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Communication: Fundamental measure theory for hard disks: Fluid and solid

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Two-dimensional hard-particle systems are rather easy to simulate but surprisingly difficult to treat by theory. Despite their importance from both theoretical and experimental points of view, theoretical approaches are usually qualitative or at best semi-quantitative. Here, we present a density functional theory based on the ideas of fundamental measure theory for two-dimensional hard-disk mixtures, which allows for the first time an accurate description of the structure of the dense fluid and the equation of state for the solid phase within the framework of density functional theory. The properties of the solid phase are obtained by freely minimizing the functional. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3687921>]

Many body systems with hard-core repulsions are of extreme significance for classical statistical mechanics. On the one hand, they are important model systems, which display phase transitions driven purely by entropy. On the other hand, they are useful reference systems for fluids or solids with a soft repulsion or attraction in addition to the hard core. In recent times, a number of dedicated experimental and simulation studies on quasi-two-dimensional (2D) systems have been performed. Such systems can be realized by an efficient trapping of colloids through laser fields or interfaces. In these studies, a wide range of the possible peculiarities associated with phase transitions in 2D have been addressed. Examples are investigations of quasicrystallinity in monolayers,^{1,2} studies on the nature of the liquid–solid transition,³ defect interactions in 2D crystals,⁴ on equilibrium structures of binary crystals,⁵ or investigations on the glass transition.^{6,7} Thus, there is an urge also for theories able to address these questions. Surprisingly, such theoretical methods are limited in 2D, even though equivalent methods are well developed in 3D.^{8,9} In this respect, classical density functional theory (DFT) is one of the most important and successful statistical mechanical approaches to study the thermodynamics and the structure of homogeneous and inhomogeneous fluids and solids in a unified manner. Especially for hard body fluids in 3D, classical DFT is well developed^{9–12} and can describe both fluid and solid phases with high accuracy. In 2D, this is not so, and it is the purpose of this letter to elaborate a DFT for hard disks which precisely allows this description.

For hard spheres in $d = 3$ fundamental measure theory (FMT) is especially successful and accurate when compared, e.g., with computer simulations. FMT is based on insight gained from the exact DFT for hard-rod mixtures in $d = 1$ and on ideas based on scaled-particle theory (SPT) and related theories. The original derivation of FMT starts with the exactly known low density limit, $\rho_i \rightarrow 0$, of the excess free

energy functional, which for any system with pair interaction $V_{ij}(r)$ and ensuing Mayer- f function $f_{ij}(r) = \exp(-\beta V_{ij}(r)) - 1$ is given by

$$\beta \mathcal{F}_{ex} \rightarrow -\frac{1}{2} \sum_{i,j} \int d\mathbf{r} \int d\mathbf{r}' \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') f_{ij}(|\mathbf{r} - \mathbf{r}'|), \quad (1)$$

with the local (inhomogeneous) density $\rho_{i[j]}(\mathbf{r})$ of species $i[j]$. In order to extrapolate this exact low density result for mixtures of different radii to higher densities, Rosenfeld realized that the Mayer- f function has to be decomposed into convolution products of weight functions that possess solely geometrical properties of particles of one component. This decomposition can be done exactly with only two weight functions for each particle species in $d = 1$. In $d = 3$, Rosenfeld found for hard spheres a decomposition using four scalar and two vector-like weight functions.⁹ An equivalent alternative was proposed by Kierlik and Rosinberg.^{13,14}

Rosenfeld also applied his FMT *recipe* to the problem of hard-disk mixtures in $d = 2$. However, in $d = 2$, as in any even space dimension, the exact deconvolution of the Mayer- f function requires an infinite number of weight functions.^{12,15} Clearly, this makes an approach based on an exact deconvolution impractical. Rosenfeld approximated the deconvolution of the two-dimensional Mayer- f function by employing scalar and vector-like weight functions¹⁵ that are analogous to those employed in $d = 3$.^{9,10} While at low densities the resulting functional performs fairly well, its accuracy decreases rapidly at intermediate and higher densities and it fails to account for the solid phase completely. Incidentally, we want to emphasize that also the original FMT functional for hard-spheres in $d = 3$ failed to account for the hard-sphere solid, however, for completely different reasons, as became clear from studies of the dimensional crossover behavior of FMT functionals.¹¹

Here, we employ the Gauss-Bonnet theorem from integral geometry as a starting point to revisit the deconvolution of $f_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$, the Mayer- f function of two disks $\mathcal{D}_i$ and $\mathcal{D}_j$ (with radii R_i and R_j) of component i and j in $d = 2$ and with centers located at $\mathbf{r}_i$ and $\mathbf{r}_j$.¹² If the disks overlap, the

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Gauss-Bonnet theorem results in

$$-2\pi f_{ij} = \int_{\partial\mathcal{D}_i \cap \mathcal{D}_j} K_i dA_i + \int_{\mathcal{D}_i \cap \partial\mathcal{D}_j} K_j dA_j + \int_{\partial\mathcal{D}_i \cap \partial\mathcal{D}_j} \phi ds, \quad (2)$$

where $K_{i[j]}$ is the Gaussian curvature of disk $i[j]$ and ϕ is the angle between the surface normals $\mathbf{n}_i$ and $\mathbf{n}_j$ of disk i and j , at their two intersecting points. The first two terms on the r.h.s. of Eq. (2) can be expressed in the standard FMT form^{9,10} as a convolution product of geometrical weight functions. However, the third term (in which the sum over the two intersection points $\partial\mathcal{D}_i \cap \partial\mathcal{D}_j$ is written as an integral), can not be expressed as a simple convolution product. Using the relation

$$\frac{2\cos^m \phi}{\sin \phi} = \int_{\partial\mathcal{D}_i \cap \partial\mathcal{D}_j} (\mathbf{n}_i \cdot \mathbf{n}_j)^m \frac{ds}{\sin \phi} = \omega_i^{(m)} \otimes \omega_j^{(m)}, \quad (3)$$

$$\omega_i^{(m)}(\mathbf{r}) = \underbrace{\hat{\mathbf{r}} \dots \hat{\mathbf{r}}}_{m \text{ times}} \delta(R_i - |\mathbf{r}|), \quad (4)$$

this term can be written as an infinite series in m of convolution products ($\otimes$) of rank m tensors $\omega_i^{(m)}$ and $\omega_j^{(m)}$ with complete contraction of their indices,

$$\omega_i^{(m)} \otimes \omega_j^{(m)} = \sum_{k_1 \dots k_m} \int d\mathbf{r} \omega_i^{k_1 \dots k_m}(\mathbf{r} - \mathbf{r}_i) \omega_j^{k_1 \dots k_m}(\mathbf{r} - \mathbf{r}_j).$$

Hence, we find the following deconvolution series of the Mayer- f function for hard disks:

$$-f_{ij} = \omega_2^i \otimes \omega_0^j + \omega_2^j \otimes \omega_0^i + \sum_{m=0}^{\infty} \frac{C_m}{2\pi} \omega_i^{(m)} \otimes \omega_j^{(m)}, \quad (5)$$

where the lowest three coefficients are $C_0 = \pi/2$, $C_1 = -1$, $C_2 = -\pi/4$ and all higher coefficients ($m \geq 3$) can be written as $C_m = -(m-3)!!/m!! C_{\text{mod}(m, 2)}$. Here, $\omega_2^i(r) = \Theta(R_i - r)$ and $\omega_0^i(r) = \omega_i^{(0)}(r)/(2\pi R_i) = \delta(R_i - r)/(2\pi R_i)$.

To proceed, we introduce weighted densities of the v -component mixture^{9,10}

$$n_\alpha = \sum_{i=1}^v \rho_i \otimes \omega_\alpha^i, \quad n^{(m)} = \sum_{i=1}^v \rho_i \otimes \omega_i^{(m)}, \quad (6)$$

employing the convolution $\rho_i \otimes \omega = \int d\mathbf{r}' \rho_i(\mathbf{r}') \omega(\mathbf{r} - \mathbf{r}')$ where ω stands for the weight functions $\omega_\alpha^i, \omega_i^{(m)}$ ($\alpha = 0, 2$ and $m \in \mathbb{N}$). Using these weighted densities, we make an ansatz for the excess free energy density $\beta^{-1}\Phi$ where Φ must have dimensions of $1/\text{length}^2$,^{9,10}

$$\Phi(\{n_\alpha, n^{(m)}\}) = f(n_2)n_0 + \sum_{m=0}^{\infty} g_m(n_2) C_m n^{(m)} \cdot n^{(m)}.$$

The scalar functions f and g_m of the dimensionless packing fraction n_2 can be determined from the SPT differential equation for the bulk pressure p ,^{9,10}

$$\beta p = \lim_{R_i \rightarrow \infty} \frac{\beta \mu_i}{A_i} = \frac{\partial \Phi}{\partial n_2} \stackrel{!}{=} \sum_i \beta \mu_i^{ex} \rho_i - \Phi + n_0, \quad (7)$$

where the particles of one fixed species i with the area $A_i = R_i^2 \pi$ are scaled up. The excess chemical potentials for species i are given by $\beta \mu_i^{ex} = \partial \Phi / \partial \rho_i$. The differential equations for f and g_m are readily integrated and the integration

constants can be fixed such that $g_m \equiv g$ for all m . The excess free energy density $\Phi(\{n_\alpha, n^{(m)}\})$ results in

$$\Phi = -n_0 \ln(1 - n_2) + \frac{1}{4\pi(1 - n_2)} \sum_{m=0}^{\infty} C_m n^{(m)} \cdot n^{(m)}. \quad (8)$$

For bulk systems, this free energy is the same as the SPT free energy for a mixture. We note that in the case of one-component systems our result is equivalent to a functional derived by Tarazona and Rosenfeld¹¹ using a completely different route (dimensional crossover). Indeed, one can show¹⁶ that the second term on the right hand side of Eq. (8) can be written as a double convolution in the form $\sum_{ij} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho_i(\mathbf{r} - \mathbf{r}_1) \rho_j(\mathbf{r} - \mathbf{r}_2) F_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ with a nontrivial convolution kernel $F_{ij}(\mathbf{r}_1, \mathbf{r}_2)$ which fully agrees with the corresponding double convolution term in Ref. 11 (one component) and Ref. 17 (multicomponent mixture).

The free energy density (Eq. (8)) is still numerically intractable through the appearance of an infinite number of weighted densities. We recall that in Rosenfeld's original attempt¹⁵ the truncation of the generalized tensor weighted densities $n^{(m)}$ to just $n^{(0)}$ (scalar) and $n^{(1)}$ (vector) has proved clearly insufficient. Therefore, a minimal truncation going beyond this consists in taking into account also the rank 2 tensor-weighted densities $n^{(2)}$. However, any truncation of the series in Eq. (8) while keeping the coefficients C_m given above results in two serious deficiencies: (i) the SPT equation of state is violated (or equivalently the second virial coefficient is wrong) and (ii) the free energy of sharply peaked density profiles (as occurring in crystals) is severely affected. In the language of dimensional crossover this means a departure from the known free energy of a cavity which can hold only one particle and is only slightly larger than the particle itself. Both deficiencies can be remedied by considering $C_0 \dots C_2$ as free parameters. The correct second virial coefficient requires $C_0 + C_2/2 = 1$ and the correct free energy for a single, sharp density peak requires $C_0 + C_1 + C_2 = 0$. Thus, one finds $C_0 = (2 + a)/3$, $C_1 = (a - 4)/3$, $C_2 = (2 - 2a)/3$ with a single fit parameter a which we fixed to $a = 11/4$ by a least-squares fitting criterion on the Mayer- f function. Rosenfeld's original functional¹⁵ also fulfills the above criteria through $C_0 = -C_1 = 1$, $C_2 = 0$. The final form of the free energy density according to our considerations is given by

$$\Phi(\{n_\alpha, n^{(m)}\}) = -n_0 \ln(1 - n_2) + \frac{1}{4\pi(1 - n_2)} \times \left(\frac{19}{12} (n^{(0)})^2 - \frac{5}{12} n^{(1)} \cdot n^{(1)} - \frac{7}{6} n^{(2)} \cdot n^{(2)} \right). \quad (9)$$

As a first test for the functional we calculate the pair correlation function $g(r)$ in the fluid phase using the test particle route, where one particle is fixed at the origin and is made an external potential for the fluid. The pair correlation function follows from $g(r) = \rho(r)/\rho$, where ρ is the bulk density and $\rho(r)$ is the fluid density profile obtained by minimizing the functional subject to this external potential. While for low values of the packing fraction $\eta = \pi \rho R^2$ the performance of the present functional is similar to that of

FIG. 1. The pair correlation function $g(r)$ in a hard-disk fluid with a packing fraction of $\eta = 0.65$. The results of the present functional (full line) are in excellent agreement with data from Monte Carlo simulations (symbols). Note that the difference between the result of the present functional and that of the Rosenfeld functional for hard-disks (dashed line) is large. The inset shows the difference between DFT and the simulations.

Rosenfeld's FMT for hard disks, at higher packing fractions clear deviations between the two approaches can be seen. As an example we show in Fig. 1 the results for $\eta = 0.65$, a rather high value of the packing fraction. There are clear deviations between the present functional (full line) and Rosenfeld's FMT (dashed line). In particular, the kink for $r = 4R$ (very pronounced for the Rosenfeld functional) is much weaker in the result obtained by the present functional. In addition, when comparing the results using the present functional to data from our Monte Carlo simulations we find excellent agreement.

Having established the quality of the present functional to describe the fluid phase we now turn to the hard-disk solid. To this end we consider a unit cell of a hexagonal lattice, which we extend to the thermodynamic limit by periodic boundary conditions in both directions. The use of periodic boundaries introduces an idealization and hence some approximations. First, this assumes long-ranged positional order, which for short-ranged interactions in two dimensions can not exist.¹⁸ Second, this rules out any fluid-solid phase transition scenario other than first order for the hard-disk model. With our calculations we can (at present) not contribute to the still open discussion of the order of the freezing transition for hard disks in two dimensions. However, quantitative differences in the equation of state between a weak first order and a Kosterlitz–Thouless scenario may be small, thus we are confident that we obtain a good account for the solid properties.

In order to obtain the density profile of the solid, following Ref. 19, we start by fixing the packing fraction η^r of the reservoir. In a defect-free two-dimensional solid with hexagonal order there would be $N = 2$ particles per unit cell. Due to strong thermal fluctuations in $2d$ we have to consider the possibility of a relatively high (compared to three or higher dimensions) concentration of vacancies

n_{vac} , which changes the effective number of particles in the unit cell to $N = 2(1 - n_{vac})$. For given values of η^r and n_{vac} , we *freely* minimize the grand potential functional $\beta\Omega[\rho] = \int d\mathbf{r} [\Phi[\rho] + \rho(\mathbf{r})(\ln \rho(\mathbf{r}) - 1 - \beta\mu(\eta^r))]$ in order to obtain the inhomogeneous density profile $\rho(x, z)$ of the solid in a unit cell. This is in clear contrast to the usual parametric minimization of the solid assuming Gaussian peaks, which is numerically less demanding but results in a simplified description of the solid. At this stage n_{vac} is an input parameter. The equilibrium state of the solid is determined by minimizing the free energy per particle in the solid with respect to n_{vac} . The output of this calculation is the density profile $\rho(x, z)$ of the solid, the vacancy concentration n_{vac} , the chemical potential $\mu(\eta^r)$, and the pressure $p(\eta^r)$.

The attempt to produce a stable solid with the Rosenfeld functional for hard disks failed for all values of the reservoir packing fraction η^r , despite the choice of coefficients C_0 and C_1 (see Eq. (8)) which preserved an accurate fluid equation of state and guaranteed the finite, correct free energy of single sharp density peaks. Thus, the failure of Rosenfeld's FMT for disks is much more subtle than in $3d$.¹¹

For the present functional we obtain solids for reservoir packing fractions $\eta^r \geq 0.718$. An example for the freely minimized inhomogeneous density profile $\rho(x, z)$ of the solid in a unit cell is shown in Fig. 2 for a reservoir packing fraction $\eta^r = 0.75$. The vacancy concentration that minimizes the free energy per particle for this solid is $n_{vac} \approx 0.00558$.

We calculate the structure and corresponding thermodynamic quantities, n_{vac} , μ , and p , for reservoir packing fractions $\eta^r \geq 0.718$. In Fig. 3, we show the chemical potential $\mu(\eta^r)$ (dotted line) and the equation of state $p(\eta^r)$ (full line) of the solid. Note that the agreement with simulations is good for the chemical potential while the pressure is overestimated a bit. Instead of determining the free parameter a using the low-density properties of the functional (see the discussion before Eq. (9)), one may fit it to the bulk crystal properties: we find a good description of the simulated pressure for $a = 3$. In the inset of Fig. 3, we also show the vacancy concentration n_{vac} as a function of η^r . It can be seen that n_{vac} is substantial for $\eta^r < 0.8$, however, our n_{vac} is roughly 5 times higher than in simulations.²²

For the determination of the coexisting fluid and solid densities we assume from the onset a first order phase transition. We obtain $\eta_f = 0.7062$, and $\eta_s = 0.7201$ for the coexisting packing fractions by imposing equal pressure and chemical potential in the fluid (f) and the solid (s). Interestingly, these coexistence densities approximately coincide with the densities of the putative fluid–hexatic and hexatic–solid transitions extracted from large-scale computer simulations.²³ Note that very recent simulation data suggest a first order fluid–hexatic transition with coexisting packing fractions of 0.700 and 0.716 and a continuous hexatic–solid transition at a packing fractions of ~ 0.720 .²⁴

In summary, we have presented an improved fundamental measure theory functional for hard-disk mixtures. While it is obvious that due to the geometry in two dimensions the FMT approach in $2d$ (or in general in even dimensions) requires additional approximations compared with FMT in $3d$ (or in odd dimensions), we have shown that an additional

FIG. 2. The density profile $\rho(x, z)$ in a unit cell of a hard-disk solid at a reservoir packing fraction of $\eta^r = 0.75$ resulting from a free minimization of the functional. We extend the solid by using periodic boundary conditions in both directions.

tensorial weighted density is sufficient to allow for a simultaneous description of the fluid and solid phase. While further refinements are possible, this functional appears to be very suitable starting point to describe properties of ordered 2d systems which have been recently and are currently under investigation.

FIG. 3. The chemical potential $\beta\mu$ (dotted line) and the pressure βp (full line) of the crystal as a function of the packing fraction η^r , obtained from free minimization of the new functional. The thin lines are predictions of cell theory for the pressure (dashed line) and the chemical potential (dashed-dotted line) of a two-dimensional crystal²⁰ and the symbols are computer simulation data for the pressure (squares) (Refs. 21 and 23) and the chemical potential (circles).²⁰ There is still a moderate but clear deviation between the DFT results and both the cell theory prediction and the computer simulation. In the inset, we show the vacancy concentration n_{vac} of the crystal. Note that for $\eta^r < 0.7201$ the crystal is metastable.

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