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## Condensation of fluids in the gravitational field

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### Abstract

An analytical expression for the contact value of the density of  $n$ -component mixtures under gravity has been obtained by means of the inhomogeneous pressure equation within fluids. The gravity-induced liquid–solid transition temperature has been estimated for hard spheres, Lennard-Jones spheres, and binary hard sphere mixtures and has been compared with those of other approximations. The density functional approximation based on the weighted density has also been used to calculate the density profile and the pressure of hard spheres and Lennard-Jones spheres at the liquid–solid interface.

Sedimentation of model particles under gravity has long been of scientific interest since the early work of Jean Perrin. Model particles in a suspension under gravity show spatial inhomogeneities due to the symmetry breaking induced by the gravitational field. A few years ago, Biben *et al* [1] had shown through Monte Carlo simulations and the weighted-density approximation (WDA) that the hard spheres can become unstable in the presence of gravity.

Recently, Hong and co-workers [2, 3] have studied the sedimentation of hard spheres under gravity and argued that there exists a critical temperature at which the density at the bottom layer becomes the close-packed density. They have defined the transition temperature  $T_c$  to be the temperature at which the local volume density at the bottom within a thickness of one particle diameter reaches the close-packed value, and identified it as a function of external parameters, i.e.,

$$k_B T_c = \frac{mg\sigma\mu\phi_c}{\mu_0} \quad (1)$$

where  $\mu\phi_c = \sigma^{d-1} \int_{\sigma/2}^{\infty} \rho(z) dz$  is the number of particles piled up over the area  $\sigma^{d-1}$  of the bottom wall,  $m$  the mass of hard spheres,  $g$  the gravitational strength,  $\sigma$  the diameter,  $d$  the dimension,  $k_B$  the Boltzmann's constant,  $\mu_0$  and  $\phi_c$  the constants that reflect the particular manner in which a system packs upon condensing, and  $\rho(z)$  the density profile in a gravitational field [3]. They have also argued that if the temperature is lowered below  $T_c$ , the first layer should remain at the close-packed state, while the particles at the second layer try to compact

and crystallize. On the other hand, Levin [4] has proposed a simple argument to account for the crystallization of hard spheres under the action of a gravitational field: the first bottom layer will crystallize when the pressure at the bottom reaches the bulk coexistence pressure corresponding to the structural fluid–solid transition of hard spheres. Here, one interesting point is that the contact value of the density of a fluid under gravity is the same as the pressure at the bottom. This implies that the transition temperature is closely related to the pressure within a fluid, and the transition temperature can be defined as the contact density at the bottom. Another interesting point is how to extend equation (1), which was identified as a function of external parameters, to systems of  $n$ -component mixtures in the gravitational field, and to apply it to explain gravity-induced segregation such as the Brazil nut type segregation [5, 6].

In this paper, we will derive the inhomogeneous pressure equation within fluids in the presence of gravitation, and show that at the critical temperature  $\mu_0$  is exactly the same as the contact density  $\rho(z = \sigma/2)\sigma^d$  (or the pressure  $\beta P_c(z = \sigma/2)\sigma^d$ ) at the bottom of the system. We calculate the transition temperature of hard spheres and Lennard-Jones spheres based on Levin's argument for the crystallization of fluids. The density functional theory in the simplified WDA is used to calculate the density profiles and the pressure of hard spheres and Lennard-Jones spheres at the liquid–solid interface. In addition, we extend the contact-value theorem to  $n$ -component mixtures under gravity. We apply it to study the gravity-induced liquid–solid transition. Finally, we briefly discuss the segregation of binary hard sphere mixtures under gravity.

The static pressure  $P(z)$  within a fluid in the action of a gravitational field satisfies

$$\frac{d\beta P(z)}{dz} = -\beta mg\rho(z), \quad (2)$$

and it can be integrated

$$\beta P(z) = \beta P(z = \sigma/2) - \beta mg \int_{\sigma/2}^z \rho(z') dz', \quad (3)$$

where  $\beta = 1/k_B T$  is the inverse temperature and  $P(z = \sigma/2)$  is the pressure when the centre position of particles ( $z = 0$ ) is located at the bottom [8]. It is known that  $P(z = \sigma/2)$  is the kinetic pressure which arises from the momentum transferred per unit time to the bottom layer. For the gravitational field,  $P(z)$  decreases rapidly and approaches zero as  $z$  tends to infinity ( $z \rightarrow \infty$ ). Then, equation (3) yields

$$\beta P(z = \sigma/2) = \beta mg \int_{\sigma/2}^{\infty} \rho(z') dz'. \quad (4)$$

To obtain the relationship between the contact value of the density and the pressure of a system at the bottom, we consider the force balance on a slab of fluids with thickness  $z$  adjacent to a wall at  $z = 0$ . The pressure  $P(z)$  is given by

$$\beta P(z) = - \int_{\sigma/2}^z \frac{\partial \beta u_{\text{ext}}(z')}{\partial z'} \rho(z') dz', \quad (5)$$

where  $u_{\text{ext}}(z)$  is the potential due to the wall at the bottom [7].

If the bottom is a hard wall and has an additional gravitational interaction with the system particles such as

$$\beta u_{\text{ext}}(z) = \begin{cases} \infty, & z < \sigma/2, \\ \beta mgz, & z > \sigma/2, \end{cases} \quad (6)$$

equation (5) becomes

$$\rho(z = \sigma/2) = \beta mg \int_{\sigma/2}^{\infty} \rho(z') dz', \quad (7)$$

since  $\partial u_{\text{ext}}(z)/\partial z = \delta(z - \sigma/2) - \beta mg$  and  $P(z)$  rapidly approaches zero as  $z$  tends to infinity. Here,  $\rho(z = \sigma/2)$  is the contact density of fluids at the bottom and  $\delta(z)$  is Dirac's delta function. In this case, the dimensionless gravitational strength (or Peclet number),  $\alpha_{\text{gr}}$ , is given by

$$\alpha_{\text{gr}} = \frac{mg\sigma}{k_{\text{B}}T} = \frac{\rho(z = \sigma/2)\sigma^d}{\sigma^{d-1} \int_{\sigma/2}^{\infty} \rho(z') dz'}. \quad (8)$$

This describes the ratio of the potential energy gain to the thermal energy  $k_{\text{B}}T$  of a particle.

Finally, equations (4) and (7) yield the simple relationship between the pressure at the bottom and the contact value of the density,

$$\beta P(z = \sigma/2) = \rho(z = \sigma/2), \quad (9)$$

and the pressure equation (3) becomes

$$\beta P(z) = \rho(z = \sigma/2) - \beta mg \int_{\sigma/2}^z \rho(z') dz'. \quad (10)$$

We may easily show that for a planar hard wall ( $z \rightarrow \infty$ ) the contact value of the density is fixed by the wall theorem, i.e.,  $\beta P = \rho(z = \sigma/2)$ , where  $P$  is the bulk pressure, irrespective of whether the phase is liquid or solid [8].

To determine the transition temperature for crystallization, let us consider Levin's argument, which was introduced to explain the crystallization of hard spheres [4]. Following this argument, the first bottom layer will crystallize when  $\beta P(z = \sigma/2)$  at the bottom reaches the (bulk) pressure at coexistence, i.e.,

$$k_{\text{B}}T_c = \frac{mg \int_{\sigma/2}^{\infty} \rho(z') dz'}{\rho_c(z = \sigma/2)} = \frac{mg \int_{\sigma/2}^{\infty} \rho(z') dz'}{\beta P_c}, \quad (11)$$

where  $P_c$  and  $\rho_c(z = \sigma/2)$  are the pressure and the contact density at coexistence, respectively. Equation (11) indicates that the transition temperature can be defined as the contact density at the bottom as well as the bulk pressure at coexistence. Then, equations (1) and (11) show that

$$\mu_0 = \beta P_c \sigma^d = \rho_c(z = \sigma/2) \sigma^d. \quad (12)$$

For the one-dimensional (1D) hard-rod system, we can show that the condensation transition occurs at zero temperature ( $T_c = 0$ ) because  $\beta P_c$  has a singularity at the close-packed density ( $\rho_c \sigma = 1$ ) [8, 9]. For the two-dimensional (2D) hard-disc system, the solid-liquid coexistence occurs when  $\beta P/\rho_{\text{cp}}$  (where  $\rho_{\text{cp}}$  is the close-packed density) is the dimensionless pressure at coexistence. Here, we have used  $\beta P_c \sigma^2 \approx 8.08 \times 2/\sqrt{3}$  obtained from the Monte Carlo simulation results of Hoover and Rhee [10]. Then, the critical temperature  $T_c$  at which the first bottom layer will crystallize becomes  $k_{\text{B}}T_c \approx \sqrt{3}mg\sigma^2 \int_{\sigma/2}^{\infty} \rho(z') dz' / (8.08 \times 2)$ . In this case,  $\mu_0 \approx 8.08 \times 2/\sqrt{3} \approx 9.33$ . If the temperature is lowered further, the additional fluid layer will solidify and a growing crystal will coexist with the diminishing fluid phase. However, the WDA based on the simple weighting function gives  $\mu_0 \approx 4.31$  [3, 11], which is smaller than  $\mu_0 \approx 9.33$ . It is noted that Hong and co-workers have defined the condensation temperature to be that temperature at which the local average density,  $\int_0^\sigma \rho(z) dz$ , reaches the close-packed value. For the three-dimensional (3D) hard sphere system, the transition temperature is given by  $k_{\text{B}}T_c \approx mg\sigma^3 \int_{\sigma/2}^{\infty} \rho(z') dz' / (8.23 \times \sqrt{2})$  since  $\beta P_c \sigma^3 \approx 8.23 \times \sqrt{2} \approx 11.69$ . (At the fluid-solid transition, the coexisting fluid/solid densities are  $\rho_l \sigma^3 \approx 0.941$  and  $\rho_s \sigma^3 \approx 1.041$ , respectively [10]). In this case,  $\mu_0 \approx 11.69$ , while the WDA theory [3] yields  $\mu_0 \approx 7.32$ . For the Lennard-Jones system, computer simulation data [14] were used to determine the transition temperature. The calculated results are presented in table 1. The transition temperature decreases with increasing the temperature  $T^* = k_{\text{B}}T/\epsilon$ . This shows that at low temperature the Lennard-Jones fluid will easily solidify.

**Table 1.** Transition temperature  $T_c^*/mg\sigma\mu\phi_c$  for Lennard-Jones spheres. The reduced melting pressure ( $P_c\sigma^3/\epsilon$ ) and density ( $\rho_c\sigma^3$ ) have been taken from computer simulation data [14].

$T^* \equiv k_B T/\epsilon$	$\rho^* \equiv \rho_s\sigma^3$	$P^* \equiv P_c\sigma^3\epsilon$	$T_c^*/mg\sigma\mu\phi_c$	$\mu_0$
0.75	0.973	0.67	1.12	0.89
1.15	1.024	5.68	0.20	4.94
1.35	1.053	9.00	0.15	6.67
2.74	1.150	32.2	0.085	11.75

In density functional theory, the density profile,  $\rho(z)$ , of fluids in the presence of a gravitational field is determined by the Euler–Lagrange minimization for the Helmholtz free energy per unit area, i.e.,  $\delta F[\rho]/\delta\rho(z) = \mu_{\text{ch}} - u_{\text{ext}}(z)$ , where  $\mu_{\text{ch}}$  represents the chemical potential. The density profile [8] becomes, after some manipulations,

$$\rho(z) = \begin{cases} \xi \exp[-\beta mgz + c^{(1)}(z; [\rho])], & z > \sigma/2, \\ 0, & z < \sigma/2, \end{cases} \quad (13)$$

where the fugacity  $\xi = \exp(\beta\mu_{\text{ch}})/\lambda^3$  is chosen to satisfy the normalization condition, i.e.,  $\xi = \int_{\sigma/2}^{\infty} \rho(z) dz / \int_{\sigma/2}^{\infty} \exp[-\beta mgz' + c^{(1)}(z'; [\rho])] dz'$ . Here,  $c^{(1)}(z; [\rho])$  is the one-particle direct correlation function (DCF) and is defined as the functional derivative of the excess free energy  $F_{\text{ex}}[\rho]$  of the system with respect to the density such as  $c^{(1)}(z; [\rho]) \equiv -\delta\beta F_{\text{ex}}[\rho]/\delta\rho(z)$ . Then, equation (7) yields

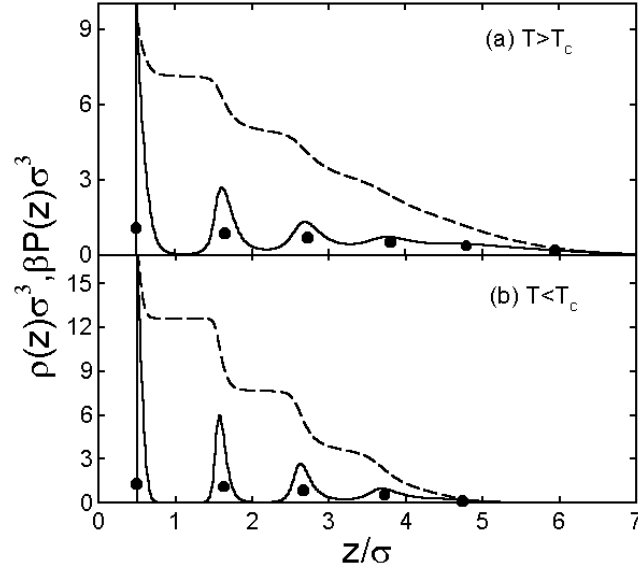
$$\exp[c^{(1)}(z = \sigma/2; [\rho])] = \beta mg \int_{\sigma/2}^{\infty} \exp[-\beta mgz' + c^{(1)}(z'; [\rho])] dz', \quad (14)$$

and the dimensionless gravitational strength  $\alpha_{\text{gr}}$  is given by

$$\alpha_{\text{gr}} = \frac{\sigma \exp[c^{(1)}(z = \sigma/2; [\rho])]}{\int_{\sigma/2}^{\infty} \exp[-\beta mgz' + c^{(1)}(z'; [\rho])] dz'}. \quad (15)$$

This is an exact relation which applies for fluids in the presence of gravity, and it can be very useful for checking numerical accuracy in the calculation of the density profile and the inhomogeneous pressure of fluids.

The WDA theory [3, 11] based on the simple weighting function  $\omega(r) = 3/4\pi\sigma^3\theta(\sigma - r)$  is used to calculate the density profile  $\rho(z)\sigma^3$  and the pressure  $\beta P(z)\sigma^3$  of hard spheres under gravity, where  $\theta(r)$  is the Heaviside step function. The calculated density profile and the pressure for  $\mu = 4$  ( $\mu = \int_{\sigma/2}^{\infty} \rho(z) dz$ ) are presented in figure 1. The transition temperature was taken to be that temperature at which  $\beta P(z = \sigma/2)\sigma^3 = \rho_c(z = \sigma/2)\sigma^3 \approx 11.69$ . At the transition temperature,  $\alpha_{\text{gr}} = 2.66$ . It is noted here that the transition temperature is slightly different from that of Both and Hong, but its difference is small [3]. For  $T > T_c$ , there is layering near the bottom wall due to packing effects. For  $T < T_c$ , however, a strong oscillation appears which is a clear indication of the crystalline phase. The peak-to-peak density oscillation is slightly greater than the hard sphere diameter, while the peak-to-peak pressure corresponding to the solid phase is almost the same as the hard sphere diameter. The pressure diagram shows the discontinuous properties at the matching density such as the layering transition of fluids in the confined systems [12]. The number of layers in the solid phase can be determined by comparing  $\beta P(z)$  with  $\beta P_c\sigma^3 \approx 11.69$ . Figure 1(b) shows the two crystal layers. The average density, represented as the solid circles, also shows the two crystal layers. The overall picture indicates that the WDA theory can be applied to explain the condensation of hard spheres sufficiently well even for the high gravitational field. When the temperature is reduced further, it is expected that the additional fluid layer will solidify.



**Figure 1.** Density profile ( $\rho(z)\sigma^3$ : solid curves) and pressure ( $\beta P(z)/\sigma^3$ : dotted curves) of hard spheres as a function of the dimensionless length  $z/\sigma$ ; (a)  $T > T_c$  ( $\mu = 4$  and  $\alpha_{gr} = 2.41$ ), (b)  $T < T_c$  ( $\mu = 4$  and  $\alpha_{gr} = 4.58$ ). The solid circles are average values of the density peaks.

Figure 2 shows the calculated density profile and the pressure of Lennard-Jones spheres at the reduced temperature  $T^* \equiv k_B T/\epsilon = 1.35$  ( $\mu = 4$ ). According to the prescription of Week, Chandler and Andersen (WCA) the Lennard-Jones potential was divided into a repulsive part and an attractive contribution. The equivalent hard sphere diameter corresponding to the repulsive contribution was chosen according to the Barker–Henderson prescription [13]. A mean-field approximation was used to calculate the excess free energy  $F_{att}[\rho]$  for the attractive part of interaction potentials. Here, the transition temperature was taken to be the temperature at which  $\beta P(z = \sigma/2)\sigma^3 = P^*/T^* \approx 6.67$  [14]. In this case,  $\alpha_{gr} = 1.92$  at the critical temperature  $T_c$ . As can be seen in this figure, the strong oscillation appears for  $T < T_c$ . The peak-to-peak pressure corresponding to the solid phase is almost the same as the hard sphere diameter  $\sigma$ . Figure 2(b) also shows the two crystal layers.

The same argument can be extended to  $n$ -component mixtures. We assume that the bottom is the hard wall and that it has the additional gravitational interactions with the system particles

$$\beta u_{ext}^i(z) = \begin{cases} \infty, & z < \sigma_i/2, \\ \beta m_i g z, & z > \sigma_i/2. \end{cases} \quad (16)$$

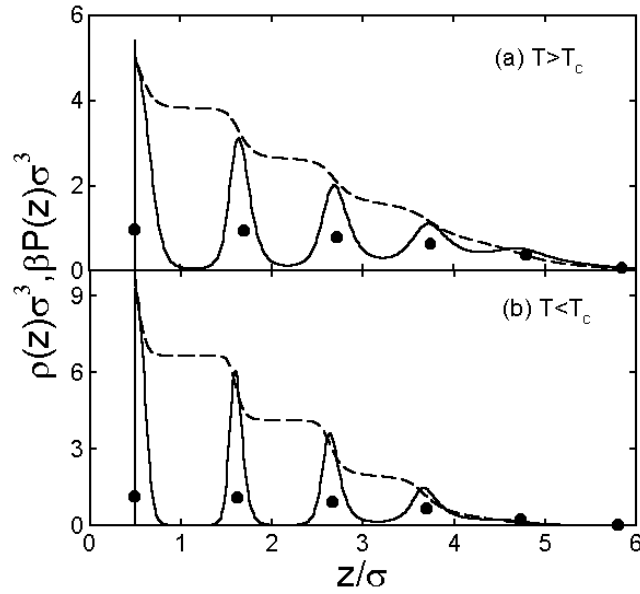
In this case, the pressure at height  $z$  is given by

$$\beta P(z) = \sum_{i=1}^n \rho_i(z = \sigma_i/2) - \sum_{i=1}^n \beta m_i g \int_{\sigma_i/2}^z \rho_i(z') dz'. \quad (17)$$

Then, equation (17) becomes

$$\sum_{i=1}^n \rho_i(z = \sigma_i/2) = \sum_{i=1}^n \beta m_i g \int_{\sigma_i/2}^{\infty} \rho_i(z') dz', \quad (18)$$

since  $\beta P(z) \rightarrow 0$  as  $z \rightarrow \infty$ . For a planar hard wall, equation (17) becomes  $\beta P = \sum_{i=1}^n \rho_i(z = \sigma_i/2)$ , where  $P$  is the bulk pressure of a  $n$ -component mixture. This is the



**Figure 2.** Density profile ( $\rho(z)\sigma^3$ : solid curves) and pressure ( $\beta P(z)/\sigma^3$ : dotted curves) of Lennard-Jones spheres ( $T^* = 1.35$ ) as a function of the dimensionless length  $z/\sigma$ ; (a)  $T > T_c$  ( $\mu = 4$  and  $\alpha_{gr} = 1.26$ ), (b)  $T < T_c$  ( $\mu = 4$  and  $\alpha_{gr} = 2.32$ ). The solid circles are average values of the density peaks.

well-known contact-value theorem [8]. Comparison with equations (1) and (18) suggests that the transition temperature for  $n$ -component mixtures can be defined as

$$k_B T_c = \frac{\sum_i^n m_i g \sigma_i \mu_i \phi_c}{\mu_0} \quad (19)$$

where  $\mu_i \phi_c = \sigma^{d-1} \int_{\sigma_i/2}^{\infty} \rho_i(z) dz$ .

If we take the pressure at the bottom as the bulk coexistence pressure corresponding to the fluid–solid transition, the transition temperature becomes

$$k_B T_c = \frac{\sum_i^n m_i \sigma_i g \int_{\sigma_i/2}^{\infty} \rho_i(z') dz'}{\beta P_c} = \frac{\sum_i^n m_i \sigma_i g \int_{\sigma_i/2}^{\infty} \rho_i(z') dz'}{\sum_{i=1}^n \rho_{ci}(z = \sigma_i/2)}, \quad (20)$$

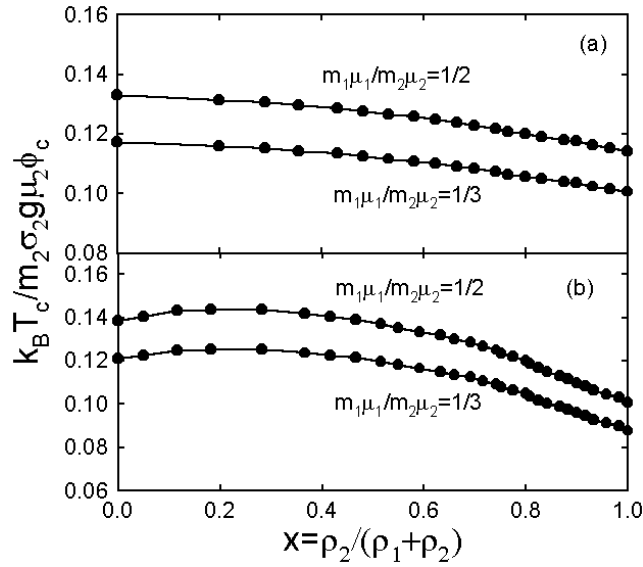
in which  $\rho_{ci}(z = \sigma_i/2)$  is the contact density of an  $i$ th component fluid at the bottom. Equation (20) shows that the transition temperature of  $n$ -component mixtures is determined to be the temperature at which  $\beta P_c = \sum_{i=1}^n \rho_{ci}(z = \sigma_i/2)$ .

We can extend the density profile equation in equation (13) to systems of  $n$ -component mixtures. In this case, the density profile  $\rho_i(z)$  is given by

$$\rho_i(z) = \begin{cases} \xi_i \exp[-\beta m_i g z + c_i^{(1)}(z; [\rho])], & z > \sigma_i/2, \\ 0, & z < \sigma_i/2, \end{cases} \quad (21)$$

where  $\xi_i = \exp(\beta \mu_{ch}^i) / \lambda_i^3$  and  $c_i^{(1)}(z; [\rho])$  is the one-particle DCF for the  $i$ th-component fluid. Then, equation (21) satisfies

$$\exp[c_i^{(1)}(z = \sigma_i/2; [\rho])] = \beta m_i g \int_{\sigma_i/2}^{\infty} \exp[-\beta m_i g z' + c_i^{(1)}(z'; [\rho])] dz'. \quad (22)$$



**Figure 3.** Transition temperature  $T_c$  of binary hard sphere mixtures as a function of the concentration of large spheres  $x = \rho_2/(\rho_1 + \rho_2)$ ; (a)  $\sigma_1/\sigma_2 = 0.95$ , (b)  $\sigma_1/\sigma_2 = 0.9$ .

For binary ( $n = 2$ ) mixtures, equation (20) simply becomes

$$k_B T_c = \frac{m_2 \sigma_2 g \mu_2 \phi_c}{\beta P_c \sigma_2^d} \left( 1 + \frac{m_1 \mu_1 \sigma_2^{d-1}}{m_2 \mu_2 \sigma_1^{d-1}} \right). \quad (23)$$

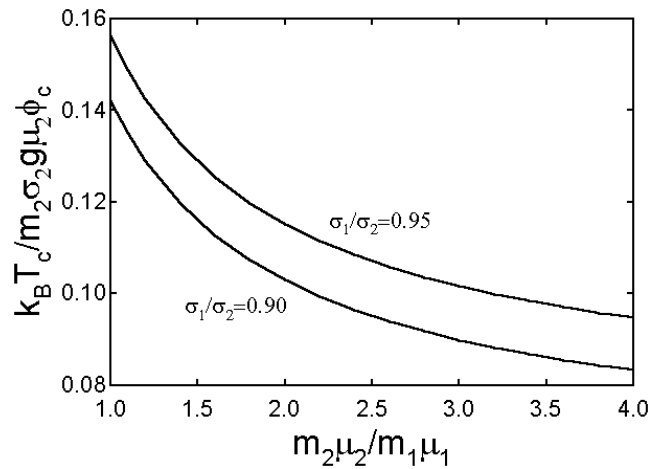
Equation (23) shows that the transition temperature increases linearly with increasing mass ratio  $m_1/m_2$ , while it decreases quadratically with increasing particle diameter ratio  $\sigma_1/\sigma_2$ . When we follow the convention  $x = \rho_2/(\rho_1 + \rho_2)$ ,  $\beta P_c$  depends on the particle diameter ratio  $\sigma_1/\sigma_2$  and the concentration  $x$  of a fluid. Then,  $\mu_0$  becomes

$$\mu_0 = \beta P_c \sigma_2^d = \sum_{i=1}^n \rho_{ci} (z = \sigma_i/2) \sigma_2^d. \quad (24)$$

Figures 3 and 4 show the transition temperature for binary hard sphere mixtures. Here, the computer simulation results done by Kranendonk and Frenkel [15], in which data can be scaled in order to match the transition parameter in the one-component limitation ( $x = 0$  and  $1$ ), were used to evaluate the transition temperature  $k_B T_c / m_2 \sigma_2 g \mu_2 \phi_c = 1/\mu_0$ . All lengths were measured in units of larger particle diameter  $\sigma_2$ . The calculated results show that the transition temperature decreases with increasing  $x$ -values or the concentration of larger particles. At the size ratio  $\sigma_1/\sigma_2 = 0.9$  in figure 3,  $T_c$  is a non-monotonic function of  $x$ . The effect is actually more pronounced for large size differences, since the transition temperature is closely related to the bulk pressure at coexistence [15].

In summary, we have derived an analytical expression for the contact value of the density of  $n$ -component mixtures under gravity. We have here defined the condensation temperature to be the temperature at which the pressure at the bottom reaches the liquid/solid coexistence pressure and determined the critical temperature for the crystallization of hard spheres and Lennard-Jones spheres. The calculated result suggests that the simple WDA theory can be applied to explain the condensation of hard spheres well enough even for the high gravitational field.





**Figure 4.** Transition temperature  $T_c$  of binary hard sphere mixtures ( $x = 0.9$ ) as a function of  $m_2 \mu_2 / m_1 \mu_1$ .

As a comment, Hong *et al* [5] have recently claimed that following Rosato *et al* [16] the crossover condition of gravity-induced segregation for binary hard spheres is given when the ratio of two critical temperatures is equal to the volume ratio of the two particles, which leads to the relationship  $m_2/m_1 = (\sigma_2/\sigma_1)^{d-1}$ . They have introduced the ratio of the centre of mass of the two spheres as the factor to quantify the segregation;  $\langle z_i \rangle = \int_{\sigma_i/2}^{\infty} z \rho_i(z) dz / \int_{\sigma_i/2}^{\infty} \rho_i(z) dz$ . However, we can show that the crossover condition can be obtained from the pressure equation (18) by choosing a simple condition for the segregation. Specifically,  $\rho_1(z = \sigma_1/2) < \rho_2(z = \sigma_2/2)$  indicates the condition for the Brazil nut type segregation,  $\rho_1(z = \sigma_1/2) = \rho_2(z = \sigma_2/2)$  for the crossover, and  $\rho_1(z = \sigma_1/2) > \rho_2(z = \sigma_2/2)$  for the reverse Brazil nut type segregation [17].

In the simulation studies investigated by Dzubiella *et al* [18] for the sedimentation of the star polymer with re-entrant melting behaviour, they observed the phase transition between the fluid and the fluid with the intercalated solid below the critical gravitational strength, and confirmed that this transition comes from the long-ranged tail in the interaction potential. On the other hand, Hong *et al* [5] have used a variational method which is based on the local density approximation (LDA) to study the binary hard sphere segregation under gravity. They have shown that the LDA yields the excited granular materials under gravity, such as the Brazil nut problem. However, it is generally known that the LDA fails to account for the strong density oscillation near the bottom. Thus, it would be interesting to apply the pressure equation employed in this work for  $n$ -component mixtures to check the solidification of the star polymer solution and the segregation of binary hard sphere mixtures under gravity. We will study these problems in the near future.

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