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# Effect of quantum dispersion on the radial distribution function of a one-component sticky-hard-sphere fluid

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**Abstract.** In this short communication we present a possible scheme to study the radial distribution function of the quantum slightly polydisperse Baxter sticky hard sphere liquid at finite temperature thorugh a semi-analytical method devised by Chandler and Wolynes.

**Keywords:** correlation functions, quantum fluids, rigorous results in statistical mechanics

**Contents**

It is well known that a one-component classical sticky-hard-sphere (SHS) liquid [1] is thermodynamically unstable [2].

Nonetheless, when studied with a Monte Carlo computer simulation the fluid *is* stable [3]. This is due to the fact that a computer can only work with numbers with a finite number of decimal figures. The computer arithmetics in fact differs from the arithmetics of real number because the standard representation of numbers must use a finite and fixed number of bits. So that the fluid studied through the computer simulation will necessarily be polydisperse (in size). And it has been proven that the polydisperse SHS fluid is indeed thermodynamically stable [2].

It is then legitimate to pose the following questions: what would the outcome for the radial distribution function of a quantum SHS fluid, obeying to Boltzmann statistics (for the sake of simplicity), calculated through the path integral Monte Carlo simulation, be? Can one find a reasonable approximation for it, through other means? The relevant parameters of the problem will be the inverse temperature $\beta = 1/K_B T$, the density $\rho$, the spheres mass $m$ and diameter $\sigma$, and $\alpha$ the adhesion coefficient.

The aim of the note is to show how one may try to answer these questions using an approach devised by Chandler and Wolynes [4] which relies on an *isomorphism* between the quantum statistical mechanics of a many body system and the classical statistical mechanics of a particular *polyatomic* fluid. Using the path integral formulation of quantum statistical mechanics it can be shown (see appendix) that the canonical partition function of a system of $N$ quantum identical particles of mass $m$ obeying to Boltzmann statistics and interacting through a pair potential $v(r)$, at absolute temperature $T$, is approached in the $P \to \infty$ limit by the classical partition function of $N$ indistinguishable ring *molecules* made up of $P$ distinguishable *atoms*, at temperature $TP$, with a total potential energy

$$V(R_0, \ldots, R_{P-1}) = \sum_{t=0}^{P-1} \left\{ \frac{|R_t - R_{t+1}|^2}{4\lambda\varepsilon^2} + \sum_{i<j}^{N} v(|\mathbf{r}_i^{(t)} - \mathbf{r}_j^{(t)}|) \right\}, \tag{1}$$

where $R_t \equiv (\mathbf{r}_1^{(t)}, \ldots, \mathbf{r}_N^{(t)})$ are the positions of the atoms at *site* (imaginary thermal time slice) $t$ of the $N$ molecules, with $R_p = R_0$, and

$$\lambda = \frac{\hbar^2}{2m}, \tag{2}$$

$$\varepsilon = \frac{\beta}{P}. \tag{3}$$

This is known as the primitive action as explained in the appendix.

Note that for the SHS Baxter model [1] one has

$$\mathrm{e}^{-\beta v(r)} - 1 \overset{\text{sticky limit}}{\longrightarrow} -\theta(\sigma - r) + \sigma\alpha\delta(r - \sigma), \tag{4}$$

where the adhesion coefficient $\alpha = \epsilon/\epsilon_0 = 1/12\tau$, with $\epsilon_0$ a characteristic energy scale, is a *monotonous function* of $\beta$. We can say that $\tau = \tau(\beta)$ is a monotonously increasing function of the absolute temperature $T$ representing a reduced temperature. The problem is then well set only upon assigning the function $\tau(\beta)$.

The radial distribution function of the quantum system is then given by

$$g(r; \beta) = \lim_{P \to \infty} \frac{1}{P} \sum_{t=0}^{P-1} g_{0t}(r; \beta/P), \tag{5}$$

where $g_{tt'}$ is the intermolecular site-site radial distribution function of the isomorphic classical system.

The idea of Chandler and Wolynes is to use the reference interaction site model (RISM) theory [5] to determine the $g_{0t}$ for $t = 0, \dots, P-1$ for a given $P$ ($P = 2$ being the simplest but less accurate approximation). That is, one needs to solve the following integral equation subject to a given closure

$$\hat{\mathbf{h}}(k; \varepsilon) =$$
$$\hat{\boldsymbol{\omega}}(k; \varepsilon)\hat{\mathbf{c}}(k; \varepsilon)[1 - \rho\hat{\boldsymbol{\omega}}(k; \varepsilon)\hat{\mathbf{c}}(k; \varepsilon)]^{-1}\hat{\boldsymbol{\omega}}(k; \varepsilon), \tag{6}$$

where $\hat{\mathbf{h}}(k; \varepsilon)$ and $\hat{\mathbf{c}}(k; \varepsilon)$ are the matrices whose elements are the Fourier transform of the intermolecular site-site total correlation function $h_{tt'}(r; \varepsilon) = g_{tt'}(r; \varepsilon) - 1$ and direct correlation function $c_{tt'}(r; \varepsilon)$ respectively and the elements of $\hat{\boldsymbol{\omega}}(k; \varepsilon)$ are the Fourier transform of

$$\omega_{tt'}(\mathbf{r}; \varepsilon) = \delta_{tt'}\delta(\mathbf{r}) + (1 - \delta_{tt'})s_{tt'}(r; \varepsilon),$$
$$= \begin{cases} \delta(\mathbf{r}) & t = t' \\ s_{tt'}(r; \epsilon) & t \neq t' \end{cases} \tag{7}$$

where $s_{tt'}(r; \varepsilon)$ are the intramolecular site-site radial distribution functions of the isomorphic classical system, for which a reasonable approximation is

$$s_{tt'}(r; \varepsilon) \approx \gamma_{tt'}\, \mathrm{e}^{-\frac{r^2}{4\lambda|t-t'|\varepsilon}} y_{\text{SHS}}(r; \tau(|t - t'|\epsilon)), \tag{8}$$

where the normalization constant $\gamma_{tt'}$ should be determined from the condition

$$\int s_{tt'}(r; \varepsilon)\,\mathrm{d}\mathbf{r} = 1, \tag{9}$$

and $y_{\text{SHS}}(r; \tau)$ is the cavity radial distribution function of a system of classical SHS of diameter $\sigma$, with reduced temperature $\tau$ at a packing fraction $\eta = \pi\rho\sigma^3/6$, $\rho = N/V$ being the density. That is $y_{\text{SHS}}(r; \tau) = g_{\text{SHS}}(r; \tau) \exp[\tau v(r)]$ which is a continuous function of $r$ even when the radial distribution function of the SHS model, $g_{\text{SHS}}$, and/or $v$ are discontinuous.

In equation (8) the exponential factor stems from the kinetic part of the action and again we used the functional dependence of the adhesion coefficient $\tau$ on the inverse temperature $|t - t'|\varepsilon$.

Clearly we will have $y_{\mathrm{SHS}}(r;\tau) = g_{\mathrm{SHS}}(r;\tau)$ for $r > \sigma$. The Laplace transform of $rg_{\mathrm{SHS}}(r;\tau)$ in the Percus–Yevick approximation for the SHS system is given by [6]

$$
\begin{aligned}
\widehat{G}_{\mathrm{SHS}}(s) &= \int_0^\infty \mathrm{d}r\, \mathrm{e}^{-sr} rg_{\mathrm{SHS}}(r;\tau) \\
&= \frac{\mathrm{e}^{-s}}{s^2} \frac{\Lambda_0 + \Lambda_1 s + \Lambda_2 s^2}{1 - 12\eta[\varphi_2(s)\Lambda_0 + \varphi_1(s)\Lambda_1 + \varphi_0(s)\Lambda_2]},
\end{aligned}
\tag{10}
$$

where,

$$
\varphi_k(x) = x^{-(k+1)} \left( \sum_{l=0}^{k} \frac{(-x)^l}{l!} - \mathrm{e}^{-x} \right),
\tag{11}
$$

and

$$
\Lambda_0 = \frac{1+2\eta}{(1-\eta)^2} - \frac{12\eta}{1-\eta}\Lambda_2,
\tag{12}
$$

$$
\Lambda_1 = \frac{1+\eta/2}{(1-\eta)^2} - \frac{6\eta}{1-\eta}\Lambda_2.
\tag{13}
$$

$$
\Lambda_2 = \frac{1 - (1-\tau^{-1})\eta - w}{2\tau^{-1}(1-\eta)\eta},
$$
$$
w = \sqrt{(1-\eta)\left[1 - \eta\left(1 - 2\tau^{-1} + \frac{\tau^{-2}}{3}\right)\right] + \frac{\tau^{-2}}{2}\eta^2}.
\tag{14}
$$

In figure 1 we show the intramolecular site-site radial distribution functions of the isomorphic classical system assuming an adhesion coefficient independent from temperature.

For the closure one may use the modified mean spherical approximation (mMSA) [7]

$$
c_{tt'}(r) = f_{tt'}(r) = \mathrm{e}^{-\beta v_{tt'}(r)} - 1, \quad r > d_{tt'},
\tag{15}
$$

where

$$
v_{tt'}(r) = \begin{cases} v(r) & t = t' \\ 0 & t \neq t' \end{cases},
\tag{16}
$$

and

$$
d_{tt'} = \begin{cases} \sigma & t = t' \\ 0 & t \neq t' \end{cases}.
\tag{17}
$$

Here we are neglecting the fact that the size of a path (or polymer), its thermal wavelength, is $\Lambda_\beta = \sqrt{\beta\hbar^2/m}$[1]. Combined with the exact relation valid for $r \leqslant d_{tt'}$

[1] One may take into account of the size of the path by taking for example $d_{tt'} = \{\sigma$ for $t = t'$, $\{0$ for $\sigma < \Lambda_\beta, \sigma - \Lambda_\beta$ for $\sigma > \Lambda_\beta\}$ for $t = t' \pm 1$, $0$ otherwise$\}$.
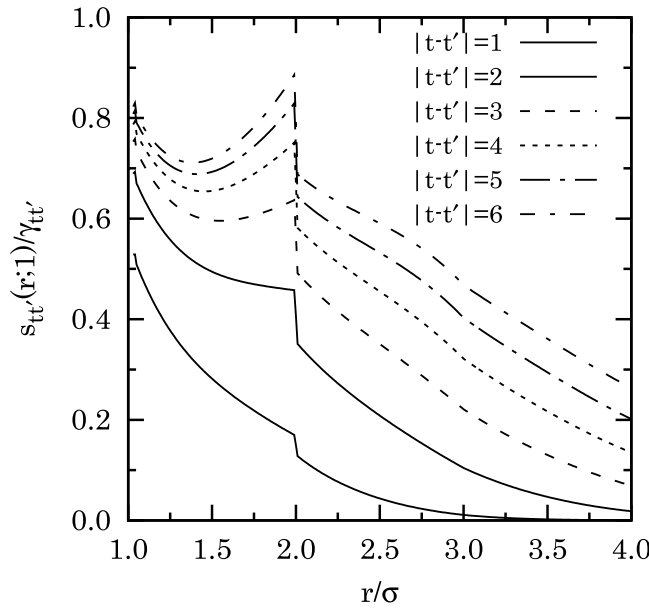
**Figure 1.** The intramolecular site-site radial distribution functions of the isomorphic classical system $s_{tt'}(r;1)$ for $\lambda = 1$, $\eta = 0.32$, and $\tau = 0.2$.

$$h_{tt'}(r) = \begin{cases} \frac{\sigma}{12\tau} y_{tt}(d_{tt}) \delta(r - d_{tt}) - 1 & t = t' \\ -1 & t \neq t' \end{cases}, \tag{18}$$

where $y_{tt}(d_{tt})$ are the intermolecular site-site cavity functions at contact which in the mMSA are [7]

$$y_{tt}(d_{tt}) = 1, \quad t = 0, \ldots, P - 1. \tag{19}$$

Then, for the closure, we will have

$$c_{tt'}(r) = 0, \quad r > d_{tt'}, \tag{20}$$

$$h_{tt'}(r) = \begin{cases} \frac{\sigma}{12\tau} \delta(r - \sigma) - 1 & t = t' \\ -1 & t \neq t' \end{cases}, \quad r \leqslant d_{tt'}. \tag{21}$$

The RISM integral equation (6) can be rewritten as the following Ornstein–Zernike-like relation,

$$\hat{\mathbf{h}}(k;\varepsilon) = \hat{\boldsymbol{\omega}}(k;\varepsilon) \hat{\mathbf{c}}(k;\varepsilon) \hat{\boldsymbol{\omega}}(k;\varepsilon) + \rho \hat{\boldsymbol{\omega}}(k;\varepsilon) \hat{\mathbf{c}}(k;\varepsilon) \hat{\mathbf{h}}(k;\varepsilon). \tag{22}$$

The main obstacle in solving this integral equation reside in the fact that the intramolecular site-site radial distribution function of the isomorphic classical system, $s_{tt'}(r;\epsilon)$, is known only numerically through Laplace inversion of equation (10) obtained for example using the algorithm of Abate and Whitt [8].

The uncontrolled approximations in this treatment reside in: (i) equation (8), where we have approximated the full equilibrium distribution function for *P cavities* forming a molecule with the cavity pair distribution function of the SHS classical fluid (this approximation becomes worse and worse as $P$ decreases). Since the primitive

approximation error goes like $\lambda\varepsilon^2$ [9] it is reasonable to expect that a good enough approximation would require $\lambda\beta^2/P^2 \sim 0.01$. Of course one reasonably expects that solving RISM equations numerically becomes rapidly a difficult task (including non-convergence problems) as P increases; (ii) equation (17), where we are neglecting the thermal wavelength of a polymer.

To our knowledge the quantum slightly polydisperse Baxter sticky hard spheres liquid has never been studied before either through computer simulations of the one-component system or through other means. To assess the existence of thermodynamic and structural properties of such a physical model from a rigorous mathematical point of view seems to be a quite formidable task. In this respect the theory of path integrals should probably be the place to start to look at. It is infact out of doubt that at any finite $P$ the classical isomorphic system is thermodynamically ($N \to \infty$ at constant $\rho$) well defined, but understanding the effect of the slightly polydisperse adhesion (the last term in equation (4)) in the $P \to \infty$ (Feynman–Kac-)limit does not seem so easy. There are three different limits we have to deal with: (i) the sticky limit, (ii) the path integral limit, and (iii) the thermodynamic limit. While it is quite customary to take the thermodynamic limit in the end, the order of the first two limits should be immaterial. Moreover we expect the path integral solution to depend crucially on the choice of the function $\tau(T)$.

We plan to adopt the present scheme to obtain semi-analytical quantitative results for the radial distribution function of the extension to the quantum regime of some of the classical fluids studied in [10–24], in the near future.

## Acknowledgments

## Appendix. The primitive action

In this appendix we give a brief review of the derivation of the primitive approximation given in [9]. Suppose the Hamiltonian is split into two pieces $\mathcal{H} = \mathcal{T} + \mathcal{V}$, where $\mathcal{T}$ and $\mathcal{V}$ are the kinetic and potential operators. Recall the exact Baker–Campbell–Hausdorff formula to expand $\exp(-\varepsilon\mathcal{H})$ into the product $\exp(-\varepsilon\mathcal{T})\exp(-\varepsilon\mathcal{V})$. As $\varepsilon \to 0$ the commutator terms which are of order higher than $\varepsilon^2$ become smaller than the other terms and thus can be neglected. This is known as the *primitive approximation*

$$\mathrm{e}^{-\varepsilon(\mathcal{T}+\mathcal{V})} \approx \mathrm{e}^{-\varepsilon\mathcal{T}}\mathrm{e}^{-\varepsilon\mathcal{V}} \tag{A.1}$$

hence we can approximate the exact density matrix by product of the density matrices for $\mathcal{T}$ and $\mathcal{V}$ alone. One might worry that this would lead to an error as $P \to \infty$, with small errors building up to a finite error. According to the Trotter [25] formula, one does not have to worry

$$\mathrm{e}^{-\beta(\mathcal{T}+\mathcal{V})} = \lim_{P\to\infty}\left[\mathrm{e}^{-\varepsilon\mathcal{T}}\mathrm{e}^{-\varepsilon\mathcal{V}}\right]^P. \tag{A.2}$$

The Trotter formula holds if the three operators $\mathcal{T}$, $\mathcal{V}$, and $\mathcal{T} + \mathcal{V}$ are self-adjoint and make sense separately, for example, if their spectrum is bounded below. [26] This is the case for the Hamiltonian describing SHS.

Let us now write the primitive approximation in position space $R = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ with $\mathbf{r}_i$ the coordinate of the $i$th particle,

$$\rho(R_0, R_2; \varepsilon) \approx \int dR_1 \langle R_0 | e^{-\varepsilon \mathcal{T}} | R_1 \rangle \langle R_1 | e^{-\varepsilon \mathcal{V}} | R_2 \rangle, \tag{A.3}$$

and evaluate the kinetic and potential density matrices. Since the potential operator is diagonal in the position representation, its matrix elements are trivial

$$\langle R_1 | e^{-\varepsilon \mathcal{V}} | R_2 \rangle = e^{-\varepsilon V(R_1)} \delta(R_2 - R_1). \tag{A.4}$$

The kinetic matrix can be evaluated using the eigenfunction expansion of $\mathcal{T}$. Consider, for example, the case of distinguishable particles in a cube of side $L$ with periodic boundary conditions. Then the exact eigenfunctions and eigenvalues of $\mathcal{T}$ are $L^{-3N/2} e^{iK_\mathbf{n} R}$ and $\lambda K_\mathbf{n}^2$, with $K_\mathbf{n} = 2\pi \mathbf{n}/L$ and $\mathbf{n}$ a $3N$-dimensional integer vector. We are using here dimensional units. Then

$$\langle R_0 | e^{-\varepsilon \mathcal{T}} | R_1 \rangle = \sum_\mathbf{n} L^{-3N} e^{-\varepsilon \lambda K_\mathbf{n}^2} e^{-iK_\mathbf{n}(R_0 - R_1)} \tag{A.5}$$

$$= (4\pi\lambda\varepsilon)^{-3N/2} \exp\left[-\frac{(R_0 - R_1)^2}{4\lambda\varepsilon}\right], \tag{A.6}$$

where $\lambda = \hbar^2/2m$. Equation (A.6) is obtained by approximating the sum by an integral. This is appropriate only if the thermal wavelength of one step is much less than the size of the box, $\lambda\varepsilon \ll L^2$. In some special situations this condition could be violated, in which case one should use equation (A.5) or add periodic 'images' to equation (A.6). The exact kinetic density matrix in periodic boundary conditions is a theta function, $\prod_{i=1}^{3N} \theta_3(z_i, q)$, where $z_i = \pi(R_0^i - R_1^i)/L$, $R^i$ is the $i$th component of the $3N$ dimensional vector $R$, and $q = e^{-\lambda\varepsilon(2\pi/L)^2}$ (see chapter 16 of [27]). Errors from ignoring the boundary conditions are $O(q)$, exponentially small at large $P$.

A *link $m$* is a pair of time slices $(R_{m-1}, R_m)$ separated by a *time step* $\varepsilon = \beta/P$. The *action $S^m$* of a link is defined as minus the logarithm of the exact density matrix. Then the exact path-integral expression becomes

$$\rho(R_0, R_P; \beta) = \int dR_1 \ldots dR_{P-1} \exp\left[-\sum_{m=1}^{P} S^m\right]. \tag{A.7}$$

It is convenient to separate out the *kinetic action* from the rest of the action. The exact kinetic action for link $m$ will be denoted $K^m$

$$K^m = \frac{3N}{2}\ln(4\pi\lambda\varepsilon) + \frac{(R_{m-1} - R_m)^2}{4\lambda\varepsilon}. \tag{A.8}$$

The *inter-action* is then defined as what is left

$$U^m = U(R_{m-1}, R_m; \varepsilon) = S^m - K^m. \tag{A.9}$$

In the primitive approximation the inter-action is

$$U_1^m = \frac{\varepsilon}{2}[V(R_{m-1}) + V(R_m)], \tag{A.10}$$

where we have symmetrized $U_1^m$ with respect to $R_{m-1}$ and $R_m$, since one knows that the exact density matrix is symmetric and thus the symmetrized form is more accurate.

A capital letter $U$ refers to the total link inter-action. One should not think of the exact $U$ as being strictly the potential action. That is true for the primitive action but, in general, is only correct in the small-$\varepsilon$ limit. The exact $U$ also contains kinetic contributions of higher order in $\varepsilon$. If a subscript is present on the inter-action, it indicates the order of approximation; the primitive approximation is only correct to order $\varepsilon$. No subscript implies the exact inter-action.

The *residual energy* of an approximate density matrix is defined as

$$E_A(R, R'; t) = \frac{1}{\rho_A(R, R'; t)} \left[ \mathcal{H} + \frac{\partial}{\partial t} \right] \rho_A(R, R'; t). \tag{A.11}$$

The residual energy for an exact density matrix vanishes; it is a local measure of the error of an approximate density matrix. The Hamiltonian $\mathcal{H}$ is a function of $R$; thus the residual energy is not symmetric in $R$ and $R'$.

It is useful to write the residual energy as a function of the inter-action. We find

$$\begin{aligned} E_A(R, R'; t) = V(R) - \frac{\partial U_A}{\partial t} - \frac{(R - R') \cdot \nabla U_A}{t} \\ + \lambda \nabla^2 U_A - \lambda \left( \nabla U_A \right)^2. \end{aligned} \tag{A.12}$$

The terms on the right hand side are ordered in powers of $\varepsilon$, keeping in mind that $U(R)$ is of order $\varepsilon$, and $|R - R'|$ is of order $\varepsilon^{1/2}$. One obtains the primitive action by setting the residual energy to zero and dropping the last three terms on the right hand side.

The residual energy of the primitive approximation is

$$\begin{aligned} E_1(R, R'; t) = \frac{1}{2} \left[ V(R) - V(R') \right] - \frac{1}{2}(R - R') \cdot \nabla V \\ + \frac{\lambda t}{2} \nabla^2 V - \frac{\lambda t^2}{4} \left( \nabla V \right)^2. \end{aligned} \tag{A.13}$$

With a leading error of $\sim \lambda \varepsilon^2$.

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