

## Self-Diffusion as an indicator of the solid-fluid phase transition<sup>1</sup>

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### Abstract

$N$  hard disks are injected into a 2-dimensional container. The initial velocities of the disks are generated according to a centered normal distribution. The Newtonian dynamics is imposed on the (thermodynamic) system. The average quadratic displacement of the disks from their initial positions is sampled as function of time for different densities of the system. It turns out that this function depends qualitatively on whether the system is in the fluid/solid phase; the average quadratic displacement indicates the self-diffusion phenomenon in a fluid and performs a different behavior in a solid. Based on computer experimental data the density of the solid-fluid phase transition for hard disks is localized.

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# 1 Introduction

An important and conceptually simple microscopic model for a substance is the Boltzmann system of moving molecules that are described by hard spheres, or, in the 2-dimensional case, by hard disks. In this model the molecules are subject to (thermal) motion and interact through collisions. It is generally believed that the Boltzmann system undergoes a solid-liquid phase transition (melting) at some critical density which is independent of the temperature, cf. Bowen et al. (2006).

The analytical determination of the density of phase transition is to our knowledge an unsolved problem. On the other hand, there are attempts to determine the melting point by simulation studies, cf. Jaster (1998) and Watanabe et al. (2004).

The aim of the present contribution is the discussion of a possibility for detecting the phase transition in the 2-dimensional Boltzmann system by checking whether the thermal motion of hard disks performs a diffusive behavior for different densities.

In Section 2 we describe the design of a computer experiment and explain the notion of average quadratic displacement as a statistical tool for studying the self-diffusion. In Section 3 we report the outcome of this long term computer experiment whose statistical evaluation yields a small interval covering the density of the solid-fluid phase transition. In Section 4 some conclusions are drawn.

## 2 The Arrangement of the Computer Experiment

Let us consider a rectangular container

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

where

$$(2.1) \quad a_2 = \frac{\sqrt{3}}{2} \cdot a_1.$$

We inject  $N = 1661$  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.

In order to impose the temperature  $T = 300\text{K}$  on the (thermodynamic) system we put

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

where  $k_B = 1.38 \cdot 10^{-23} \text{J/K}$  denotes Boltzmann constant; we generate the initial velocities  $v^{(1)}(0), \dots, v^{(N)}(0) \in \mathbb{R}^2$  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  $2 \times 2$ -identity matrix. This initial state complies with Maxwell hypothesis, cf. Moeschlin, Grycko (2006).

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

For the analysis of the self-diffusion phenomenon in the system we introduce the position index  $I^{(j)}$  of sphere  $j$  at time  $t$  which is initially defined according to

$$I^{(j)} := (0, 0) \in \mathbb{Z}^2;$$

if disk  $j$  is reflected at the wall  $\{a_1\} \times [-a_2, a_2]$  of container  $C$  at time  $t$ , then  $I_1^{(j)}$  is increased or decreased by 1 depending on whether  $I_1^{(j)}$  is even or odd,

respectively; if disk  $j$  is reflected at  $\{-a_1\} \times [-a_2, a_2]$ , then  $I_1^{(j)}$  is decreased or increased by 1 depending on whether  $I_1^{(j)}$  is even or odd, respectively. A corresponding rule for changing the second component  $I_2^{(j)}$  of  $I^{(j)}$  is applied if disk  $j$  is reflected at  $[-a_1, a_1] \times \{a_2\}$  or at  $[-a_1, a_1] \times \{-a_2\}$ .

If position  $x^{(j)}(t)$  and index  $I^{(j)}$  of disk  $j$  at time  $t$  are given, then its virtual position  $y^{(j)}(t) = (y_1^{(j)}(t), y_2^{(j)}(t)) \in \mathbb{R}^2$  at time  $t$  is defined by:

$$y_i^{(j)}(t) := \begin{cases} x_i^{(j)}(t) + a_i \cdot I_i^{(j)} & \text{if } I_i^{(j)} \text{ is even} \\ -x_i^{(j)}(t) + a_i \cdot I_i^{(j)} & \text{if } I_i^{(j)} \text{ is odd} \end{cases}$$

for  $i = 1, 2, j = 1, \dots, N, t \geq 0$ .

Put

$$(2.2) \quad q(t) := \frac{1}{N} \cdot \sum_{j=1}^N |y^{(j)}(t) - x^{(j)}(0)|^2 \quad (t \geq 0)$$

where  $|\cdot|$  denotes the Euclidean norm on  $\mathbb{R}^2$ .  $q(t)$  expresses the average quadratic displacement of the disks at time  $t$  from their initial positions. Since we have used the virtual positions  $y^{(j)}(t)$  and not  $x^{(j)}(t)$  in (2.2), the average quadratic displacement  $q(t)$  is not biased by boundary effects. An analogous concept of quadratic displacement is applied in Grycko (2007) to the estimation of the self-diffusion coefficient of a fluid.

In the course of the computer experiment imitating the (thermal) motion of the disks, the temporal evolution of  $q(t)$  has been stored for different values of the volume  $4a_1a_2$  of container  $C$ .

### 3 The Outcome of the Computer Experiment and its Evaluation

If  $N$  disks are confined to a container of volume  $4a_1a_2$ , the number density  $\varrho$  of the thermodynamic system is given by

$$\varrho = \frac{N}{4a_1a_2};$$

the relative density  $\varrho_r$  is defined according to:

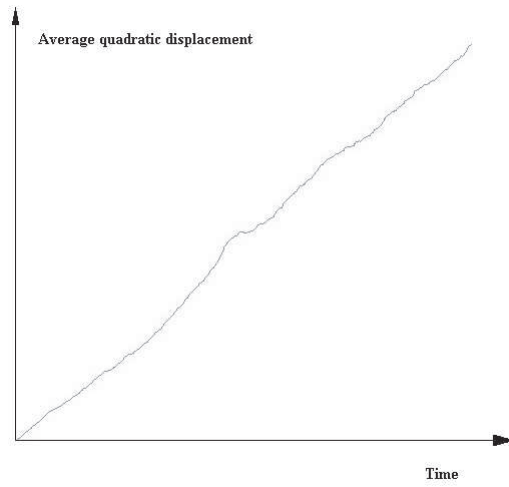
$$\varrho_r := \frac{2\sqrt{3} \cdot r^2 \cdot N}{4a_1a_2}$$

where  $2\sqrt{3} \cdot r^2$  is the inverse density of the close packing.

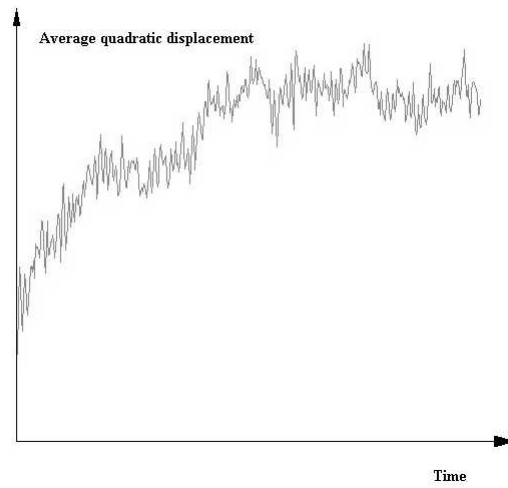
In the course of experimentation the edge lengths  $2a_1$  and  $2a_2$  of the container have been varied such that the validity of (2.1) has been maintained; the relative density  $\varrho_r$  has ranged between 0.5 and 1.0; for each choice of relative density the dynamics has been run until  $5 \cdot 10^6$  collisions between the disks have occurred; the average quadratic displacement  $q(t)$  has been stored as function of time. In Figure 1 the graph of the observed function  $q$  is shown for the relative density  $\varrho_r = 0.6784$ ; here  $q$  can be approximated by a linear function,

$$q(t) \approx D \cdot t \quad (t \geq 0)$$

where parameter  $D$  can be interpreted as coefficient of self-diffusion, which is typical for the fluid phase.

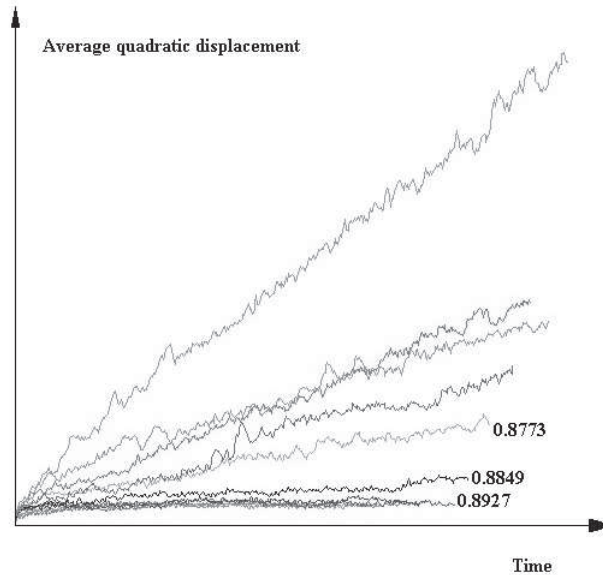


**Fig. 1:** Average quadratic displacement as function of time;  $q_r = 0.6784$ .



**Fig. 2:** Average quadratic displacement as function of time;  $q_r = 0.9252$ .

In Figure 2 the graph of  $q$  is shown for the relative density  $\varrho_r = 0.9252$ . Here function  $q$  increases initially and starts to oscillate around a constant value which corresponds to the oscillations of the micro-constituents around their mechanical equilibrium positions; this phenomenon indicates the solid phase.



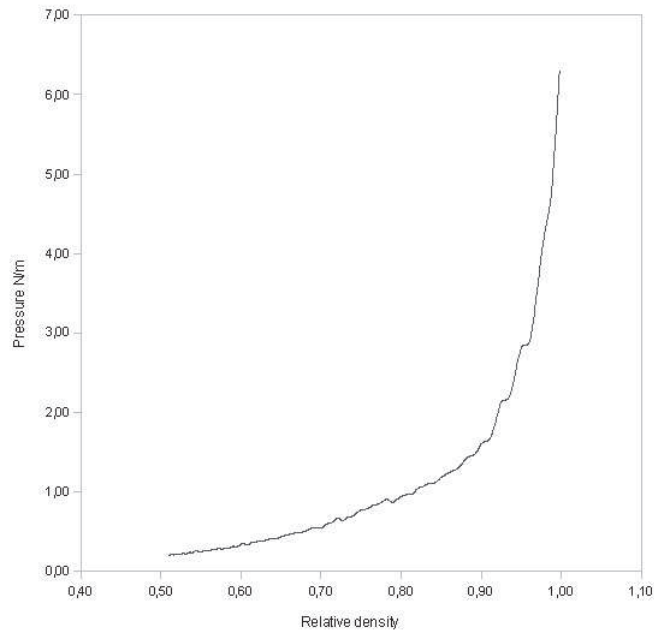
**Fig. 3:** Average quadratic displacement as function of time for different densities

In Figure 3 the average quadratic displacement as function of time is shown for different densities; the numerical values of relative density are attached to the three curves that indicate the solid-fluid phase transition. The visual impression suggests that the relative density of phase transition  $\bar{\varrho}_r$  lies in the interval  $I_L = [0.8773, 0.8927]$ ; the index  $L$  has been settled on the occasion of 65th birthday of Professor Hansjörg Linden from the University of Hagen. The task of a sharper localization of  $\bar{\varrho}_r$  would require a longer observation of the average quadratic displacement for relative densities in the critical range and the application of mathematically justified methods

from Inferential Statistics.

## 4 Conclusions

In the course of the long term computer experiment the pressure has been estimated in the range 0.5-1.0 of relative density by an application of a pressure estimator introduced in Moeschlin, Grycko (2006), chap. 5. Figure 4 shows the isotherm ( $T = 300\text{K}$ ) where the horizontal axis corresponds to the (relative) density of the system and the vertical axis to the estimated pressure; the diagram indicates that a localization of a phase transition based on this isotherm should be difficult.



**Fig. 4:** Estimated pressure as function of density

On the other hand, the localization of the melting point based on the temporal evolution of the average quadratic displacement of the molecules is



straightforward, cf. Figure 3. The resulting Linden interval for  $\bar{\varrho}_r$  is in a good agreement with Jaster (1998) and Watanabe et al. (2004) who used a Monte-Carlo method to study the dependence of an order parameter on the density of the hard disk system and obtained similar melting points.

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