

Quantum Hard Spheres with Affine Quantization

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We study a fluid of quantum hard-spheres treated with affine quantization. Assuming that the fluid obeys to Bose-Einstein statistics we solve for its the structure and thermodynamics using the path integral Monte Carlo method.

Keywords: Hard-Spheres; Affine-Quantization; Bose-Einstein Statistics; Path Integral Monte Carlo; Structure; Thermodynamics

I. INTRODUCTION

The simplest model of a fluid [1] is a system of hard spheres, for which the pair potential $\Phi_{\text{HS}}(r)$ at a separation r is

$$\Phi_{\text{HS}}(r) = \begin{cases} +\infty & r < \sigma \\ 0 & \text{else} \end{cases}, \quad (1.1)$$

where σ is the hard-sphere diameter. This simple potential is ideally suited to the study of phenomena in which the hard core of the potential is the dominant factor. Much of our understanding of the properties of the hard-sphere model come from computer simulations [2, 3]. Such calculations have revealed very clearly that the structure of a hard-sphere fluid does not differ in any significant way from that corresponding to more complicated interatomic potentials, at least under conditions close to crystallisation.

The most important feature of the pair potential of a liquid is the strong repulsion that appears at short range and is due to the overlap of the outer electron shells inhibited by the Pauli exclusion principle. This strongly repulsive forces are responsible for the short range order characteristic of the liquid state. The attractive forces acting at long range are much more smooth and play only a minor role in determining the structure of the liquid. They provide an almost uniform attractive background giving rise to the cohesive energy that stabilizes the liquid.

However, although simulations show that the hard-sphere *classical* fluid undergoes a freezing transition at a reduced number density $\rho^* = \rho\sigma^3 \approx 0.945$, the absence of attractive forces means that there is only one fluid phase. The properties of hard-spheres are better understood in terms of the so called packing fraction $\eta = \rho v_d \sigma^d$ where

$$v_d = \frac{(\pi/4)^{d/2}}{\Gamma(1 + d/2)}, \quad (1.2)$$

is the volume of a d -dimensional sphere of unit diameter (for instance $v_3 = \pi/6$, so that $0 < \eta < v_3\sqrt{2}$ since one cannot pack spheres more than their closest packing configuration in three dimensions).

The hard-sphere fluid is also considered as the reference system for a pair potential perturbation theory [1, 4–6].

Least but not least the classical hard-sphere fluid admits exact analytic solution for the Percus-Yevick integral equation theory through the Wiener-Hopf factorization [7–12]

Now the *quantum* version of the hard-sphere fluid has seldomly been treated. This can be explained by the difficulties that one faces when treating hard-walls in quantum mechanics [13]. In order to overcome the difficulty of having to deal with a canonical momentum that is not anymore a self-adjoint operator a possible way out strategy is to use *affine quantization* instead of the usual Dirac canonical quantization [14].

In this work we will define the model of Quantum Hard-Spheres treated with Affine Quantization (AQHS) and then we will carry out some Path Integral Monte Carlo (PIMC) simulations for a canonical ensemble of the fluid of AQHS in thermal equilibrium at finite non-zero temperature.

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II. THE MODEL

The Hamiltonian for a d -dimensional system of N Bose (BHS) Quantum (QHS) Hard-Spheres (HS) treated with Affine-Quantization (AQ) is as follows [15]

$$H = \lambda \sum_{i=1}^N \frac{\partial^2}{\partial \mathbf{r}_i^2} + \sum_{i < j} \phi_{\text{AQ}}(r_{ij}) + \sum_{i < j} \phi_{\text{HS}}(r_{ij}), \quad (2.1)$$

where σ is the diameter of the spheres of mass m , $\lambda = \hbar^2/2m$, \mathbf{r}_i is the position of the i th sphere center, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, the HS pair potential $\phi_{\text{HS}}(r)$ of Eq. (1.1), and the AQ effective pair potential

$$\phi_{\text{AQ}}(r) = \hbar^2 \frac{2r^2 + \sigma^2}{(r^2 - \sigma^2)^2}. \quad (2.2)$$

The latter has a repulsive spike at contact $r = \sigma$. So that the QHS repel each other before getting into (classical) contact. And at large r , $\phi(r) \approx a^2/r^2$, with $a = \hbar\sqrt{2}$, which has a long range repulsive character in $d > 1$. So, in order for the system to admit a thermodynamic limit one needs to add a uniform background with the effect to modify the AQ pair potential as follows

$$\phi_{\text{AQ}}(r) \rightarrow \phi_{\text{AQ}}(r) - \frac{N}{N-1} D_d, \quad (2.3)$$

$$D_d = \frac{1}{\Omega} \int_{\Omega, r > \sigma} \phi_{\text{AQ}}(r) d\mathbf{r} \approx \begin{cases} 24(L - \sigma)/L^3 & d = 3 \\ 16 \ln(L/\sigma)/L^2 & d = 2 \end{cases} \quad (2.4)$$

where $\Omega = L^d$ is the volume of the cubic box (approximated to a sphere of radius $L/2$ in Eq. (2.4) containing the system of QHS in thermal equilibrium at an inverse temperature $\beta = 1/k_B T$ with k_B the Boltzmann constant and T the absolute temperature. This procedure is justified by requiring that the total potential energy $\hat{V} = \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \phi_{\text{AQ}}(|\mathbf{r} - \mathbf{r}'|)$ remains unchanged under the transformation (2.3) keeping the local number density $\rho(\mathbf{r}) = \sum_i \delta^d(\mathbf{r} - \mathbf{r}_i)$, where δ^d is the d -dimensional Dirac delta function, or under the transformation $\rho(\mathbf{r}) \rightarrow \rho(\mathbf{r}) + \rho_b$, where $\rho_b = -\rho = -N/\Omega$ is the uniform background density, keeping the pair potential $\phi_{\text{AQ}}(\mathbf{r})$ constant.

III. THE PATH INTEGRAL MONTE CARLO METHOD

The basis for our quantum simulation is imaginary time path integral [16]. We will treat the N AQHS as bosons interacting with the Hamiltonian of Eq. (2.1). Then the quantum statistical mechanics problem reduces to use path integral [17] to calculate the thermal *density matrix* elements $\langle R | e^{-\beta H} | R' \rangle$ as the following path average

$$\langle R | e^{-\beta H} | R' \rangle = (4\pi\lambda\tau)^{-dNM/2} \int dR_1 \int dR_2 \cdots \int dR_{M-1} e^{-S(R_0, R_1, R_2, \dots, R_M)}, \quad (3.1)$$

where $R_i = (\mathbf{r}_{1,i}, \mathbf{r}_{2,i}, \dots, \mathbf{r}_{N,i})$ for $i = 1, 2, \dots, M$ are the “beads” attached to the M timeslices that form the “polymer” of the Feynman “classical-quantum” isomorphism [18]. And $R_0 = R = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$, $R_M = R' = (\mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N)$. In the limit that $\tau = \beta/M \rightarrow 0$ the action S has the following simple “primitive approximation” form [18]

$$S(R_0, R_1, R_2, \dots, R_M) = \sum_{i=1}^M \left(\sum_{k=1}^N \frac{(\mathbf{r}_{k,i} - \mathbf{r}_{k,i-1})^2}{4\lambda\tau} + \tau \sum_{k < l} [\phi_{\text{AQ}}(r_{kl,i}) + \phi_{\text{HS}}(r_{kl,i})] \right), \quad (3.2)$$

where $r_{kl,i} = |\mathbf{r}_{k,i} - \mathbf{r}_{l,i}|$ and in $\mathbf{r}_{i,j}$ the first index i is a particle label and the second index j is a bead label. We then measure an observable \mathcal{O} through the following trace

$$\langle \mathcal{O} \rangle = \sum_{\mathcal{P}} \int dR \langle R | \mathcal{O} e^{-\beta H} | \mathcal{P} R \rangle, \quad (3.3)$$

where the sum is over all permutations of particle positions $\mathcal{P}R$. If \mathcal{O} is diagonal in position representation

$$\langle \mathcal{O} \rangle = \sum_{\mathcal{P}} \int dR \mathcal{O}(R) \langle R | e^{-\beta H} | \mathcal{P} R \rangle. \quad (3.4)$$

We perform the dNM multidimensional integral and the permutation sum with the *Metropolis algorithm* [19, 20]¹. Monte Carlo (Metropolis or Markov Chain) is a random walk through phase space using rejections to achieve detailed balance and thereby sample the density matrix. In particular, for the spatial integral we propose a displacement move of the position of a single timeslice k of a single particle i according to $\mathbf{r}_{k,i} \rightarrow \mathbf{r}_{k,i} + \mathbf{\Delta}(\eta - 1/2)$ where η is a uniform pseudo-random number in $[0, 1)$ and $\mathbf{\Delta}$ a fixed d -dimensional vector whose magnitude is chosen so to have acceptance ratios close to $1/2$. Whereas, for the permutation sum, we propose a swap move of two randomly chosen particles. This particular sampling of the permutations sum will never be able to change the winding number of 3 or more particles [18], so we will not be able to measure the superfluid fraction (see our code listing in the supplementary material).

We will measure the following observables:

- i. The potential energy $\mathcal{O} = \hat{V} = \frac{1}{M} \sum_{i=1}^M \sum_{k < l=1}^N \Phi(r_{kl,i})$, where $\Phi = \phi_{\text{AQ}} + \phi_{\text{HS}} = \phi_{\text{AQ}}$ since the overlap of any two particles is forbidden.
- ii. The kinetic energy $\mathcal{O} = \hat{T} = \frac{1}{M} \sum_{i=1}^M \sum_{k=1}^N (\mathbf{r}_{k,i} - \mathbf{r}_{k,i-1})^2 / 4\lambda\tau$.
- iii. The total internal energy $\mathcal{O} = \hat{U} = \hat{T} + \hat{V}$.

Note that in the classical HS fluid the potential energy will vanish identically. Not so in the quantum AQHS fluid where the repulsive spiked AQ effective pair potential will prevent any two HS from touching since the spike will produce a smooth repulsive potential profile in a neighborhood of the pair classical contact $r_{ij} = \sigma^+$ that tends to keep apart the pair of particles: they will never be able to touch each other and will instead slip away one from the other contact. We expect this effect to affect the structure of the fluid, its radial distribution function or its structure factor profiles.

IV. NUMERICAL RESULTS

We chose units such that: $\hbar = k_B = \sigma = 1$.

¹ Note that a brute force integration with Monte Carlo is not feasible here because the integrand of Eq. (3.4) is very sharply peaked in many dimensions. By doing a random walk rather than a direct sampling, one stays where the integrand is large. But this advantage is also a curse because it is not obvious whether any given walk will converge to its equilibrium distribution in the time available; this is the ergodic problem. This aspect of simulation is experimental; there are no useful theorems, only lots of controlled tests, the lore of the practitioners, and occasional clean comparisons with experimental data. Other subtleties of these methods are how to pick the initial and boundary conditions, determine error bars on the results, compute long-range potentials quickly, and determine physical properties [21].

AQHS Bose d=3 N=30 M=250 $\rho=0.1$ T=0.05

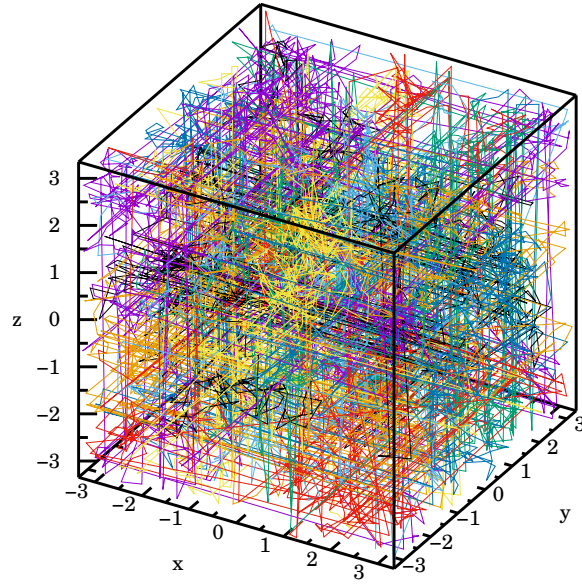


FIG. 1. We show a snapshot of the paths of 30 AQHS made of 250 timeslices each. At a density $\rho = 0.1$ and temperature $T = 0.05$. During the simulation we measured a total kinetic energy $\langle \hat{T} \rangle = 52.6(2)$ and a total potential energy $\langle \hat{V} \rangle = -19.95(5)$.

V. CONCLUSIONS

[22? –33]

AUTHOR DECLARATIONS

Conflicts of interest

None declared.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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