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ON THE THERMAL CONDUCTIVITY OF THE HARD SPHERE FLUID

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Abstract: We consider the hard sphere fluid confined to a container. We realize two heat baths at two opposite ends of the container entailing a stationary heat flow through the fluid. Based on a simulation experiment, the heat conductivity can be estimated. A formula for the heat conductivity of the hard sphere fluid is proposed; the formula is valid for arbitrary temperature and for a wide range of fluid density. As an application, the obtained formula is discussed in the light of laboratory values of thermal conductivity for noble gases and for water.

AMS Subject Classification: 82C70
Key Words: molecular dynamics, Nadaraya-Watson estimator, weighted regression

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. In this model the molecules are subject to thermal motion and interact through collisions.

In the present contribution we consider a container C filled with hard

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spheres; a prescribed initial temperature of the hard sphere fluid can be adjusted by generating initial velocities of the spheres according to an appropriate distribution. We realize heat baths at two opposite walls of container C entailing a slope of temperature along the container; the position dependent temperature can be estimated by the Nadaraya-Watson estimator. Since the resulting heat flow can be assessed during the computational process, we are able to estimate the thermal conductivity of the hard sphere fluid depending on temperature and density. Based on a long term computer experiment, we establish a formula for the thermal conductivity; this formula is valid for arbitrary temperatures T and relative densities $\varrho_r \in [0, 0.33]$. As an application, we explore a possibility of microscopic explanation of empirical thermal conductivity values for noble gases and for liquid water.

2. The Distribution of Velocities of Spheres Approaching a Wall

In the present section we explore statistically the distribution of velocities of spheres approaching a container wall. The obtained computer experimental result can be interpreted as a guidance for the design of a heat bath, which is utilized in Section 3.

Let us consider a 3-dimensional container

$$C := [0, a] \times [-b, b]^2 \subset \mathbb{R}^3$$

where $a = 8b > 0$. We inject N hard spheres of mass $m = N_A^{-1}$ and radius $r = 10^{-10}\text{m}$ into C according to the uniform distribution where $N_A = 6.022 \cdot 10^{26}\text{kg}^{-1}$ denotes the modified Avogadro number.

We generate the initial velocities of the disks according to the normal distribution $N(0, \sigma^2 \cdot I_3)$ with mean vector $0 \in \mathbb{R}^3$ and covariance matrix $\sigma^2 \cdot I_3$ where I_3 denotes the 3×3 – identity matrix. This initial state complies with Maxwell hypothesis, cf. [1].

The system can be interpreted thermally according to

$$\sigma^2 = \frac{k_B \cdot T}{m} \tag{2.1}$$

where $k_B = 1.38 \cdot 10^{-23}\text{J/K}$ and T denote Boltzmann constant and temperature, respectively.

Newtonian dynamics is imposed on the micro-constituents of the fluid. During the computational process reflections of spheres at the right wall

$$W_R := \{a\} \times [-b, b]^2 \subset \partial C$$

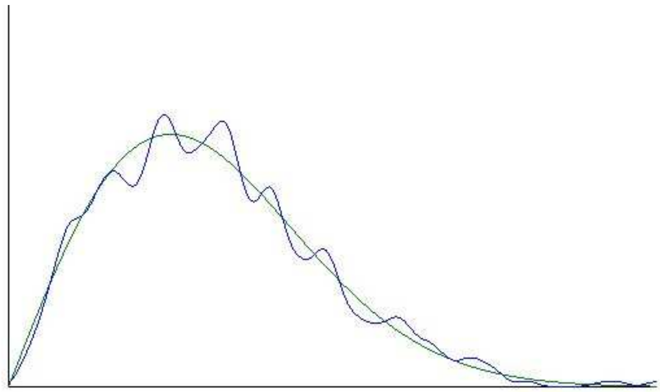

Figure 1: Model density f_σ and its kernel estimate

of container C occur. We sample velocity vectors $u^{(1)}, u^{(2)}, \ldots$ of spheres approaching wall W_R. Plausibility considerations entail that the components $u_1^{(1)}, u_1^{(2)}, \ldots$ of vectors $u^{(1)}, u^{(2)}, \ldots$ orthogonal to wall W_R are distributed according to a distribution P_σ whose probability density is given by

$$f_\sigma(u) = \frac{u}{\sigma^2} \cdot \exp\left(-\frac{u^2}{2\sigma^2}\right) \qquad (u \geq 0).$$

Let $K : \mathbb{R} \to \mathbb{R}_+$ denote the Gaussian kernel:

$$K(x) := \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{x^2}{2}\right).$$

The kernel estimate of the probability density of the velocity components $u_1^{(1)}$, $\ldots, u_1^{(n)}$ orthogonal to W_R is given by

$$\widehat{f}_n(u) = \frac{1}{nh} \cdot \sum_{i=1}^{n} K\left(\frac{u - u_1^{(i)}}{h}\right)$$

where $h > 0$ is an appropriate bandwidth. (For an introduction to the method of kernel density estimation cf. [4]).

In Figure 1 the graphical comparison between f_σ and $\widehat{f}_n$ is presented where $n = 1000$. Since the noisy graph of $\widehat{f}_n$ approximates the smooth graph of f_σ, Figure 1 confirms the validity of f_σ for the description of the distribution of velocity components $u_1^{(1)}, u_1^{(2)}, \ldots$ of spheres approaching wall W_R. This confirmation is obtained independently of the adjusted temperature T and of the selected density

$$\varrho = \frac{N}{4ab^2} \tag{2.2}$$

of the fluid.

3. The Computer Experiment and its Outcome

In the computer experiment considered in the present section $N = 5000$ hard spheres are injected into container C introduced in Section 2. The initial velocities of the spheres are generated according to the normal distribution $N(0, \sigma^2 \cdot I_3)$ with the thermal interpretation of the variance given in (2.1) and with the specification $T = 300$K of the initial temperature of the fluid. Newtonian dynamics is imposed on the spheres.

The walls $W_L := \{0\} \times [-b, b]^2$ and W_R are exposed to two heat baths with temperatures $T_L = 200$K and $T_R = 400$K, respectively. If sphere j approaches wall W_L, then it is reflected and its velocity component $v_1^{(j)}$ orthogonal to wall W_L is generated according to distribution P_σ where

$$\sigma := \sigma_L := \sqrt{\frac{k_B \cdot T_L}{m}};$$

cf. Section 2. The velocity components $v_2^{(j)}$ and $v_3^{(j)}$ tangential to wall W_L are generated according to the normal distribution $N(0, \sigma_L^2)$. An analogous heat bath with $T_R = 400$K is implemented at wall W_R.

The dynamics and the heat baths entail a heat flow from W_R to W_L.

The heat input $H_R(t)$ at W_R and the heat output $H_L(t)$ at W_L can be sampled as functions of time; after some experimental time τ the approximative equality

$$H_L(\tau) \approx H_R(\tau)$$

is observed, which indicates a stationary heat flow through the container.

Let $x^{(j)}(t) \in C$ and $v^{(j)}(t) \in \mathbb{R}^3$ denote the position and velocity of sphere j at time t, respectively. Based on a momentary microstate

$$(x^{(1)}(t), \ldots, x^{(N)}(t); v^{(1)}(t), \ldots, v^{(N)}(t))$$

temperature T as function of the horizontal position coordinate ξ can be esti-

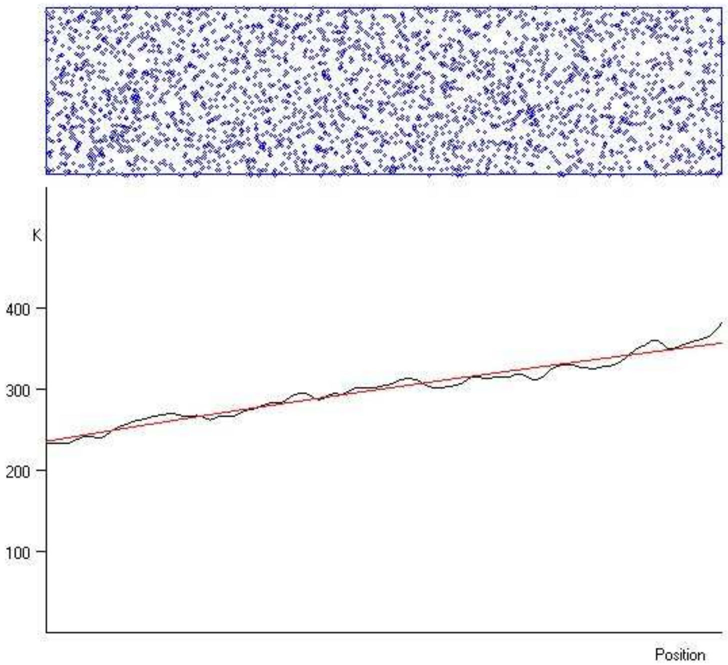

Figure 2: Screen shot of the experiment

mated by the Nadaraya-Watson estimator

$$\widehat{T}_t(\xi) = \frac{m \cdot \sum_{j=1}^{N} \langle v^{(j)}(t), v^{(j)}(t) \rangle \cdot K\left(\frac{\xi - x_1^{(j)}(t)}{h}\right)}{3k_B \cdot \sum_{j=1}^{N} K\left(\frac{\xi - x_1^{(j)}(t)}{h}\right)}$$

where $h > 0$ denotes an appropriate bandwidth and $\langle , \rangle$ the standard scalar product on $\mathbb{R}^3$.

In Figure 2 container C filled with the hard sphere fluid is shown. In the diagram a typical Nadaraya-Watson estimate of temperature is visualized (noisy line). The smooth line corresponds to the function

$$T_t(\xi) = \beta_T \cdot (\xi - \xi_T)^{\alpha_T} \tag{3.1}$$

where parameters α_T, β_T, ξ_T are fitted to the nonparametric estimate $\widehat{T}_t$.

The (nonparametric) kernel estimate of the relative density of the fluid as a function of the horizontal position coordinate ξ is given by

$$\widehat{\varrho}_r^t(\xi) = \frac{\sqrt{32}r^3}{b^2 \cdot h} \cdot \sum_{j=1}^{N} K\left(\frac{\xi - x_1^{(j)}(t)}{h}\right)$$

where $\sqrt{32}r^3$ denotes the inverse density of the close packing of spheres. Analogously, $\widehat{\varrho}_r^t$ can be approximated by the smooth function

$$\widehat{\widehat{\varrho}}_r^t(\xi) = \beta_\varrho \cdot (\xi - \xi_\varrho)^{\alpha_\varrho} \tag{3.2}$$

by fitting parameters $\alpha_\varrho, \beta_\varrho, \xi_\varrho$ to estimate $\widehat{\varrho}_r^t$.

The principle of corresponding states entails that heat conductivity κ of the hard sphere fluid is proportional to

$$\frac{\sigma}{r^2} = \frac{\sqrt{\frac{k_B \cdot T}{m}}}{r^2};$$

this suggests the formula

$$\kappa = k_B \cdot \gamma(\varrho_r) \cdot \sqrt{\frac{k_B \cdot T}{m}} \cdot \frac{1}{r^2} \tag{3.3}$$

where function γ reflects the dependence of κ on the relative density of the fluid.

We repeat the described experiment adjusting different average relative densities

$$\varrho_r = \sqrt{32}r^3 \cdot \frac{N}{4ab^2}$$

by varying volume $4ab^2$ of container C. At each repetition we sample the estimates

$$\widehat{\kappa}_\tau := \frac{H_R(\tau)}{\tau \cdot b^2 \cdot T_\tau'(\xi_0)},$$

$\widehat{\widehat{\varrho}}_r^\tau(\xi_0)$ and

$$\widehat{\sigma}_\tau := \sqrt{\frac{k_B \cdot T_\tau(\xi_0)}{m}}$$

where T_τ' denotes the derivative of function T_τ w.r.t. the position variable ξ (gradient of temperature). For a large value τ of experimental time we obtain pairs (ϱ_i, γ_i) where

$$\varrho_i := \widehat{\widehat{\varrho}}_r^\tau(\xi_0)$$

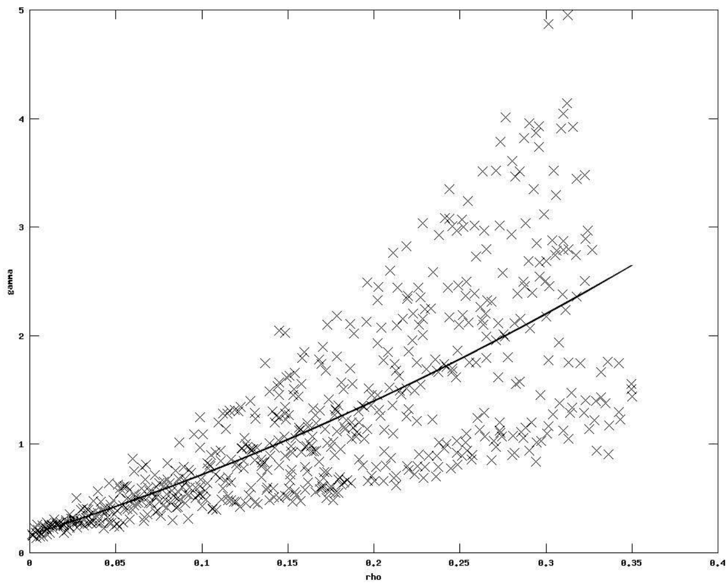

Figure 3: Sampled pairs (ϱ_i, γ_i)

is an estimate of the relative density and

$$\gamma_i := \frac{\widehat{\kappa}_\tau \cdot r^2}{k_B \cdot \widehat{\sigma}_\tau}$$

is an estimate of the value $\gamma(\rho_i)$ of function γ expressing the dependence of κ on relative density according to (3.3).

In Figure 3 the sampled pairs $(\varrho_i, \gamma_i), i = 1, \ldots, n$ of estimates are visualized. The diagram shows a strong dispersion of estimates γ_i in particular for high densities. The data visualized in Figure 3 carries statistical information about the dependence of coefficient γ in (3.3) on the relative density of the fluid. The visual impression suggests the ansatz

$$\widehat{\gamma}(\varrho_r) = \gamma_0 + \gamma_1 \varrho_r + \gamma_2 \varrho_r^2 \tag{3.4}$$

for approximating function γ. The weighted least squares estimates of the parameters in (3.4) based on computer experimental data are given by

$$\gamma_0 = 1.6497 \cdot 10^{-1}, \qquad \gamma_1 = 4.9295, \qquad \gamma_2 = 6.1836,$$

where the weight function $w(\varrho_r) = 1/\varrho_r$ has been applied. Note that estimate γ_0 compares well with the corresponding theoretical constant $\pi^{-3/2}$ obtained for dilute gases, cf. [2], p. 481.

The announced formula for heat conductivity κ of the hard sphere fluid is given by

$$\kappa = k_B \cdot (\gamma_0 + \gamma_1 \varrho_r + \gamma_2 \varrho_r^2) \cdot \sqrt{\frac{k_B \cdot T}{m}} \cdot \frac{1}{r^2}. \tag{3.5}$$

Based on our computer experimental experience we claim that (3.5) is valid for arbitrary temperature T and for relative density $\varrho_r \in [0, 0.33]$.

4. Comparison with Laboratory Data

Since thermal conductivity of real fluids can be determined in laboratory, it is natural to compare formula (3.5) with measurements. In [3] laboratory values of thermal conductivity of the noble gas Ne are reported for the temperature range $50\text{K} \le T \le 2000\text{K}$. Since these data are sampled at constant pressure $p = 1.01 \cdot 10^5 \text{N/m}^2$ and not at constant density ϱ, we utilize the equation of state of the ideal gas,

$$p = \varrho \cdot k_B \cdot T, \tag{4.1}$$

to determine the corresponding relative density in the hard sphere model

$$\varrho_r = \sqrt{32} \cdot r^3 \cdot \varrho = \sqrt{32} \cdot r^3 \cdot \frac{p}{k_B \cdot T}$$

which can be inserted into (3.5).

In Figure 4 the horizontal axis corresponds to temperature and the vertical axis to heat conductivity. The dotted line shows laboratory measurements of κ for Ne; the continuous line corresponds to prediction (3.5) where $m := m_r/N_A$ and $m_r = 20.18$ denotes the relative atomic mass of Ne; radius r is fitted to the data by the least square method yielding the realistic value $\widehat{r} = 1.1627 \cdot 10^{-10}\text{m}$.

Figure 4 shows an essentially good agreement between theory and laboratory measurements. It should be emphasized that atomic radius r is the only parameter required here for microscopic explanation of thermal conductivity of Ne as function of temperature. An attentive look at Figure 4 reveals, however, a slight discrepancy between measurements and the fitted line which can be interpreted as a limitation of the description of a real fluid by the hard sphere model.

Analogous comments apply to heat conductivity of other noble gases and, surprisingly, also to liquid water.

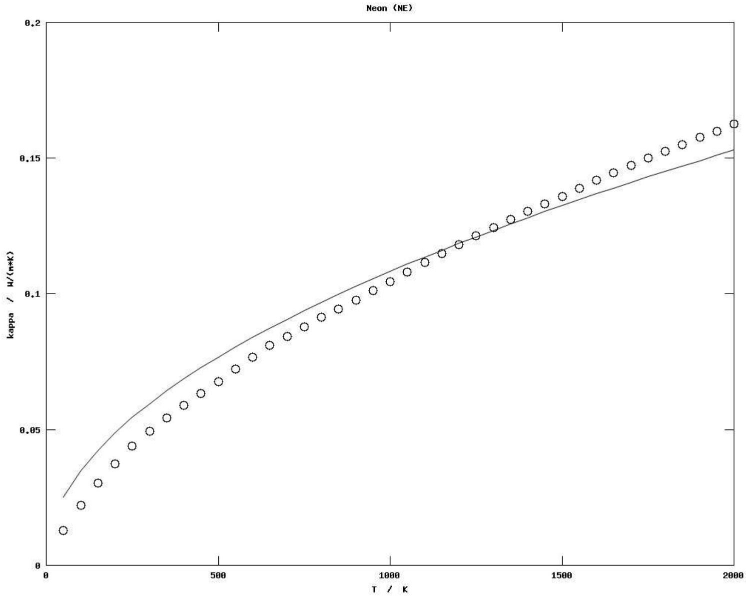

Figure 4: Thermal conductivity of Ne

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