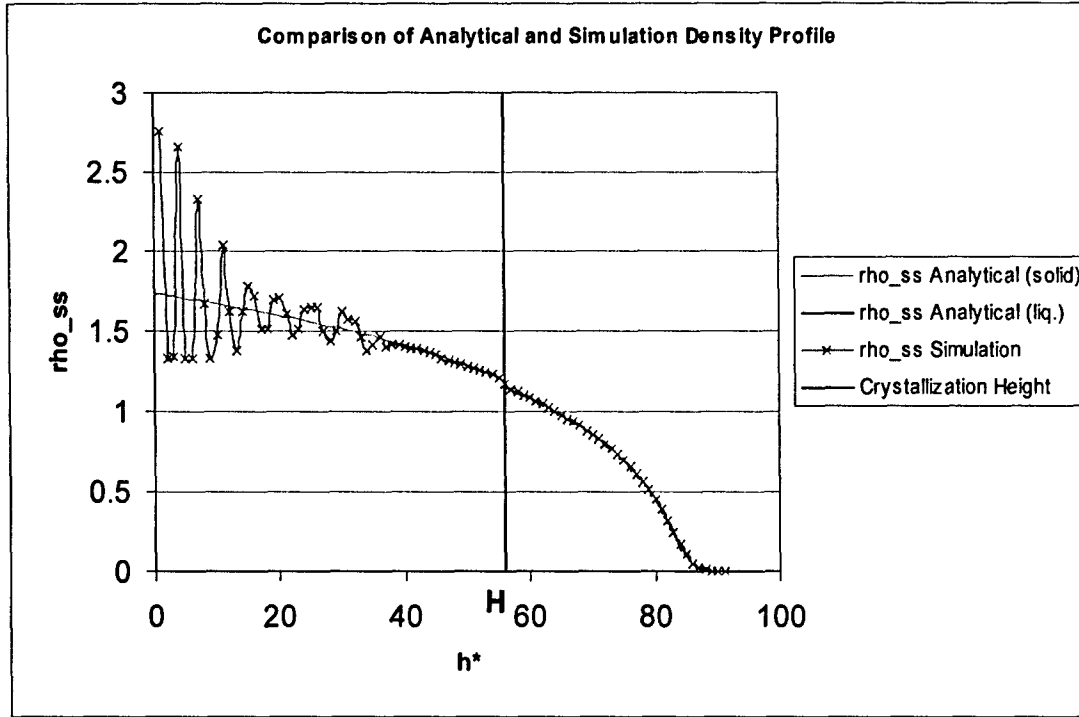
Figure 10 Predicted and simulation density profile; system F is at N/A* = 106.995 and T* = 1 undergoes crystallization

At a sufficiently low temperature/high gravity/ high pressure, the system crystallizes, and an interface is formed which separates the solid at the bottom and fluid phase of the higher layers, as shown in the figure 10. The density profile in the solid phase region can be obtained by substituting the solid equation of state [4] in equation 11 and integrating, i.e., $f_{liquid/solid}(\widetilde{\rho}_{ss}) = f_{solid}(\widetilde{\rho}_{ss})$.

$$-\frac{(h*-h_{0,s}^*)}{T*} = 7\ln\widetilde{\rho}_{SS} + \frac{5}{8}C_{latt}\widetilde{\rho}_{SS}{}^4 - 3C_1\widetilde{\rho}_{SS}{}^{-4} - 7C_2\widetilde{\rho}_{SS}{}^{-8} - \mu_{0,s}^*$$

Equation 15

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$$\mu_{0,s}^* = 7\ln \tilde{\rho}_{SS0,s} + \frac{5}{8}C_{latt}\tilde{\rho}_{SS0,s}{}^4 - 3C_1\tilde{\rho}_{SS0,s}{}^{-4} - 7C_2\tilde{\rho}_{SS0,s}{}^{-8}$$

<div align="right">Equation 16</div>

In the present study of small systems, Hoover's value [4] for 500 particles was used for the system-size dependent constants C_1 and C_2.

As in the previous section, $\tilde{\rho}_{SS0,s}$ is the soft-sphere reduced density of the crystal phase at $h_{0,s}^*$ and can be determined by considering the pressure at the base of the box, which is simply the weight of the simulation divided by the base area of the box. The following equation can be solved for $\tilde{\rho}_{SS0,s}(h_{0,s}^*)$,

$$\left(\frac{N}{A*}\right)\left(\frac{1}{T*}\right)^{\frac{5}{4}} = 7\tilde{\rho}_{SS0,s} + 0.5C_{latt}\tilde{\rho}_{SS0,s}{}^5 - 4C_1\tilde{\rho}_{SS0,s}{}^{-3} - 8C_2\tilde{\rho}_{SS0,s}{}^{-7}$$

<div align="right">Equation 17</div>

For the system in figure 10, solving equation 17 gives, $\tilde{\rho}_{SS0,s} = 1.734$. The coexistence pressure for the freezing transition is $\tilde{P}_{ss} = 22.6$ [7] and from the solid equation of state this corresponds to $\tilde{\rho}_{SSH,s} = 1.194$. Equations 15 to 17, thus allow us to compute the height, H*=55.915, the height of freezing transition, at which the pressure is equal to the freezing transition pressure. The interfacial layer is predicted to form at H*.

Similarly, from the fluid equation of state, the coexistence density of the fluid at H* is found to be $\tilde{\rho}_{SSH,l} = 1.150$. In equations 12 and 13, instead of $h_{0,l}* = 0$, we now use $h_{0,l}* = H$ and $\tilde{\rho}_{SS0,l}(H)$ as the boundary condition. The fluid density profile can once again be obtained from equations 12 and 13.

Thus, from the point thermodynamic approximation and a knowledge of the equation of state and freezing transition pressure of bulk soft-sphere systems, we can predict the height H* at which the small inhomogeneous system under gravity would undergo a transition from the solid to the fluid phase and we can predict the density and pressure profiles in both the fluid and solid regions. The analytical and simulation profiles in figure 10 show good agreement.

Hard spheres under gravity have been studied and the formation of the crystal region is referred to as "condensation"[11]. As in their analysis, with the knowledge of the coexistence pressure at the melting transition, $\widetilde{P}_{ss} = 22.6$, we can predict the "condensation temperature" T^*_c, i.e., the temperature at which the solid phase begins to form at the base of the box. For the system with N/A*=106.995, from equation 17, T^*_c was found to be equal to 3.469. The surface density, N/A* versus the inverse of the calculated condensation temperature $\beta^*_c = 1/T^*_c$ is plotted in figure 11 below.
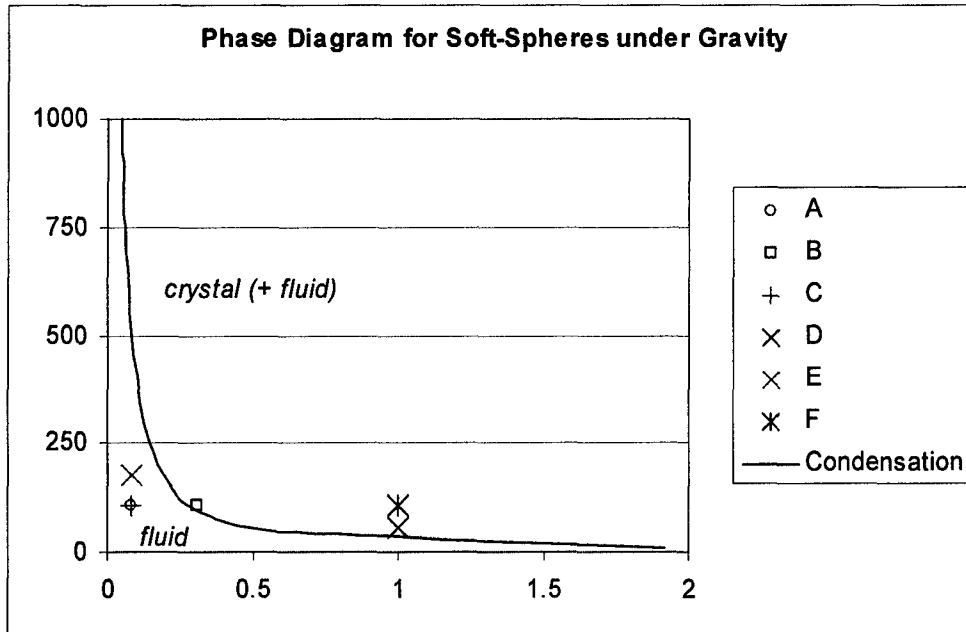
Phase Diagram for Soft-Spheres under Gravity

Figure 11 Comparison of inverse condensation temperature, $1/T^*_c$ versus N/A^* for the the 3-D soft-sphere system. Points for simulation systems A-F described in Figures 3- 10 are plotted. Pressure at the base of the simulation systems B, D and F has exceeded the soft-sphere freezing pressure while systems A=C and E are completely fluid.

In these systems temperature and gravity cannot be varied independently. If we use another system of reduced units, where the temperature is fixed at 1.0 and the gravity is not fixed, then we could define a "condensation gravity".

It should be noted, that the pressure at any layer is determined due to the mechanical equilibrium condition and is simply equal to the weight of the particles above it. The density at the layer can then determined from the pressure via the accurately known equation of state. Density can be considered as the "slave variable". The equation of state expresses pressure as a function of density and can be a little misleading in this sense.

Within the solid-fluid interface, the pressure is not isotropic and the density variation is large, and so, in this "interface layer", the point-thermodynamic assumption is not valid. To predict properties of the system at the interface more sophisticated treatment using local and non-local approximations is required [2].

The peaks in the density profile due to normal layering near the wall and crystallization, cannot be predicted from our simple model. But the predicted solid phase density profile appears to be an average of the peak and trough pair in the oscillating simulation density profile and so in that sense agrees well with the simulation result.

9.   Chemical potential

At equilibrium, the total chemical potential, $\mu = \mu_{int}(h) + mg(h - h_0)$ should be constant over all phases throughout the system which is inhomogeneous in the Z-direction along the height, h. In addition to the characteristic density and pressure profiles discussed previously, the system also has a characteristic intrinsic chemical potential profile, μ_{int} (h). The local intrinsic chemical potential is defined as the component of μ, is independent of the external field and corresponds to the chemical potential of the homogenous soft-sphere system whose bulk density [4] is same as the local density.

In the fluid phase, the Helmholtz free energy is given by [8]:

$$F(\rho) = F_{id}(\rho) + NkT \int_0^\rho \left(\frac{P}{\rho kT} - 1 \right) \frac{d\rho}{\rho}$$

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$F_{id}(\rho) = -kT \ln\left(\dfrac{V^N}{N!\Lambda^{3N}}\right)$ is the free energy of the ideal gas.

From the soft-sphere fluid equation of state[7], in soft-sphere reduced units,

$$\mu_{int}^*(\tilde{\rho}_{SS}(h^*,T^*),T^*) = K_{fluid}(T^*) + \mu_{config,l}^*(\tilde{\rho}_{SS}(h^*,T^*),T^*) \quad K_{fluid}(T^*) = T^* \ln\left(\tilde{\Lambda}_{SS}^{\ 3}\right)$$

<div align="right">Equation 18</div>

$$\mu_{config,l}^*(\tilde{\rho}_{SS}(h^*,T^*),T^*) = (T^*)\left(\ln(\tilde{\rho}_{SS}) + 2B_2\tilde{\rho}_{SS} + \frac{3}{2}B_3\tilde{\rho}_{SS}^{\ 2} + \frac{4}{3}B_4\tilde{\rho}_{SS}^{\ 3} + \frac{5}{4}B_5\tilde{\rho}_{SS}^{\ 4} + \frac{6}{5}B_6\tilde{\rho}_{SS}^{\ 5}\right)$$

<div align="right">Equation 19</div>

$$\tilde{\Lambda}_{SS} = \left[\frac{\Lambda}{\sigma}\left(\frac{kT}{\varepsilon}\right)^{\frac{1}{12}}\right] = \left(\frac{h^2}{2\pi mkT\sigma^2}\right)^{\frac{1}{2}}\left(\frac{\varepsilon}{kT}\right)^{\frac{1}{12}} \qquad \text{Equation 20}$$

In equation 18, the intrinsic chemical potential contains a term $K_{fluid} = T^* \ln\left(\tilde{\Lambda}_{SS}^{\ 3}\right)$

which is independent of $\tilde{\rho}_{SS}$, while the remaining terms of the μ_{int}^* depend on $\tilde{\rho}_{SS}$ and are

grouped together as the configurational component of the intrinsic chemical potential,

$\mu_{config,l}^*$. The temperature dependence of $K_{fluid}, \tilde{\rho}_{ss}$ and $\mu_{config,l}^*$ is not shown explicitly in

the following discussion.

The expression for the total chemical potential of a soft-sphere system under gravity in

the liquid phase is given by:

$$\mu^* = K_{fluid} + \mu_{config,l}^*(\tilde{\rho}_{SS}(h^*)) + (h^* - h_0^*) \qquad\qquad \text{Equation 21}$$

$$\frac{\mu^*}{T^*} =$$

$$\frac{K_{fluid}}{T^*} + \left(\ln(\widetilde{\rho}_{SS}) + 2B_2\widetilde{\rho}_{SS} + \frac{3}{2}B_3\widetilde{\rho}_{SS}{}^2 + \frac{4}{3}B_4\widetilde{\rho}_{SS}{}^3 + \frac{5}{4}B_5\widetilde{\rho}_{SS}{}^4 + \frac{6}{5}B_6\widetilde{\rho}_{SS}{}^5 \right) + \frac{h^* - h_0{}^*}{T^*}$$

<div align="right">Equation 22</div>

The zero of gravitational potential energy is taken to be at an arbitary height, $h_0{}^*$.

Since, the total chemical potential is the same at any height h^* in the simulation box and at the height, $h_{0,l}^*$, which could be the base of the box filled with a fluid or in the case of an interfacial system, at the height of freezing transition , H*, we have for the fluid phase,

$$\frac{K_{fluid}}{T^*} + \frac{\mu_{config,l}^*(h_{0,l}^*)}{T^*} + \frac{h_{0,l}^* - h_0^*}{T^*} = \frac{K_{fluid}}{T^*} + \frac{\mu_{config,l}^*(h^*)}{T^*} + \frac{h^* - h_0^*}{T^*}$$

<div align="right">Equation 23</div>

$$-\frac{h^* - h_{0,l}^*}{T^*} = \frac{\mu_{config,l}^*(h^*)}{T^*} + \frac{\mu_{config,l}^*(h_{0,l}^*)}{T^*} \qquad \text{Equation 24}$$

Equations 12 and 13 are retrieved and it should be noted that $\mu_{config,l}^*(h_{0,l}^*)$ of equation 24 is equal to $(\mu_{0,l}^*)T^*$ of equation 13. Thus, apart from the condition of mechanical equilibrium, the condition of chemical equilibrium also provides a route to the density profile of this system.

Similarly for the solid phase,

$$F(\rho) = -kT \ln Z_{anharmonic} \quad , \quad \mu_{int}(\rho) = \frac{dF(\rho)}{dN} \quad \text{and}$$

<div align="center">30</div>

$$Z_{anharmonic} = \exp\left(\frac{-\Phi_0}{kT}\right)\frac{V}{N}\frac{N^{\frac{3}{2}}}{\Lambda^3}\prod_{j=1}^{3N-3}\frac{kT}{h\upsilon_j}\exp\left(-NC_1\tilde{\rho}_{SS}^{-4}-NC_2\tilde{\rho}_{SS}^{-8}+...\right)$$

The constants can be found in [7, 14] and the expression for the canonical partition function, above, was given in [6].

Carrying out the differentiation and expressing in reduced units, we have:

$$\frac{\mu^*}{T^*} = \frac{K_{solid}}{T^*} + \frac{\mu_{config,s}^*(\tilde{\rho}_{SS}(h^*))}{T^*} + \frac{(h^*-h_0^*)}{T^*} \qquad\qquad \text{Equation 25}$$

$$\mu_{config,s}^*(\tilde{\rho}_{SS}) = T^*\left(7\ln(\tilde{\rho}_{SS}) + \frac{5}{8}C_{latt}\tilde{\rho}_{SS}^{4} - 4C_1\tilde{\rho}_{SS}^{-4} - 8C_2\tilde{\rho}_{SS}^{-8}\right) \qquad\qquad \text{Equation 26}$$

h_0^* is chosen to be the zero of gravitational potential energy as before. The exact form of K_{solid} is not important for the present analysis as it will cancel out. The total chemical potential of the crystal phase is constant at the base of the simulation box $h^* = h_{0,s}^*$, $\tilde{\rho}_{SS} = \tilde{\rho}_{SS0,s}$ and at any intermediate height h^*,

$$\frac{K_{solid}}{T^*} + \frac{\mu_{config,s}^*(h_{0,s}^*)}{T^*} + \frac{h_{0,s}^* - h_0^*}{T^*} = \frac{K_{solid}}{T^*} + \frac{\mu_{config,s}^*(h^*)}{T^*} + \frac{h^* - h_0^*}{T^*}$$

$$\text{Equation 27}$$

$$-\frac{(h^*-h_{0,s}^*)}{T^*} = \frac{\mu_{config,s}^*(h^*)}{T^*} - \frac{\mu_{config,s}^*(h^*_{0,s})}{T^*} \qquad\qquad \text{Equation 28}$$

The equations 15 and 16 for the density profile in the solid phase are retrieved.

$\mu_{config,s}^*(h_{0,s}^*)$ of equation 28 is equal to $(\mu_{0,s}^*)T^*$ of equation 16.

Lastly, we knew *a priori* from [7], that the coexistence pressure for these systems is at $\widetilde{P}_{SS} = 22.6$, but we could also deduce this from the equation of state by solving for the density at which the intrinsic chemical potential of the two phases would be equal, i.e., density/height at which, the right-hand-side of equations 24 and 28 would be equal. Thus, in order to determine the complete set of thermodynamic properties of this system within the point local thermodynamic approximation, all that is needed is the accurate equations of state for the soft-sphere fluid and crystal phases. It is also noted that the inhomogeneous equilibrium soft-sphere system under gravity provides a reversible thermodynamic path connecting the solid and liquid phases.

10.   Conclusions

The soft-sphere model of a molecular fluid/crystal, with purely repulsive r^{-12} potential under a gravitational field, exhibits characteristic properties of a small thermodynamic system, that is phenomenologically similar to the behavior of a wide range of atomic and molecular nano-systems undergoing self-assembly . There exists a detailed knowledge of the macroscopic properties of soft spheres in the thermodynamic large-system limit. This, together with the unique scaling properties that enables temperature to scale with gravitational potential as a single state variable, means that the model is uniquely valuable as a tool to research the thermodynamics of small system self assembly in the first instance.

The equations that have been derived here, to predict thermodynamic profiles of small

inhomogeneous systems using the infinite-system equation of state, and the local density

approximation, can be easily tested against the results of computer simulations. The

comparison between experiment and theory show that, in this case, the inhomogeneous

thermodynamic property profiles are essentially quantitatively predictable, from top to

base, and over the whole range of state variables, surface density, gravitational field

and/or temperature. The predictions are accurate for all systems to a small fraction of 1%.

Configurational temperature profiles for these inhomogeneous systems studied here were

also computed and the agreement between kinetic and configurational temperatures was

found to be useful in checking whether equilibrium had been reached. For non-

equilibrium and some metastable states, the configurational and kinetic temperatures are

different. These results confirm that all the systems for which we have reported

simulation results are in states of thermodynamic equilibrium. The agreement between

the predicted profiles and simulation profile, generated from molecular dynamic

simulations, is very good over the range of state points that were tested.

A reduced set of state parameters can be identified to define thermodynamic states, and

hence state functions, for all small inhomogeneous systems.. Systems with identical state

parameters will exhibit identical profiles of thermodynamic properties like density,

pressure and intrinsic chemical potential, measured in the direction of the applied

conservative field of gravity. Althought there is excellent agreement, at high fields, and

hence pressure gradients, there will in more complex models Hamiltonian systems, be

several different crystal structures on top of one another. The detailed structure prediction, especially at the crystal fluid interface, and crystal-crystal interfaces, will prove especially troublesome. Early indications are that, even in thi s simple model, crystal phases that are not found to exist in the thermodynamic limit, make an appearance in the inhomogeneous systems as narrow mesophases. Future work, therefore, should involve using a higher-order approximation for extremely strong fields, the next best approximation being the square-gradient approximation [3]. This higher level of approximation may be necessary to obtain very accurate representation at the fluid-crystal interface.

The thermodynamics of small systems has important applications in systems other than inhomogeneous equilibrium systems. Hill and Chamberlain [13], for example, have applied the thermodynamics of small equilibrium systems to open metastable states which are not strictly equilibrium states. The treatment of metastable states and non-equilibrium steady-states as small-systems might finally allow for the development of a complete description of these the self-assembly into local metastable states on time-scales that do not permit a global thermodynamic equilibration.of the system.

11. Referenced reports and papers

1. EOARD contract grant # 033080 Deliverable 1: Submitted January 2004 to AFRL via EOARD by Professor L V Woodcock Scientific Simulation Services in part fulfillment of A review of recent developments and literature survey of the field: *"The Thermodynamics of Small Inhomogeneous Systems"* 2004

2. EOARD contract grant # 033080Deliverable 2 (submitted June 2004) Submitted to AFRL via EOARD by Professor Leslie V Woodcock *"A computer program for the thermodynamic profiles of small inhomogeneous systems of spherical particles in a gravitational field, together with test results and report"* , 2004

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12.   Appendix: commentary on self-assembly of nanomaterials

Colloidal suspensions can be regarded as thermodynamically small systems; the molecular theory of which has been reviewed by Rowlinson. "Small" here does not necessarily mean that the system has a limited number of particles, it refers to the fact that the system is far from the thermodynamic limit. The system is affected by the external gravitational or other surface forces to the extent that it is inhomogeneous. Its thermodynamic properties and in some cases, its actual phase, varies spatially when the system is in thermodynamic equilibrium. All equilibrium systems in the thermodynamically large limit are homogeneous, even in the 2-phase region of a phase diagram.

Colloidal suspensions and fine powders comprising nanoparticles 10-1000 nanometers in diameter, in which all the particles are the same size, shape, etc. are said to be "monodisperse" in that property. Monodisperse size and shape colloids, and mixtures of monodisperse colloids readily form colloidal crystals, colloidal films, and colloidal "molecules", i.e. self-assembling clusters. Monodispersity can then give rise to phase behaviour and colloidal and granular crystalline phase in which the granules themselves self- assemble with varying degrees of crystallinity or order. These colloidal assemblies are potentially a new source of modern materials, or precursors to new materials, with new properties, yet to be researched or discovered.

Colloidal suspensions are truly, small thermodynamic systems, in the sense that they will, if allowed to equilibrate thermally, obey the laws of statistical thermodynamics. Colloidal suspensions will have osmotic excess properties, and obey Gibbs phase rule, etc. Granular fluidised suspensions of particles are not in that sense thermodynamic but they can be made to behave as such,. Here, however, .we have examined the properties of a soft-sphere model that could equally model the properties of colloidal suspension or of dry colloidal inelastic spheres, that are not in thermodynamic equilibrium with a host solvent, or neighbouring interface, but which are fluidised under gravity by small amplitude vibrations or some other non intrusive means.

. Previous studies have demonstrated that the essential requirement is that the amplitude of vibration should be less than a characteristic correlation length, i.e., less than the smallest characteristic distance scales that determine the physics of the system In the soft-sphere model simulations performed in the tests reported above, , the correlation length was identified as the characteristic path length $\Lambda = \rho^{-1/3}$. For the soft-particle model used in the present work, the characteristic distance is of the order of a mean vibrational amplitude of the particles.

The use of mesoscale modeling to study such idealiszed powders yields information about the conditions under which, powders fluidized by external vibration, can also behave like thermodynamically small atomic liquids and atomic crystals. Our computer simulation studies have shown that when external vibrations at a surface fluidised powders, under certain conditions the principle of equipartition is upheld. This, in turn, implies that the statistical conditions for adherence to laws of thermodynamics, for a

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system of sufficient numbers of particles, are obeyed. This leads to a definition of thermodynamic properties of powders as state functions of a granular "temperature" and a granular "pressure". The essential requirement is that the amplitude of vibration should be less than the correlation lengths between particles or the distance scales that determine the physical properties of the system.

If powders can be made to behave thermodynamically by vibration fluidization, it follows that we can utilize the laws of thermodynamics to predict the conditions under which powders would prefer to be two separate phases, or to be mixed. A very simple consideration of the mixing criteria for two powders of hard spheres that differ only in size, suggests that all powders will mix if vibrated at a sufficiently small amplitude and characteristic frequency. If we consider a two component powder which may be two separate phases, A + B, or homogeneously mixed like a molecular solution, A/B, then the criterion for the mixing process at equilibrium, given by equation 1a-c), is that the excess Gibbs free energy of mixing, should be negative.

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad \Delta H_m = \Delta E_m + p\Delta V_m$$

$$\Delta S_m = -R(X_A \ln X_A + X_B \ln X_B)$$

The effect of granular pressure is to enhance mixing if ΔV_m is negative and to enhance segregation if ΔV_m is positive. The effect of granular temperature, on the other hand, is always to favor mixing. This simple consideration leads to the deduction that most difficult-to-mix binary powders will mix with sufficient granular "temperature". These calculations and subsequent thermodynamic considerations may result in the prediction and discovery of self-assembled phases of binary powders. In these fluidised systems, the

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granular "pressure' varies undeʳ gravity from zero at the top to the weight of the system at the bottom. The pressure gradiⱥnt results in pure segregated phases above a homogeneously mixed phase. Theseᵉ powders cannot hitherto be homogeneously mixed by any other means.

Now that we can treat these systems thermodynamically, we have a means of predicting the conditions whereupon the various mixed or demixed, ordered or disordered phases will exist, and to reproduce those conditions in materials processing.

We have here reported upon the conditions whereby inhomogeneous systems composed of nano-particles can be induced to obey the laws of thermodynamics when fluidised either by thermal or other means. A knowledge and understanding of such conditions will allow for the application of a new "granular thermodynamics" to predicting the position of granular equilibrium of nano- and micro- particle assemblies, by analogy with the application of chemical thermodynamics by chemical engineers to predict physical and chemical equilibrium states of molecular fluids. In thermodynamically small systems, assemblies of particles which may not be in thermodynamic equilibrium, can obey a quasi-thermodynamics that, if understood, can be used to predict stable new structures.