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Structure of two-dimensional hard disk systems. Simple geometric method

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ABSTRACT

Two-dimensional systems, especially systems of hard disks, have been studied intensively during the last years both by simulation methods and theoretically; modified density functional theory has been applied most often. Recently, we have proposed an improved expression for the residual Helmholtz energy, ΔA, of the mixtures of 2D convex figures, which makes it possible to develop another, more simple "geometric" method. By differentiating ΔA with respect to the number of particles of type j, the chemical potential $\Delta\mu_j$ might be obtained and consequently the logarithm of the radial distribution function expressed in terms of $\Delta\mu_k$ of the considered pair of particles and the corresponding combined figure. The resulting equation is very simple, only two geometric quantities – figure areas and mean curvature integrals (mean radii) are to be evaluated. The used method is extremely simple and yields accurate prediction of the radial distribution functions of both the one- and multi-component systems in the most important interval of distances.

1. Introduction

In the last decade we have witnessed renewed interest in the two-dimensional (2D) systems of hard disks, ellipses and two-dimensional Lennard–Jones fluids [1–8]. This interest is connected with the studies of adsorption, catalysis, behavior of colloids and planar nano-systems by statistical thermodynamic methods. To this end, simulation data were obtained for the simplest models of such systems, i.e. systems with hard body repulsions [7–16]. Quite often the modification of the density functional theory has been applied [8–15] to predict the structure of these systems via radial distribution function or the surface density profile.

In the recent paper [17] we dealt with the equation of state of the 2D convex figures (including hard disks), derived from the self-consistent-like expression [18] for the residual Helmholtz energy, ΔA. The corresponding equation of state is valid for all the convex figures, and includes – besides of the 2D non-sphericity factor – only one constant (adjusted to the virial coefficients); it predicts accurately the behavior of the pure hard disks and their mixtures up to the highest densities. Predictions agree fairly well with results from many-constant equations of state for disks.

Our knowledge of the equation for the residual Helmholtz function for the whole family of convex figures makes it possible to derive an expression for the residual chemical potential of different convex figures including hard disks. By applying Meeron–Siegert relation [19] (see also [20–22]) the expression for the 2D radial distribution function can be formulated, in which – besides of the pair of particles we consider the "enlarged combining figure" (the geometric quantities of which are tractable via expressions of the convex figures). The resulting expression for the distribution function, g, possesses the form corresponding to the three-dimensional case [23], however in terms of only two geometric quantities – difference in areas, ΔS and difference in the 2D mean curvature integral (divided by 2π). These differences are so far well known only for the interval of distances of the pair of considered particles $r_{12} \in (0, 2)$; this fact limits the range of our present results.

2. Theory

In the recent paper [17] we have proposed an accurate equation of state for two-dimensional hard disks, two-dimensional prolate sphero-cylinders, ellipses and other convex figures. The equation for the residual Helmholtz energy, ΔA, reads as

$$\frac{\Delta A}{N_A kT} = -\ln(1-\eta) + \frac{\gamma\eta(1+c\eta)}{(1-\eta)} \tag{1}$$

where N_A stands for the Avogadro number, k denotes Boltzmann constant, T – temperature, η – packing fraction and c possesses value $\gamma/14$; γ is the 2D non-sphericity (non-circular) factor [23], $\gamma = \pi\left(\sum x_i R_i\right)^2 / \sum x_i S_i$ and R_i, S_i denote "mean radius" and area of the

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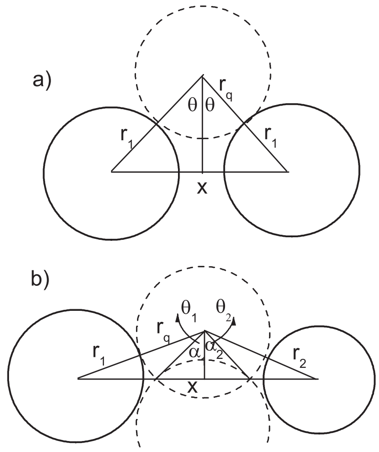

Fig. 1. Geometry of the combined figure (*CF*) of the 2D hard disks (a) for pure fluid with $x = r_{12}/\sigma$, $r_q = r_1 = \sigma/2$; θ – characteristic angle, (b) for the i–j pair in a mixture of hard disks; θ_i, α_i – characteristic angles (the latter determined by the intersection of the probe circle with the site-site connecting line.

ith figure. (For pure hard disks $\gamma = 1$.) The corresponding equation of state of the form

$$\frac{P}{\rho kT} = \frac{1}{(1-\eta)} + \frac{\gamma\eta[1+\gamma(\eta/7-\eta^2/14)]}{(1-\eta)^2} \tag{2}$$

has proved [17] to describe the state behavior of hard disks in the broad interval of surface densities and that of other convex figures in the isotropic phase.

By differentiation of ΔA with respect to number of molecules of the j-type, N_j, one obtains the residual chemical potential, $\Delta\mu_j$. Thus for $\Delta\mu_j$ we have (cf. [19–23])

$$\frac{\Delta\mu_j}{kT} = -\ln(1-\eta) + z(2\gamma R_j^* + S_j^*) + \gamma z^2[S_j^*(1+c\gamma\eta) + c\gamma(1-\eta)(4R_j^*-1)] \tag{3}$$

where $z = \eta/(1-\eta)$ and R_j^*, S_j^* are the dimensionless quantities,

$$X_j^* = \frac{X_j}{\sum_i x_i X_i} \tag{4}$$

Similarly as in the three-dimensional case, the expression for the distribution function, g, in terms of the chemical potentials of particles i, j and that of the combined figure, CF, holds true

$$\ln g_{ij} = \beta\Delta\mu_i + \beta\Delta\mu_j - \beta\Delta\mu_{CF} \tag{5}$$

where $\beta = 1/kT$. In the case of 2D disks, the combined figure (for shorter distances $x = r_{ij}/\sigma$) is given by two disks and area determined by the probe circle with diameter, q, see Fig. 1a). After substitution from Eqs. (3) and (5) one has

$$\ln g_{ij} = -\ln(1-\eta) + z(2\gamma\Delta R^* + \Delta S^*) + \gamma z^2[\Delta S^*(1+c\gamma\eta) + c\gamma(1-\eta)(4\Delta R_j^*-1)] \tag{6}$$

Here

$$\Delta R^* = \frac{(\Delta R_i^* + \Delta R_j^* - \Delta R_{CF}^*)}{\sum x_i R_i} \qquad \Delta S^* = \frac{(\Delta S_i^* + \Delta S_j^* - \Delta S_{CF}^*)}{\sum x_i S_i} \tag{7}$$

2.1. Pure hard disks

In the case of the pure hard disks, the diameter of the probe circle, q, is taken to be equal to that of the studied hard disk, i.e. $q = p = 1$, and the reduced quantities – $R^* = 2R_i/\sigma$ and $S^* = 4S_i/(\pi\sigma^2)$ possess values $R^* = S^* = 1$. For values of $x < \sqrt{3}$ the quantities of the combined figure are

$$R_{CF}^* = \left[p + \frac{2(p+q)\theta}{\pi}\right] = 1 + \frac{4\theta}{\pi} \tag{8}$$

$$S_{CF}^* = p^2 + \frac{2(p^2-q^2)\theta}{\pi} + \frac{2(p+q)^2\cos(\theta)\sin(\theta)}{\pi} = 1 + \left(\frac{8}{\pi}\right)\cos(\theta)\sin(\theta) \tag{9}$$

where the expression for R_{CF}^* follows from differentiation of S_{CF}^* with respect to p and $(-q)$; θ is the characteristic angle, $\theta = \arcsin(x/2)$. Then,

$$\Delta R^* = 1 - \frac{4\theta}{\pi}, \quad \Delta S^* = 1 - \left(\frac{8}{\pi}\right)\cos(\theta)\sin(\theta) \tag{10}$$

For the reduced distances $x \in (\sqrt{3}, 2.0)$ we have

$$R_{CF}^* = 1 + \frac{4\theta}{\pi} - \frac{2q\alpha}{\pi} + \frac{q\sin(\alpha)}{(2\pi)}$$

$$S_{CF}^* = 1 + \left(\frac{8}{\pi}\right)\cos(\theta)\sin(\theta) + \frac{2q^2\alpha}{\pi}$$

and for $x > 2.0$ we take value $g = 1$. (The last term of the expression for R_{CF}^* has a slightly empirical character and is not considered in the case of mixtures.)

2.2. Mixtures of hard disks

Firstly we will consider a binary mixture of 2D hard disks with the diameter ratio $p = \sigma_2/\sigma$ ($\sigma = \sigma_1 = 1$), mole fraction x_1 and packing fraction $\eta = \rho\sum x_i S_i$, where ρ denotes the surface density. If $p_1 = 1$ and $p_2 = p$ and

$$q = \frac{\sum x_i p_i^2}{\sum x_i p_i} \tag{11}$$

then we write for the combined figure of the pair i–j (see Fig. 1b)

$$R_{ij} = \left(\frac{1}{2}\right)\sum_{k=i,j}\left[p_k + \frac{2(p_k+q)\theta_k}{\pi} - \frac{2q\alpha_k}{\pi}\right] \tag{12}$$

and

$$S_{ij} = \left(\frac{1}{2}\right)\sum_{k=i,j}\left[p_k^2 + \frac{2(p_k^2-q^2)\theta_k}{\pi} + \left(\frac{2}{\pi}\right)(p_k+q)^2\cos(\theta_k)\sin(\theta_k) + \frac{2q^2\alpha_k}{\pi}\right] \tag{13}$$

Here θ_k and α_k denote characteristic angles of the part of the combined figure, corresponding to the k-disk with $R_k^* = p_k$ and $S_k^* = p_k^2$. Angle α_k is related to θ_k via the expression

$$(p_k+q)\cos(\theta_k) = q\cos(\alpha_k) \tag{14}$$

Then

$$\Delta R_{ij}^* = \frac{1}{(2R_s)}\sum_{k=1,2}\left[p_k - (p_k+q)\left(\frac{2\theta_k}{\pi}\right) + q\left(\frac{2\alpha_k}{\pi}\right)\right] \tag{15}$$

$$\Delta S_{ij}^* = \frac{1}{(2S_s)}\sum_{k=1,2}\left[p_k^2 - 2(p_k^2-q^2)\left(\frac{\theta_k}{\pi}\right) - \left(\frac{2}{\pi}\right)(p_k+q)^2\cos(\theta_k)\sin(\theta_k) - q^2\left(\frac{\alpha_k}{\pi}\right)\right] \tag{16}$$