Structural Properties of Binary Repulsive Systems in Two Dimensions

G. Ziegenhain*

(Dated: August 28, 2007)

The radial distribution function $g_{\alpha\beta}(r)$ and the direct correlation function $c_{\alpha\beta}(r)$ are routinely calculated numerically from the potential $V_{\alpha\beta}(r)$ by iterating the Ornstein-Zernicke (OZ) and Percus-Yevick (PY) / Hypernetted-Chain (HNC) equations. As the first maximum of these correlators increases for $d = 2$ in comparison to $d = 3$ a stable solution of the set of equations is not easy to find for long ranged potentials. We will present a suiting algorithm for solving these equations here and compare the obtained $g_{\alpha\beta}(r)$ to MD simulations.

I. INTRODUCTION

a. Physical Motivation and State-of-the-Art In the recent years an experimental realization of a two dimensional glass former [6] raised the question on the validity of the mode coupling theory[5, 9] for two dimensional repulsive systems. Some research on this topic has been done[2]. As mentioned there, considerable effort has to be made to obtain the static structure factors for this system using the classical PY/HNC approximations. In this paper we will present a fast and yet stable numerical method to overcome this difficulty.

b. Considered System Directly motivated by the experimental system [6] we consider the following system. Two sorts of dipolar hard spheres with radii $r_1 = 1.4[\mu\text{m}]$, $r_2 = 2.3[\mu\text{m}]$ and susceptibilities $\chi_1 = 6.6[\text{p}\frac{\text{Am}^2}{\text{T}}]$ and $\chi_2 = 62[\text{p}\frac{\text{Am}^2}{\text{T}}]$ interact with a potential

$$V_{\alpha\beta}(r) := \begin{cases} \infty & r \leq \frac{\sigma_{12}}{\sigma_{\alpha\beta}} \\ \frac{\mu_0}{4\pi}\frac{\chi_\alpha \chi_\beta B^2}{r^3} & r > \frac{\sigma_{12}}{\sigma_{\alpha\beta}} \end{cases} \tag{1}$$

Here $\sigma_{\alpha\beta} = r_\alpha + r_\beta$. The system is described by the parameters $\delta = r_1/r_2$, $\delta' = \chi_1/\chi_2$ and the packing fraction $\eta := \rho\frac{\pi}{4}\left[x_1\sigma_{11}^2 + x_2\sigma_{22}^2\right]$, where $\rho = N/V$ is the particle density. For $\eta \ll 1$ the system is driven by the average dipolar interaction energy $\Gamma := \frac{\mu_0}{4\pi}B^2\frac{(\rho\pi)^{\frac{3}{2}}}{k_bT}\chi^2$.

c. Static Correlators With this system in mind, we turn to the OZ equation [7] in matrix form with $\mathbf{P} = diag(x_1, x_2)\rho$ and $\mathbf{H} := \mathbf{G} - 1$. As usual this equation is closed with the Fourier transformation and PY / HNC approximation. Following [3] the smooth correlator $\gamma(r) := \mathbf{h}(r) - \mathbf{c}(r)$ is introduced and the set of equations to be solved is

$$\mathbf{H}(q) = \mathbf{C}(q)[\mathbb{1} - \mathbf{P}\mathbf{C}(q)]^{-1} \tag{2}$$

$$\mathbf{h}(r) = e^{-\beta\mathbf{v}(r)} \cdot e^{\mathbf{h}(r)-\mathbf{c}(r)} + 1 \tag{3}$$

$$\mathbf{h}(r) = e^{-\beta\mathbf{v}(r)} \cdot [\mathbf{h}(r) + 1 - \mathbf{c}(r)] + 1$$

II. TWO DIMENSIONAL DIFFICULTY

d. Fourier Bessel Transformation The angular part in the Fourier transformation cannot be integrated analytically in two dimensions, moreover it is included in a Bessel function of 0th order: $\mathcal{F}[\mathbf{f}(r)] = \int_{\mathbb{R}^+} drr\mathbf{f}(r)J_0(qr)$. Due to this an equidistant discretisation of impulse and spatial space leads to oscillations in the correlators. These can be avoided following [8] by choosing a discretisation of M points along the zeroes λ_i of J_0: $r_i := \lambda_i/Q$ and $q_m := \lambda_m/R$, where the maximal radius R for the correlators has to be chosen and $Q = \lambda_{M-1}/R$. The zeroes of J_0 are exact to at least 10^{-5} with $\lambda_i \approx \frac{\pi(4i-1)}{4} + \frac{1}{2\pi(4i-1)} - \frac{31}{6\pi^3(4i-1)} + \frac{3779}{15\pi^5(4i-1)^5}$ [4] or can be calculated numerically [1] alternatively.

*Electronic address: gerolf@ziegenhain.com

This leads us to the Fourier-Bessel transformation

$$F_m = \frac{4\pi}{Q^2}\sum_{j=0}^{M-1} f_j \frac{J_0(q_m r_j)}{J_1^2(Q r_j)} \tag{4}$$
$$f_i = \frac{1}{\pi R^2}\sum_{n=0}^{M-1} F_n \frac{J_0(q_n r_i)}{J_1^2(q_n R)}$$

e. Gillans Resort in 2d for Monodisperse Systems This set of equations can be solved by simple Picard iteration with adaptive iteration steps for pure hard spheres. Nevertheless the numerics is more sensitive as in $d = 3$ due to the increased first extrema of the correlators, which is a result of the different closed-packed structure in $d = 2$. As expected to stability is more difficult to achieve for growing η. Even though this simple method is quite stable for more complex systems (...) in $d = 3$ it doesn't work for systems with a small repulsive contribution (X). Gillan proposed a resort in [3] by splitting up the correlators in a coarse and a fine part. Therefore we select basis functions $0 \le P_i^\alpha \le 1$ of piecewise averaging in the high oscillation region

$$\alpha = 0 \quad P_i^{\alpha=0} = \begin{cases} \frac{i_1 - i}{i_1} & 0 \le i \le i_1 \\ 0 & i_1 < i < M \end{cases} \tag{5}$$
$$\alpha = 1 \quad P_i^{\alpha=1} = \begin{cases} \frac{i}{i_1} & 0 \le i \le i_1 \\ \frac{i_2 - i}{i_2 - i_1} & i_i < i \le i_2 \\ 0 & i_2 < i < M \end{cases}$$
$$\alpha \ge 2 \quad P_i^{\alpha} = \begin{cases} 0 & 0 \le i \le i_{\alpha-2} \\ \frac{i - i_{\alpha-2}}{i_{\alpha-1} - i_{\alpha-2}} & i_{\alpha-2} < i \le i_{\alpha-1} \\ \frac{i_{\alpha} - i}{i_{\alpha} - i_{\alpha-1}} & i_{\alpha-1} < i \le i_{\alpha} \\ 0 & i_{\alpha} < i < M \end{cases}$$

The conjugated basis is constructed with completeness and orthogonality:

$$Q_i^\alpha = \sum_\beta \left(\left[\sum_j P_j^\alpha P_j^\beta \right]^{-1} \right)_{\alpha\beta} P_i^\beta \tag{6}$$

As we choose only one basis set for all four components (this is reasonable because the correlators are in the same orders of magnitude), the generalization to binary systems is done by only changing the decomposition to

$$a_\alpha = \sum_{i=0}^{M-1} \gamma_i Q_i^\alpha \tag{7}$$
$$\Delta\gamma_i = \gamma_i - \sum_{\alpha=0}^{\nu-1} a_\alpha P_i^\alpha$$

An elementary step is now $\gamma(r) \to \mathbf{c}(r) \to \mathbf{C}(q) \to \mathbf{\Gamma}(q) \to \gamma'$.

If one directly generalizes the Gillan approach with a Newtonian iteration for the coarse coefficients, the new coarse part is evaluated with respect to

$$a_\alpha^{\mu\nu} = a_\alpha^{\mu\nu} - \sum_{\beta=0}^{\nu-1}\sum_{\rho,\sigma=0}^{1} \left\{ \left(\frac{\partial}{\partial a_\beta^{\rho\sigma}} \left[a_\alpha^{\mu\nu} - a_\alpha^{'\mu\nu} \right] \right)^{-1} \right\}_{\alpha\beta} \left(a_\beta^{\rho\sigma} - a_\beta^{'\rho\sigma} \right) \tag{8}$$

For a monodisperse system the Jacobian matrix can be calculated analytically analogous to [3]

$$J_{\alpha\beta} := \frac{\partial}{\partial a_\beta}\left[a_\alpha - a_\alpha^{'} \right] = \delta_{\alpha\beta} - \sum_{i,j=0}^{M-1} Q_i^\alpha \frac{\partial \gamma_i^{'}}{\partial \gamma_j} P_j^\beta \tag{9}$$
$$= \delta_{\alpha\beta} - \left(\frac{2}{QR} \right)^2 \sum_{m=0}^{M-1} \left(-1 + \frac{1}{(-1 + \rho C_m)^2} \right) \times \tag{10}$$
$$\times \sum_{i,j=0}^{M-1} Q_j^\alpha P_i^\beta \frac{J_0(q_m r_j) J_0(q_m r_i)}{J_1^2(q_m R) J_1^2(Q r_i)} \left(e^{-\beta V_i} - 1 \right)$$

This set of equations has been solved numerically.

f. Extension to Binary Systems The Jacobian matrix can be calculated with the equation system in component form to

$$J^{\mu\nu,\rho\sigma}_{\alpha\beta} = \frac{\partial}{\partial a^{\rho\sigma}_{\beta}} \left[a^{\mu\nu}_{\alpha} - a^{'\mu\nu}_{\alpha} \right] \tag{11}$$

$$= \delta_{\alpha\beta}\delta_{\mu\rho}\delta_{\nu\sigma} - \sum_{i,j=0}^{M-1} \sum_{\zeta,\xi=0}^{1} Q^{\alpha}_{i} \frac{\partial \gamma^{'\rho\sigma}_{i}}{\partial \gamma^{\zeta\xi}_{j}} P^{\beta}_{j} \tag{12}$$

$$= \delta_{\alpha\beta}\delta_{\mu\rho}\delta_{\nu\sigma} - \left(\frac{2}{QR} \right)^{2} \sum_{i,j=0}^{M-1} Q^{\alpha}_{i} P^{\beta}_{j} \left(e^{-\beta V^{\rho\sigma}_{i}} - 1 \right) \sum_{m=0}^{M-1} \frac{J_0(q_m r_i) J_0(q_m r_j)}{J_1^2(q_m R) J_1^2(Q r_i)} \frac{\partial \Gamma^{\mu\nu}_{m}}{\partial C^{\rho\sigma}_{m}} \tag{13}$$

Even after using the symmetry there are 9 components left to be calculated. This results in a very high computational overhead and the approach has to be condemned. Tersely: Calculating the inverse Jacobian matrix is numerically too circumstantial.

g. Optimizing the Coarse Part We conclude that the difficulty in finding the static correlators for a pure repulsive system in two dimensions is twofold: Conventional iteration schemes are not stable and/or not efficient enough. Reason for this problem is the first peak in the correlators, which is increased in comparison to three dimensions, in combination with the long ranged oscillations caused by the repulsive interaction.

This problem can be evaded, if the Jacobian is not evaluated analytically but numerically: our approach is to iterate the coarse coefficients $a^{\mu\nu}_{\alpha}$ by a levenberg-marquardt method [10]. In the spirit of Gillan the old iteration scheme is kept and only the calculation of the coarse coefficients is replaced. This results in a extremely stable and fast algorithm.

III. SUMMARY

The mathematical basis for understanding the provided code has been given. Results obtained with this code can be found in [11].

---

[1] *GNU Scientific Library.* www.gsl.org, 2005.

[2] M. Bayer, J. Brader, F. Ebert, E. Lange, M. Fuchs, G. Maret, R. Schilling, M. Sperl, and J. Wittmer. Dynamic glass transition in two dimensions. *PRE*, 76:011508, 2007.

[3] M. J. Gillan. A new method of solving the liquid structure integral equations. *Mol. Phys.*, 38(6):1781–1794, 1979.

[4] I. S. Gradshteyn and I. M. Ryzhik. *Table of Integrals, Series, and Products.* Academic Press, INC., 1250 Sixth Avenue, San Diege, California 92101, 1980.

[5] W. Götze. *liquids, freezing and glass transition (Part 1).* North Holland, Elsevier Science Publishers B.V., P.O. Box 211, 1000 AE Amsterdam, The Netherlands, 1989.

[6] K. Zahn H. König, R. Hund and G. Maret. Experimental realization of a model glass former in 2d. *Europhys. J. E*, 18(3):287–293, 2005.

[7] J.-P. Hansen and I.R. McDonald. *Theory of simple liquids (2nd edition).* Academic Press, 32 Jamestown Road, London NW1 7BY, UK, 1986.

[8] F. Lado. Hypernetted-chain solutions for the two-dimensional classical electron gas. *Phys. Rev. B*, 17(7):2827–3832, 1978.

[9] W. Götze U. Bengtzelius and A. Sjörlander. *J. Phys. C: Solid State Phys.*, 17:5915, 1984.

[10] W. T. Vetterling B. P. Flannery W. H. Press, S. A. Teuklosky. *Numerical Recipes in C - The Art of Scientific Computing (Second Edition).* Cambridge University Press, 40 West 20th Street, New York, NY 10011-4211, USA, 1992.

[11] G. Ziegenhain. Test der modenkopplungstheorie in zwei dimensionen. Master's thesis, University Mainz, 2006.