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AN EQUATION OF STATE FOR BINARY HARD DISK FLUID MIXTURES

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Abstract: Recently an equation of state for the hard disk fluid has been proposed based on a statistical evaluation of molecular kinetic long term computer experiments. We generalize this equation to the case of binary mixtures of hard disk fluids and discuss the quality of the generalization in the light of computer experimental data. As in the case of a pure fluid, Moeschlin pressure estimator is applied revealing the usefulness of the idea of pressure superposition in a certain range of the ratio of disk radii.

Dedicated to Professor Johann Boos from Hagen on the occasion of his 65-th birthday.

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1. Introduction

An important model fluid is given by the Boltzmann system of hard disks that are subject to thermal motion within a container C. This fluid exerts pressure on the boundary of C which can be statistically estimated from computer experimental data.

The equation of state interrelates pressure with temperature and density and the properties of the micro-constituents of a fluid. A traditional approach

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to the equation of state of a model fluid is the numerical approximation of virial coefficients, cf. [4].

Recently, cf. [2], an equation of state for a pure hard disk fluid has been proposed for a wide range of particle densities based on the statistical evaluation of long term molecular kinetic computer experiments.

In the present contribution we explore hard disk fluid mixtures in the range $[1/8, 1/2]$ of relative density; a generalization of the equation of state obtained in [2] is motivated based on a superposition of the contributions of the mixture components to pressure (Section 2). We also point out that pressure of the model mixture depends linearly on temperature and does not depend on the masses of the micro-constituents (Section 3). In Section 4 the outcome of long term computer experiments is reported and the quality and validity range of the proposed equation of state are discussed.

2. The Generalized Equation of State

Let us consider a rectangular container

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

of volume (area) V, where $a_1, a_2 > 0$. We inject N hard disks of mass $m > 0$ and radius $r > 0$ into C subject to the condition of mutual non-overlapping. Let the initial velocities $v^{(1)}(0), \dots, v^{(N)}(0) \in \mathbb{R}^2$ of the disks be generated according to the bivariate 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; parameter σ can be interpreted thermally according to

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

where k_B denotes the Boltzmann constant and T the temperature of the fluid.

Let the Newtonian dynamics be imposed on the system which can be imitated on the computer. During the temporal evolution of the microstate of the system reflections of the disks at the boundary of C can be observed, which enables us to estimate pressure p according to [3], Chapter 5.

In [2] the following equation of state for the pure hard disk fluid is proposed,

$$p(N, V, T) = \frac{N k_B T}{V - N\gamma(r)} \cdot \left(1 + \sum_{j=1}^{3} A_j \cdot \left(\gamma(r) \cdot \frac{N}{V}\right)^j\right), \tag{2.1}$$

where $\gamma(r) = 2\sqrt{3} \cdot r^2$ and coefficients A_j are estimated from computer experimental data; the estimates are:

$$\widehat{A}_1 = 0.77843\,, \quad \widehat{A}_2 = 0.83254\,, \quad \widehat{A}_3 = 0.47933. \tag{2.2}$$

Let

$$\varrho_r = \gamma(r) \cdot \frac{N}{V}$$

denote the relative density of the fluid. The average relative error of 2.5% is observed in prediction (2.1) of pressure in the range $[10^{-3}, 0.75]$ of relative density.

Let us now consider a binary mixture of hard disk fluids consisting of N_j disks of mass $m_j > 0$ and radius $r_j > 0$ for $j = 1, 2$. If the mixture is confined to container C of volume V, then Newtonian dynamics can be imposed on it enabling us to estimate pressure.

We propose a generalization of (2.1) based on a superposition principle. Let

$$x_j = \frac{N_j}{N}$$

denote the fraction of disks of type j for $j = 1, 2$, where $N = N_1 + N_2$. A natural generalization of term $\gamma(r)$ in the context of the introduced mixture is given by

$$\gamma_2 = 2\sqrt{3} \cdot (x_1 \cdot r_1^2 + x_2 \cdot r_2^2).$$

Therefore the generalization of (2.1) by superposition can be written as

$$p(N_1, N_2, V, T) = \frac{N k_B T}{V - N\gamma_2} \cdot \left(1 + \sum_{j=1}^{3} A_j \left(\gamma_2 \cdot \frac{N}{V}\right)^j\right). \tag{2.3}$$

3. Disk Masses, Temperature and Pressure

In this section we show that pressure exerted by a hard disk fluid mixture depends linearly on temperature and does not depend on disk masses.

Interaction potential Φ_{jj} between two hard disks of radius r_j is given by

$$\Phi_{jj}(s) = \begin{cases} 0\,, & \text{if} \quad s \geq 2r_j\,, \\ \infty\,, & \text{if} \quad s < 2r_j\,, \end{cases} \tag{3.1}$$

for $j = 1, 2$. Analogously, interaction potential Φ_{12} between two hard disks of radii r_1 and r_2 is defined by

$$\Phi_{12}(s) = \begin{cases} 0\,, & \text{if} \quad s \geq r_1 + r_2\,, \\ \infty\,, & \text{if} \quad s < r_1 + r_2. \end{cases} \tag{3.2}$$

Let

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

denote a momentary state of the fluid mixture where $x^{(j)}$ denotes the position and $u^{(j)}$ the momentum of the j-th disk, $j = 1, \dots, N = N_1 + N_2$. The dynamic term $H_d(u)$ of Hamiltonian $H : C^N \times \mathbb{R}^{2N} \to \overline{\mathbb{R}}_+$ of the system is given by

$$H_d(u) = \frac{1}{2m_1} \cdot \sum_{j=1}^{N_1} < u^{(j)}, u^{(j)} > + \frac{1}{2m_2} \cdot \sum_{j=N_1+1}^{N} < u^{(j)}, u^{(j)} > ,$$

where $<,>$ denotes the scalar product on $\mathbb{R}^2$; the configurational term $H_c(x)$ is given by

$$\sum_{1 \le i < j \le N_1} \Phi_{11}(|x^{(i)} - x^{(j)}|) + \sum_{N_1 < i < j \le N} \Phi_{22}(|x^{(i)} - x^{(j)}|) + \sum_{i=1}^{N_1} \sum_{j=N_1+1}^{N} \Phi_{12}(|x^{(i)} - x^{(j)}|) ,$$

where $|.|$ denotes the Euclidean norm on $\mathbb{R}^2$. Now the total energy of the system can be expressed by

$$H(x;u) = H_c(x) + H_d(u).$$

Partition function Z of the fluid mixture confined to container C of volume V, as introduced in Section 2, is defined according to

$$Z(N_1, N_2, V, T) = \frac{h^{-2N}}{N_1! \cdot N_2!} \cdot \int_{C^N \times \mathbb{R}^{2N}} \exp\left(-\frac{1}{k_B T} \cdot (H_c(x) + H_d(u)) \right) dx du , \quad (3.3)$$

where h denotes Planck constant, cf. [1]; according to the thermodynamic formalism, pressure p is given by

$$p(N_1, N_2, V, T) = k_B T \cdot \frac{\partial}{\partial V} \ln Z(N_1, N_2, V, T). \quad (3.4)$$

Since the integral in (3.3) factorizes into the dynamical and the configurational terms, one recognizes that the derivative in (3.4) is independent of m_1 and m_2. Moreover, the value of the integral

$$\int_{C^N} \exp\left(-\frac{1}{k_B T} \cdot H_c(x) \right) dx$$

does not depend on T which together with (3.4) entails a linear dependence of p on T for hard disk fluid mixtures.

These observations reduce the complexity of the task of establishing an equation of state and enable us to fix m_1, m_2 and T in all computer experiments discussed in the present contribution.

4. The Computer Experiments and their Outcomes

In the computer experiments the total number N of disks constituting a binary fluid mixture has been fixed to $N = 3000$. For the masses m_1 and m_2 of the disks we have put $m_1 = m_2 = N_A^{-1}$ where $N_A = 6.022 \cdot 10^{26}\text{kg}^{-1}$ denotes the modified Avogadro number. The temperature $T = 300\text{K}$ has been adjusted by generating the initial velocities of the disks according to a bivariate normal distribution with variance

$$\sigma^2 = \frac{k_B T}{m_1} = \frac{k_B T}{m_2}.$$

The ratio r_1/r_2 of the radii of the micro-constituents of the first and second mixture components has been varied in the range $[1.2, 4.0]$ where $r_2 = 10^{-10}\text{m}$ has been fixed. For each choice of radii ratio the number N_1 of disks of radius r_1 has been varied according to

$$N_1 = 300 \cdot i \qquad (i = 1, \ldots, 9).$$

The volume V of rectangular container C has been varied to adjust relative densities

$$\varrho_r = 2\sqrt{3} \cdot \frac{N_1 \cdot r_1^2 + N_2 \cdot r_2^2}{V} = \frac{1}{2 + 0.2 \cdot i} \qquad (i = 0, \ldots, 30)$$

that constitute a dense lattice in the interval $[1/8, 1/2]$ which is our main region of interest. For each choice of parameters r_1, N_1 and V Newtonian dynamics has been imposed on the micro-constituents of the fluid mixture to register 3000 reflections of disks at the boundary of the container. Moeschlin pressure estimator has been applied to the reflection data.

The obtained pressure estimates are compared with prediction (2.3). The results are summarized in Table 1 where for appropriate values of fraction $x_1 = N_1/N$ and of radii ratio r_1/r_2 the average relative errors of the estimated value w.r.t. their predictions (2.3) are recorded (the averages are based on 31 pressure values corresponding to 31 values of relative density of the fluid mixture; for relative densities lower than 1/8, predictions (2.3) are expected to improve with decreasing relative density).

Table 1 suggests that the relative error tends to increase with increasing

r_2/r_1 \ x_1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1.2	0.6	0.7	0.6	0.6	0.7	0.5	0.6	0.6	0.6
1.4	0.7	0.8	0.8	0.9	0.9	0.7	0.7	0.8	0.7
1.6	0.9	1.3	1.4	1.4	1.2	1.1	1.0	0.9	0.7
1.8	1.3	1.5	2.0	2.0	1.6	1.6	1.5	1.0	0.9
2.0	1.6	2.4	2.5	2.5	2.4	1.9	1.8	1.3	0.8
2.2	2.1	3.0	3.1	3.1	2.8	2.2	2.1	1.3	0.9
2.4	2.8	3.7	3.9	3.7	2.8	2.7	2.1	1.7	1.1
2.6	3.6	4.1	4.7	4.1	3.9	3.2	2.5	1.7	1.1
2.8	4.1	5.0	5.0	4.6	4.2	3.4	2.6	1.8	1.1
3.0	4.7	5.6	5.8	5.2	4.7	3.6	2.7	2.1	0.9
3.2	5.0	6.1	6.1	5.7	4.9	4.0	3.0	2.0	1.2
3.4	5.8	6.9	6.5	5.8	5.1	4.3	3.2	2.4	1.2
3.6	6.4	7.2	7.2	6.3	5.5	4.4	3.4	2.3	1.4
3.8	7.1	7.9	7.3	6.5	6.0	4.7	3.7	2.4	1.3
4.0	7.6	8.3	8.0	6.9	5.8	5.0	3.6	2.3	1.3

Table 1: Average relative error in %

radii ratio; for $1.0 \leq r_1/r_2 \leq 2.0$ the prediction error does not exceed the relative error inherent in state equation (2.1) for pure hard disk fluid. Table 1 confirms the validity of state equation (2.3) for the range $[1.0, 2.0]$ of radii ratio and shows limitations of the concept of pressure superposition for mixtures of disks with significantly differing radii.

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