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On an approximation of the partition function for the hard disk fluid [1]

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Dedicated to Andrei Duma on the occasion of his 65th birthday

Abstract

The partition function of a thermodynamic system is an important tool in Statistical Physics which is, however, analytically not accessible for some models of interest, in particular for the hard disk fluid. We obtain an equation of state for this fluid by statistical evaluation of a long term computer experiment. An approximation of the partition function based on the equation of state is proposed. To test the quality of the approximation, we simulate an adiabatic compression process and observe the behavior of entropy.

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1 Introduction

The partition function plays an important role in the context of microscopic modelling of thermodynamic systems. From the partition function values of parameters describing a given system can be calculated. In particular the equation of state interrelating pressure, temperature and density of a fluid can be computed, and, moreover, the functional dependence of entropy on temperature and density can be specified.

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In typical models of interest, however, the exact determination of the partition function is impossible entailing that approximations are desirable; this is also the case for the hard disk fluid where analytical approximation is available essentially only for the dilute range of density (ideal gas).

The aim of the present contribution is the establishment of an approximation of the partition function for the hard disk fluid in the range $[0, 0.80]$ of relative density based on an equation of state which is accessible through statistical evaluation of molecular-kinetic long term computer experiments.

The paper is organized as follows. In Section 2 we present a computer experiment which enables us to estimate the pressure of the hard disk fluid under arbitrary thermodynamic conditions; the repetition of this experiment under varying fluid densities yields a data set whose statistical evaluation leads to the establishment of an (approximative) equation of state. In Section 3 an approximation of the partition function is derived by utilizing thermodynamic formalism and the equation of state obtained in Section 2. To explore the quality of this approximation we base on it to introduce an estimator for the entropy. We carry out a computer experiment imitating the adiabatic compression of the fluid by a piston and observe the behavior of entropy estimates (Section 4). It turns out that the entropy of the fluid is approximatively constant during the compression process, which confirms the applicability of thermodynamic postulates to the model fluid and underlines the quality of the proposed approximation of the partition function.

2 The computer experiment and its evaluation

Let us consider a rectangular container

$$C := [-a_1, a_1] \times [-a_2, a_2] \subset \mathbb{R}^2$$

where

$$a_2 = \frac{\sqrt{3}}{2} \cdot a_1. \tag{1}$$

We inject $N = 3691$ hard disks of mass $m = N_A^{-1}$ and radius $r = 10^{-10}$m into C where $N_A = 6.022 \cdot 10^{26}\text{kg}^{-1}$ denotes the modified Avogadro number.

To impose the temperature $T = 300$K on this thermodynamic system we put

$$\sigma^2 := \frac{k_B \cdot T}{m}$$

where $k_B = 1.38 \cdot 10^{-23}$J/K denotes Boltzmann constant; we generate the initial velocities $v^{(1)}(0), ..., v^{(N)}(0) \in \mathbb{R}^2$ of the disks according to the normal distribution $N(0, \sigma^2 \cdot I_2)$ with mean vector 0 and covariance matrix $\sigma^2 \cdot I_2$ where I_2 denotes the 2×2-identity matrix. This initial state complies with Maxwell hypothesis, cf. Moeschlin, Grycko (2006), chap. 1.

Newtonian dynamics is imposed on the system of N hard disks confined to container C enabling us to determine the positions $x^{(1)}(t), ..., x^{(N)}(t) \in C$ and velocities $v^{(1)}(t), \ldots, v^{(N)}(t) \in \mathbb{R}^2$ of the disks at any time $t \geq 0$.

During the temporal evolution of the state of the system, reflections of disks at the boundary of C occur and can be registered to estimate pressure according to Moeschlin, Grycko (2006), chap. 5.

We distinguish between fluid density

$$\varrho = \frac{N}{V}$$

and its relative density

$$\varrho_r = 2\sqrt{3} \cdot r^2 \cdot \varrho$$

where

$$V = 2\sqrt{3} \cdot a_1^2 \qquad \text{and} \qquad 2\sqrt{3} \cdot r^2$$

denote the volume (area) of C and the inverse density of close packing of disks, respectively.

The experiment is repeated 321 times for different volumes of container C covering the range $[10^{-3}, 0.85]$ of relative density of the fluid. At each repetition $3 \cdot 10^4$ reflections are involved in the pressure estimation process.

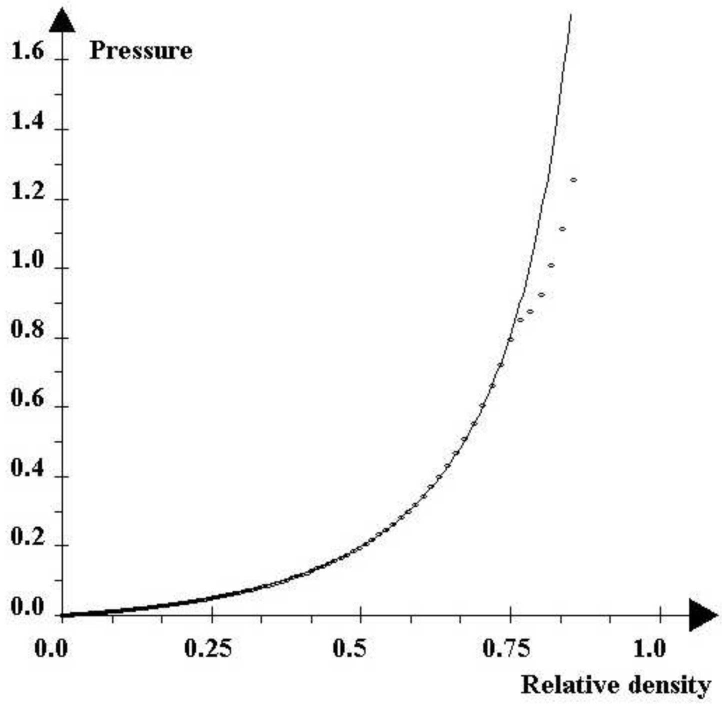

Fig. 1: Estimated pressure as function of density

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In Figure 1 the adjusted relative densities are graphed on the horizontal axis versus the estimated pressure values on the vertical axis.

For the statistical approximation of pressure as function of thermodynamic parameters (temperature T and density ϱ) the following ansatz is considered:

$$p(\varrho, T) = \frac{\varrho k_B T}{1 - \varrho_r} \cdot (1 + \sum_{j=1}^{3} A_j \cdot (2\sqrt{3} \cdot r^2 \cdot \varrho)^j\,). \tag{2}$$

(2) is motivated by the principle of corresponding states entailing a linear dependence between p and T; the denominator in (2) is justified by the fact that a singularity is expected at the relative density $\varrho_r = 1$ (close packing). Note that (2) approximates the equation of state of the ideal gas in the dilute range of fluid density.

The least-squares estimates of coefficients A_1, A_2, A_3 based on computer experimental data are given by

$$\widehat{A}_1 = 0.77843 \qquad \widehat{A}_2 = 0.83254 \qquad \widehat{A}_3 = 0.47933. \tag{3}$$

The fitted curve is also visualized in Figure 1. The average relative error based on 315 data points and the model curve attains 2.5%. The significant deviation between the last six data points and the fitted curve can be viewed as statistical evidence for a fluid/solid phase transition (cf. Grycko (2008)); therefore the last six data points are not involved in the computation of estimates (3).

3 The approximation

A momentary microstate of the fluid confined to container C is represented by

$$(x;u) := (x^{(1)},\ldots,x^{(N)};u^{(1)},\ldots,u^{(N)}) \in C^N \times \mathbb{R}^{2N} \tag{4}$$

where $x^{(j)} \in C$ denotes the position and $u^{(j)} \in \mathbb{R}^2$ the momentum of the j^{th} disk. Tuple $x = (x^{(1)},\ldots,x^{(N)})$ is called configuration. The potential energy of configuration x is given by

$$E_p(x) = \sum_{i<j} \Phi(|x^{(i)} - x^{(j)}|) \tag{5}$$

where $|.|$ denotes the Euclidean norm on $\mathbb{R}^2$ and Φ is defined according to

$$\Phi(s) = \begin{cases} 0 & \text{if} \quad s \geq 2r \\ \infty & \text{if} \quad s < 2r. \end{cases} \tag{6}$$

Φ obviously penalizes overlapping of disks.

The partition function for the hard disk fluid is defined by

$$Z(N,V,T) := \frac{1}{N! \cdot h^{2N}} \cdot \int\limits_{C^N \times \mathbb{R}^{2N}} \exp\left(-\frac{1}{k_B T} \cdot H(x;u)\right) dxdu \tag{7}$$

where h and V denote Planck constant and volume of container C, respectively. Hamiltonian

$$H : C^N \times \mathbb{R}^{2N} \to \overline{\mathbb{R}}$$

in (7) is defined by

$$H(x;u) := \sum_{j=1}^{N} \frac{1}{2m} < u^{(j)}, u^{(j)} > + \sum_{i<j} \Phi(|x^{(i)} - x^{(j)}|). \tag{8}$$

Integration w.r.t. variable u in (7) is related to handling multivariate Gaussian distributions and can be performed exactly; integration w.r.t. variable x is hard such that an approximation of Z is desirable.

On the other hand, for the case of radius $r = 0$ of the hard disks (ideal gas), the integral in (7) can be computed exactly yielding

$$\widehat{Z}(N,V,T) = \frac{V^N}{N! \cdot h^{2N}} \cdot (2\pi m k_B T)^N. \tag{9}$$

$\widehat{Z}$ can be viewed as an approximation of Z if volume V of container C is sufficiently large.

Now, state equation (2) can be rewritten as

$$p(N,V,T) = \frac{N k_B T}{V - N\gamma(r)} \cdot \left(1 + \sum_{j=1}^{3} A_j \cdot \gamma(r)^j \cdot \left(\frac{N}{V}\right)^j \right) \tag{10}$$

where $\gamma(r) := 2\sqrt{3}r^2$. According to the thermodynamic formalism (cf. Greiner et al. (1995), p. 167) pressure can be expressed by

$$p(N,V,T) = -\frac{\partial F}{\partial V} \tag{11}$$

where

$$F(N,V,T) := -k_B T \ln(Z(N,V,T)) \tag{12}$$

denotes the free energy of a system.

To approximate F for the hard disk fluid, we consider a large container of volume V_0; based on (9), $F(N,V_0,T)$ can be approximated by $\widehat{F}(N,V_0,T)$ where

$$\widehat{F}(N,V,T) := -k_B T \ln(\widehat{Z}(N,V,T)).$$

Combining (9) and (11) leads to the approximation

$$F_{V_0}(N,V,T) = \widehat{F}(N,V_0,T) - \int_{V_0}^{V} p(N,v,T)dv \tag{13}$$

of free energy where the subscript indicates that approximation F_{V_0} depends on the choice of the reference container of volume V_0; since approximation (9) improves with increasing V, we propose the approximation

$$F_\infty(N,V,T) := \lim_{V_0\to\infty} F_{V_0}(N,V,T) \tag{14}$$

which can be explicitly computed because the integral in (13) is exactly solvable for the pressure function given in (10). We obtain

$$F_\infty(N,V,T) = -Nk_BT\cdot\Bigg(1+\ln\left(\frac{2\pi m k_B T}{h^2}\right)+\ln(V/N-\gamma(r))+ +A_s\ln(1-N\gamma(r)/V)+A_{23}N\gamma(r)/V+A_3(N\gamma(r))^2/(2V^2)\Bigg) \tag{15}$$

where

$$A_s := A_1+A_2+A_3 \qquad \text{and} \qquad A_{23} := A_2+A_3.$$

(15) leads in view of (12) to the announced approximation

$$Z(N,V,T) \approx \exp\left(-\frac{F_\infty(N,V,T)}{k_BT}\right) \tag{16}$$

of the partition function for the hard disk fluid.

4 The Duma Test

According to the thermodynamic formalism, entropy S of a system can be computed by

$$S(N,V,T) = -\frac{\partial F}{\partial T} \tag{17}$$

where F denotes the free energy as function of parameters N, V and T. Approximation F_∞ given in (15) for the free energy of the hard disk fluid entails the approximation

$$S_\infty(N,V,T) := -\frac{\partial F_\infty}{\partial T} \tag{18}$$

for the entropy of this fluid.

Let us consider a rectangular tube

$$\Theta := [0, L(0)]\times[-b,b]\subset\mathbb{R}^2$$

filled with N hard disks of radius $r > 0$ and mass $m > 0$ where $L(0)$ denotes the initial length of the tube. Analogously to the experiment described in Section 2, an arbitrary initial temperature $T(0)$ of the fluid can be adjusted. Combining (18) and (15) yields the approximation

$$\widehat{S}(0) := S_\infty(N, V, T(0))$$

of the initial entropy of the fluid in the tube.

Now we propose a computer experimental test for the quality of a given approximation of the partition function of a thermodynamic system. The name of the test has been settled on the occasion of the 65th birthday of Professor Andrei Duma from Hagen.

The test idea is based on the thermodynamic postulate of entropy invariance under adiabatic compression of a fluid (cf. Greiner et al. (1995)). We exemplify the test idea for the case of the approximation given in Section 3.

Let us interpret the right edge of Θ as a piston which is initially described by $\{L(0)\} \times [-b, b]$. If the piston moves in horizontal direction with velocity v, then it describes the trajectory

$$(\{L(t)\} \times [-b, b])_{t \geq 0}$$

where $L(t) = L(0) - vt$ for $t \geq 0$. The movement of the piston entails a compression of the fluid whose temperature at time t can be estimated by

$$\widehat{T}(t) := \frac{m}{2Nk_B} \cdot \sum_{j=1}^{N} < v^{(j)}(t), v^{(j)}(t) > \tag{19}$$

if the momentary velocities $v^{(1)}(t), \ldots, v^{(N)}(t)$ of the disks are computed, cf. Moeschlin, Grycko (2006), chap. 1.

Combining (18), (19) and (15) suggests the esimator

$$\widehat{S}(t) := -\frac{\partial F_\infty}{\partial T}(N, V(t), \widehat{T}(t)) \tag{20}$$

for the entropy of the compressed fluid where $V(t) := 2L(t)b$ is the volume of the tube at the time point $t \geq 0$.

The compression process together with its statistical evaluation has been realized in a computer experiment.

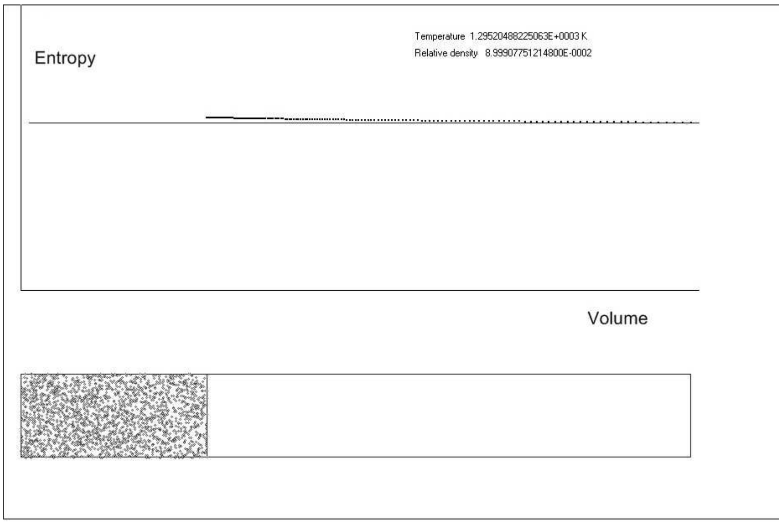

Fig. 2: Adiabatic compression and entropy

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Figure 2 presents a typical picture generated during the experiment. The tube with the piston is visualized. In the diagram the abscissa corresponds to the volume $V(t)$ of the tube and the ordinate to the entropy estimates obtained according to (20) at appropriate time points $t_1, t_2, \ldots$; the estimates are represented as dots. The ordinate of the horizontal line in the diagram is the initial estimate $\widehat{S}(0)$ of entropy.

Since entropy estimates $\widehat{S}(t_1), \widehat{S}(t_2), \ldots$ are close to the initial estimate $\widehat{S}(0)$ during the whole compression process, the test confirms the invariance of entropy under adiabatic compression of the hard disk fluid, which underlines the quality of approximation (15) involved in the construction of estimator $\widehat{S}$.

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