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Universality of the bridge functions and a semiempirical freezing criterion in two and three dimensions

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(Received 9 May 1980)

A model for systems interacting via soft inverse-power potentials enables one to express the bridge function at the origin, $B(O)$, directly in terms of the equation of state, and to find its physical meaning. The Lindemann, Ross, and van der Waals empirical melting criteria are unified by the empirical finding that $B(O)$, calculated along the freezing line, is nearly independent of the pair potential and is nearly the same in two and three dimensions.

The idea of universality of the bridge functions,¹⁻³ $B(r)$, has brought the theory of classical fluids (on the pair level) to within the accuracy of present day computer-simulation studies for nearly every physically conceivable effective pair potential. Analysis of the dense plasma statics and thermodynamics⁴ based on scaled direct correlation functions demonstrated that universality extends all the way to the origin ($r=0$). Here, I extend that analysis to mixtures of "charged" particles interacting via relatively soft inverse-power potentials. This study enables us to find semiempirical relations between the bridge functions and melting, and to assign physical meaning to $B(r=0)$. In particular (and as a generalization to the Lindemann-Ross criterion) it is found that to within the accuracy of the simulation studies, $B(r=0)$ calculated along the freezing line is independent of pair potential and is the same in two and three dimensions.

Consider a q -component mixture, containing N_i particles of type i , interacting through the pair potentials $u_{ij}(r)$. Let $N = \sum_i N_i$, V = total D -dimensional volume, $\rho = N/V$, $x_i = N_i/N$, and $\beta = 1/k_B T$. The bridge functions, $B_{ij}(r)$, represent the sum over all "basic" elementary graphs with $h_{ij}(r)$ bonds. They are related to the pair functions $g_{ij}(r) \equiv h_{ij}(r) + 1$, screening functions

$$H_{ij}(r) = \ln \{ g_{ij}(r) \exp[\beta u_{ij}(r)] \},$$

and direct correlation functions $c_{ij}(r)$ by

$$B_{ij}(r) = h_{ij}(r) - c_{ij}(r) - H_{ij}(r). \quad (1)$$

It was found possible to fit computer-simulation data for quite disparate potentials through the

thermodynamically consistent solution of the modified HNC (MHNC) equations, by means of universal q -parameter fitting functions B_{ij}^{HS} ($r, \sigma_1, \dots, \sigma_q, \rho$), appropriate to the q -component system of hard spheres (HS) with diameters σ_i ($i=1, \dots, q$).¹⁻³ The above fitting procedure is insensitive to the values of the bridge-fitting functions at small separations where the given (from computer simulations) $g_{ij}(r)$ is essentially zero. Analysis of the computer-simulation data for dense Coulomb mixtures revealed, however, that the universality of the bridge functions extends all the way to the origin, i.e., a hard-sphere bridge function that accurately fits the structure of a given system also predicts well [via Eq. (1)] the value of $H_{ij}(0)$.⁴ In other words, the equation,

$$B(0; \rho, T) = B^{\text{HS}}(0; \eta), \quad (2)$$

where B^{HS} is a hard sphere (disk, in 2D) bridge function, defines the same effective packing fraction $\eta(\rho, T)$ ($\eta = \frac{1}{6} \pi \rho \sigma^3, \frac{1}{4} \pi \rho \sigma^2$ in 3D, 2D, respectively) as the thermodynamically consistent MHNC equations. A model for soft inverse-power potentials enables to express $B(0)$ directly in terms of the equation of state of the given system.

Consider mixtures of charged particles interacting via the relatively soft inverse-power potentials, $\beta u_{ij}(r) = Q_i Q_j \Gamma_0 / r^m$ ($Q_i > 0, m/D \lesssim 4$). $\Gamma_0 \propto \beta \rho^{m/D}$ is the coupling constant and r is the distance in units of the D -dimensional Wigner-Seitz radius $a = [\pi^{-D/2} \Gamma(\frac{1}{2} D + 1) / \rho]^{1/D}$. An exact relation for these systems is⁵

$$H_{ij}(0) = \mu_{Q_i} + \mu_{Q_j} - \mu_{Q_i Q_j}, \quad (3)$$

where $\mu_{Q_i} = (\partial / \partial x_i) (\beta F_N^* / N) |_{\Gamma_0, Q, m/D}$ is the chemi-

cal potential for a particle with charge Q_i at constant total charge density and temperature (the notation is $\langle Q^s \rangle = \sum_i x_i Q_i^s$). Assume that as for plasmas with real charges⁴ these mixtures with charged soft inverse-power interactions, in the strong-coupling regime ($\Gamma_0 \gg 1$), are governed by a "one-fluid" equation of state, $(\beta U/N)_{\text{mix}}^{(m,D)} = U_0^{(m,D)}(\Gamma_0 Q_{\text{eff}}^2)$. $U_0^{(m,D)}(\Gamma_0)$ denotes the potential energy, $\beta U/N$, for the one-component system. In order to determine the effective charge Q_{eff} , a generalization of the model for plasmas is employed. The direct correlation functions are assumed to have the scaled form

$$c_{ij}^{(m,D)}(r) = \frac{-Q_i Q_j \Gamma_0}{[t_{ij} R(\Gamma_0)]^m} F^{(m,D)}\left(\frac{r}{t_{ij} R(\Gamma_0)}\right), \quad (4)$$

where $R(\Gamma_0)$ is the scaling length, and t_{ij} is a function of charges and concentrations, satisfying the identity $\sum_i x_i Q_i^2 / t_{ii}^m = \sum_{i,j} x_i x_j Q_i Q_j t_{ij}^{2-m}$. Writing the solution to this identity equation in the form $t_{ij} = [\frac{1}{2}(Q_i^{1/D} + Q_j^{1/D}) / \langle Q \rangle^{1/D}] T_{ij}(m, D)$, it can be easily verified that except for highly dissymmetric mixtures (e.g., $Q_1/Q_2 \gg 1$), T_{ij} is excellently approximated by unity. The "ion-sphere" charge averaging for multicomponent plasmas is thus generalized by

$$Q_{\text{eff}}^2 = \sum_i x_i Q_i^2 / t_{ii}^m = \langle Q \rangle^{m/D} \langle Q^{2-m/D} \rangle. \quad (5)$$

With a one-fluid equation of state for the dense inverse-power mixture and an effective charge given by (5), the exact relation (3) yields:

$$H_{ij}^{(m,D)}(0) = \frac{U_0^{(m,D)}(\Gamma_0 Q_{\text{eff}}^2)}{\langle Q^{2-m/D} \rangle} \times [Q_i^{2-m/D} + Q_j^{2-m/D} - (Q_i + Q_j)^{2-m/D}]. \quad (6)$$

Using Eq. (1) and making simple manipulations on the Ornstein-Zernike relations, one obtains

$$B(0) = \beta \left(\frac{\partial \rho}{\partial \rho} \right)_T - 1 - 2 \left(\frac{\beta U}{N} \right) - H(0) + \Delta, \quad (7)$$

for the one-component system, while a similar expression for the mixture is obtained provided one considers the average

$$\begin{aligned} \langle B(0) \rangle &\equiv \sum_i x_i B_{ii}(0) \\ &= \beta \left(\frac{\partial \rho}{\partial \rho} \right)_{T,x} - 1 - 2 \left(\frac{\beta U}{N} \right) - \sum_i x_i H_{ii}(0) + \Delta. \end{aligned} \quad (8)$$

$\beta(\partial \rho / \partial \rho)_{T,x}$ is the total inverse compressibility for the mixture, while

$$\Delta = \rho \sum_{i,j} x_i x_j \int g_{ij}(r) [c_{ij}(r) + \beta u_{ij}(r)] d\vec{r}$$

is a relatively small quantity for any dense fluid.^{2,6} Using Eqs. (6) and (7) one gets

$$\begin{aligned} [B(0) - \Delta]^{(m,D)} &= \left(\frac{m}{D} - 4(1 - 2^{-m/D}) \right) U_0^{(m,D)}(\Gamma_0) \\ &+ \left(\frac{m}{D} \right)^2 \Gamma_0 \frac{\partial}{\partial \Gamma_0} U_0^{(m,D)}(\Gamma_0), \end{aligned} \quad (9)$$

for the one-component system, and exactly the same expression, but with Γ_0 replaced by $\Gamma_0 \times Q_{\text{eff}}^2$, is obtained from (6) and (8) for the mixture average $[B(0) - \Delta]^{(m,D)}$.

It is unsafe to rely on uncontrolled approximations when assessing the subtle free-energy difference given by Eq. (3). In the absence of computer-simulation data for the mixtures treated here, I checked the result (9) for two typical cases ($m=5$ and 12 in 3D) by solving the MHNC equations to find as good agreement as found before⁴ for the one-component plasma ($m=1$).⁷

The exact result for D-dimensional hard spheres is⁸ $H_{ij}(0) = \beta \mu_j^{\text{ex}}$, where μ_j^{ex} is the excess chemical potential for the smaller spheres ($\sigma_j \leq \sigma_i$) leading to

$$[B(0) - \Delta]^{(\infty,D)} = \beta \left(\frac{\partial \rho}{\partial \rho} \right)_T - 1 - \beta \mu^{\text{ex}}. \quad (10)$$

Interesting enough (and as for soft spheres above), exactly the same expression but with the equation of state for the mixture is obtained for $[B(0) - \Delta]^{(\infty,D)}$.

Incorporating (9) and (10) in (2) one obtains the effective packing fraction, $\eta_{B(\infty)}(\Gamma_0)$, which is generally consistent with that obtained from the variational hard-sphere⁹ (VHS) calculations, $\eta_{\text{VHS}}(\Gamma_0)$. The van der Waals (vdW) model for freezing correlates the transition of the hard spheres with the melting transition of simple systems.¹⁰ It leads to a Lindemann-type criterion that associates freezing with a universal effective packing fraction⁹ (e.g., $\eta_{\text{VHS}} \approx 0.45-0.50$ in 3D). The vdW hard-sphere freezing criterion can be reformulated in terms of the new definition of effective packing via $B(0)$.

Systems of particles interacting through inverse-power potentials ($m=1, 4, 6, 9, 12, \infty$) have been studied by computer simulations,^{11,12} and accurate semiempirical fits to the equation of state were derived¹³ enabling to calculate (9) along the freezing lines (denoted by subscript f) as determined by the simulations, with the following results: (i) $D=3$. For $m=1, 4, 6, 9, 12$ at the corresponding $(\Gamma_0)_f = 155, 66, 83, 174, 540$, one obtains $[B(0) - \Delta]_f = 52, 54, 52, 50, 54$, respectively. For hard spheres at $\eta_f = 0.5$ the result is $[B(0) - \Delta]_f = 40$. (ii) $D=2$. For hard discs at $\eta_f = 0.69$ and for $m=1$ at $(\Gamma_0)_f = 125$ one gets $[B(0) - \Delta]_f = 50, 52$, respectively.

(iii) For the Lennard-Jones (LJ) potential it is justified to use the relation¹⁴ $H_{LJ}(0) = \beta\mu_{LJ}$ and by employing an accurate equation of state¹⁵ one gets $[B(0) - \Delta]_f = 49, 48$ at $T_f/\epsilon = 0.72, 1.15$, respectively. (iv) A detailed analysis in 3D shows that $\Delta_f \cong -6, +5$ for the two extreme cases $m = 1, \infty$, respectively. With allowance for small deviations from the assumed "one-fluid" laws and for uncertainties in the values of Δ , a relation of the type

$$B_f(0) = 50 \pm 10\%, \quad (11)$$

can provide a *universal* freezing indicator in both two and three dimensions. This criterion can be generalized to mixtures: $\langle B_f(0) \rangle = 50 \pm 10\%$ is manifestly the generalization of (11) to mixtures with soft inverse-power potentials.

The strong-coupling potential energy for $m/D \leq 4$ is dominated by the Madelung term, $\alpha_M \Gamma_0$, and a good approximation for $B(0)$ over a limited region near freezing is given by

$$B(0) = A_{br}(m/D) \alpha_M \Gamma_0 + b, \quad (12)$$

where

$$A_{br}(m/D) = (m/D)(m/D + 1) - 4(1 - 2^{-m/D}),$$

α_M is the fcc (or triangular lattice in 2D) Madelung constant, and b is a constant ($b \sim 1$ for $m/D \leq 2$ and $b \sim 10$ for $m = 12$ in 3D). To compare (12) with other empirical melting indicators we put them also on a linear in Γ_0 scale. Lindemann's law¹⁶ says that the system melts whenever the ratio (δ) of the root-mean-square deviation of a particle from its static lattice position, to the nearest-neighbor distance exceeds some critical value δ_{melt} . When written in terms of the Debye temperature it can be extended also to 2D.¹⁷ Upon using the lattice-dynamics approximation (LD) in 3D, one obtains

$$1/\delta^2 = A_{LD} \alpha_M \Gamma_0, \quad (13)$$

where A_{LD} is a combination of lattice sums and computer calculated numerical factors.¹⁸ Ross's criterion¹⁹ is equivalent to the statement that the thermal free energy, $f = \beta F_{\text{th}}^{\text{ex}}/N$, is constant (C_R) along the melting line. In the harmonic approximation (justified even for $m = 12$ in 3D),²⁰ $f = (D/2) \ln(A_R \alpha_M \Gamma_0)$ where $A_R = \exp(2C_R/D)/[\alpha_M(\Gamma_0)_{\text{melt}}]$, one obtains

$$\exp(2f/D) = A_R \alpha_M \Gamma_0. \quad (14)$$

The approximate equality $1/\delta^2 = \exp(2f/D)$ in 3D ($A_R \sim A_{LD}$) is exact in the harmonic cell theory for any D , and may also serve to extend Lindemann's law to 2D. Results of computer and laboratory experiments^{12, 21} indicate that δ_{melt} and C_R are roughly the same, independent of details of the potential, at least for simple systems: e.g., $\delta_{\text{melt}} = 0.125, 0.17$ and $C_R = 5.85, 6.3$ for the extreme cases $m = \infty, 1$, respectively, in 3D, and $C_R = 3.9, 4.3$ (Ref. 23) is likewise in 2D.

The numerical similarity of $B_f(0)$, $\exp(2C_R/D)$ and $1/\delta_{\text{melt}}^2$ is not accidental and reflects the similar physical meaning of these quantities: (i) In the limit of high densities near closest packing (cp) of D -dimensional spheres we have $f^{(\infty, D)} - D \ln(1 - \eta/\eta_{\text{cp}})$ and the dominance of the $\beta(\partial P/\partial \rho)_T$ term in (10) implies $B(0)^{(\infty, D)} - \exp(2f/D)^{(\infty, D)}$. 1D spheres do not undergo a melting transition yet the exact 1D relation, $B(0) = \exp(2f/D) - \exp(f/D) - f/D$ yields $B(0) \cong 50$ for $2f/D \cong 4$, in agreement with the 2D and 3D results for $2C_R/D \cong 4$. (ii) For soft interactions the $\beta(\partial P/\partial \rho)_T$ term in (12) is no longer dominant. In 3D, A_{br} , and A_{LD} vary from zero (for $m/D = 1$) to about 20 (for $m/D \sim 4$), yet they maintain a nearly constant ratio (Refs. 24 and 25) between them, e.g., $A_{LD} \alpha_M \Gamma_0 \cong 45$ vs $A_{br} \alpha_M \Gamma_0 \cong 50$ for $m = 4, 6, 9, 12$.

$B(0)$, which was originally introduced as a measure of effective packing suitable for reformulating the vdW hardsphere freezing criterion, is found to be close in physical meaning to the quantities used to formulate the Lindemann and Ross criteria. The Lindemann, Ross, and vdW criteria can now all be expressed in terms of the thermodynamic expression for $B(0)$. The D independence of $B_f(0)$ is yet to be explained, but it is correlated with that of the Ross indicator $2C_R/D$. The new freezing criterion (11) is, however, unique in two main respects: (i) $B_f(0)$ is a *universal* quantity related to melting in the sense that its precise value for one system (in either 2D or 3D) will predict the freezing densities for any system (in either 2D or 3D) to within the accuracy of present day computer studies. Note that the Ross indicator is much less universal in that sense.²⁶ (ii) The $B_f(0)$ criterion can be applied via its *structural* definition (in, e.g., the MHNC scheme) and via the *equation of state* [e.g., Eq. (9)]. In particular, the study of the possible role played by $B(0)$ [and $B(r)$] in the process of melting can proceed via a diagrammatic analysis,²⁷ providing a new angle for the vdW and Lindemann approaches.

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