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ON A COMPATIBILITY RELATION BETWEEN THE MAXWELL-BOLTZMANN AND THE QUANTUM DESCRIPTION OF A GAS PARTICLE

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Abstract: We consider a quantum particle at a thermal equilibrium and compute its Gibbs state. The transition to the thermodynamic limit reveals that the asymptotic quantum variance of the velocity operator of the particle coincides with the Maxwell-Boltzmann variance of the velocity distribution, which means that the Maxwell-Boltzmann description of the ideal gas is in some sense compatible with the quantum description of a gas in a macroscopic container at an arbitrary temperature.

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We dedicate this contribution to our colleague Karl-Eugen Spreng on the occasion of his retirement.

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1. Introduction

According to the Maxwell-Boltzmann theory the velocities of the micro-constituents of a fluid at thermal equilibrium are realizations of normal random vectors whose variance σ^2 has the physical interpretation

$$\sigma^2 = \frac{k_B \cdot T}{m} \tag{1.1}$$

where k_B, T and m denotes the Boltzmann constant, the temperature of the fluid and the mass of a micro-constituent, respectively. (1.1) can be also expressed as

$$\sigma^2 = \frac{1}{\beta \cdot m} \tag{1.2}$$

where

$$\beta := \frac{1}{k_B \cdot T}$$

denotes the inverse temperature, cf. [3].

(1.1) and (1.2) are originally valid in the context of a classical description of a fluid. In the present contribution we consider the quantum approach to the ideal gas which can be viewed as a sample of non-interacting quantum particles. For the mathematical description of the quantum gas it is convenient to consider one quantum particle confined within a 1-dimensional container (Section 2). In this context the quantum Gibbs state of the particle can be introduced as a positive operator with normalized trace (Section 3). The Gibbs state describes the quantum particle at a thermal equilibrium, cf. [4], p. 384. The consideration of the velocity operator enables us to compute its second quantum moment w.r.t. the Gibbs state which, as we show in Section 4, in the thermodynamic limit coincides with the Maxwell-Boltzmann variance of the velocity distribution of a gas particle at thermal equilibrium.

2. A Quantum Particle in a Box

Let us consider a 1-dimensional box of width $2a$ where $a > 0$ is a fixed real number. The box can be represented by the potential $U : \mathbb{R} \to \overline{\mathbb{R}}$ which we define by

$$U(x) := \begin{cases} 0 & \text{for } |x| \le a \\ +\infty & \text{elsewhere} \end{cases} \tag{2.1}$$

where $\overline{\mathbb{R}} = \mathbb{R} \cup \{-\infty, +\infty\}$ denotes the extended real line.

Let us suppose that a particle of mass $m > 0$ is confined within the box. The corresponding quantum Hamiltonian $H : C^2([-a,a]) \to L^2([-a,a])$ is given by

$$H\varphi(x) := -\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2}\varphi(x) + U(x) \cdot \varphi(x). \tag{2.2}$$

where $C^2([-a,a])$ denotes the set of twice continuously differentiable functions on $[-a,a]$ and $\hbar$ the reduced Planck constant. Operator H may be also called Schrödinger operator (cf. [1]).

From the definition (2.1) of U it follows that the solutions ψ of the eigenvalue problem

$$H\psi = \lambda \cdot \psi \tag{2.3}$$

that satisfy the Dirichlet boundary condition

$$\psi(-a) = \psi(a) = 0 \tag{2.4}$$

are given as the functions

$$\psi_k(x) := \frac{1}{c_k} \cdot \sin\left(\frac{k\pi}{a} \cdot x\right) \qquad (k = 1, 2, \ldots) \tag{2.5}$$

that correspond to the eigenvalues

$$E_k(a) = \frac{\hbar^2 \cdot \pi^2 \cdot k^2}{2m \cdot a^2} \qquad (k = 1, 2, \ldots) \tag{2.6}$$

of H where

$$c_k := \left(\int_{-a}^{a} \sin^2\left(\frac{k\pi}{a} \cdot x\right) dx \right)^{\frac{1}{2}}$$

denote the normalizing constants. The set $\{\psi_k \,|\, k = 1, 2, \ldots\}$ is an orthonormal system in the Hilbert space $L^2([-a,a])$ which can be extended in a natural way by

$$\psi_{-k}(x) := \frac{1}{c_k} \cdot \cos\left(\frac{k\pi}{a} \cdot x\right) \qquad (k = 0, 1, \ldots)$$

to the orthonormal basis $B := \{\psi_k \mid \ldots, -1, 0, 1, \ldots\}$ of the considered Hilbert space (cf. [5], p. 131f) where

$$c_0 = \frac{1}{\sqrt{2a}}.$$

Formally we put

$$\psi_k(x) := 0 \qquad \text{for} \qquad |x| > a \qquad \text{and} \qquad k = \ldots, -1, 0, 1, \ldots$$

which entails that B is a complete system of eigenfunctions of operator H whose matrix representation $(H_{k,l})_{k,l=-\infty}^{\infty}$ w.r.t. basis B is given by

$$H_{k,l} = E_k(a) \cdot \delta_{k,l} \qquad (k, l = \ldots, -1, 0, 1, \ldots) \tag{2.7}$$

where $\delta_{k,l}$ denotes the Kronecker symbol and the eigenvalues $E_k(a)$ are also given by (2.6) for $k = 0, -1, -2, \ldots$

3. The Gibbs State Associated with the Hamiltonian

To construct a quantum Gibbs state of the system described by a Hamiltonian we have to exponentiate it. In view of (2.7) the operator

$$G(a, \beta) := \tau(a, \beta)^{-1} \cdot \exp(-\beta \cdot H)$$

has the matrix representation

$$(G(a, \beta))_{k,l} = \tau(a, \beta)^{-1} \cdot \exp\left(-\beta \cdot E_k(a)\right) \cdot \delta_{k,l} \quad (k, l = \ldots, -1, 0, 1, \ldots) \tag{3.1}$$

w.r.t. basis B where $\beta > 0$ denotes the inverse temperature and $\tau(a, \beta)$ is defined according to

$$\tau(a, \beta) := \operatorname{trace}\left(\exp\left(-\beta \cdot H\right)\right) = \sum_{k=-\infty}^{\infty} \exp\left(-\beta \cdot E_k(a)\right). \tag{3.2}$$

Operator $G(a, \beta) : L^2([-a, a]) \to L^2([-a, a])$ describes the quantum state of the particle confined within the 1-dimensional box $[-a, a]$ and exposed to a heat bath of inverse temperature β.

4. The Velocity Operator and its Properties

According to the quantum formalism the velocity operator $v : C^2([-a,a]) \to Ł^2([-a,a])$ for the particle confined within the 1-dimensional box $[-a,a]$ is given by

$$v\psi(x) := \frac{p}{m} = -\frac{i \cdot \hbar}{m} \cdot \frac{d}{dx}\psi(x). \tag{4.1}$$

where

$$p := -i \cdot \hbar \cdot \frac{d}{dx}$$

is the momentum operator. The squared velocity operator $u := v^2$ can be interpreted as an operator $u : C^2([-a,a]) \to Ł^2([-a,a])$ with the representation

$$u\psi(x) = -\frac{\hbar^2}{m^2} \cdot \frac{d^2}{dx^2}\psi(x).$$

The matrix representation of u w.r.t. basis B is given by

$$u_{k,l} = \frac{k^2 \cdot \pi^2 \cdot \hbar^2}{a^2 \cdot m^2} \cdot \delta_{k,l} \qquad (k,l = \ldots, -1, 0, 1, \ldots).$$

The second moment of the velocity operator v can be expressed according to

$$\operatorname{trace}\left(G(a,\beta)v^2\right) = \tau(a,\beta)^{-1} \cdot \sum_{k=-\infty}^{\infty} \exp\left(-\frac{\beta\hbar^2\pi^2k^2}{2ma^2}\right) \cdot \frac{k^2\pi^2\hbar^2}{a^2m^2}. \tag{4.2}$$

Now we consider the thermodynamic limit $a \to \infty$. For large a the term $a^{-1} \cdot \tau(a,\beta)$ can be interpreted as an approximation of the integral

$$I_1(\beta) := \int_{-\infty}^{\infty} \exp\left(-\frac{\beta \cdot \hbar^2 \cdot \pi^2}{2m} \cdot x^2\right) dx$$

by a family of Riemann sums (cf. (3.2), (2.6) and sec. 2.1 in [2]). We conclude that

$$\lim_{a\to\infty} a^{-1}\tau(a,\beta) = I_1(\beta). \tag{4.3}$$

holds. Analogously,

$$\lim_{a\to\infty} a^{-1} \cdot \sum_{k=-\infty}^{\infty} \exp\left(-\frac{\beta \cdot \hbar^2 \cdot \pi^2 \cdot k^2}{2m \cdot a^2}\right) \cdot \frac{k^2 \cdot \pi^2 \cdot \hbar^2}{a^2 \cdot m^2} = I_2(\beta) \tag{4.4}$$

where $I_2(\beta)$ is defined by

$$I_2(\beta) := \int_{-\infty}^{\infty} \exp\left(-\frac{\beta \cdot \hbar^2 \cdot \pi^2}{2m} \cdot x^2\right) \cdot \frac{\pi^2 \cdot \hbar^2}{m^2} \cdot x^2 dx. \tag{4.5}$$

(4.2)-(4.5) imply that the thermodynamic limit of the second moment of the velocity operator can be expressed by

$$\lim_{a\to\infty} \text{trace}\left(G(a,\beta)v^2\right) = \frac{I_2(\beta)}{I_1(\beta)} = \frac{1}{m \cdot \beta} \tag{4.6}$$

which is exactly the variance of the Maxwell-Boltzmann velocity distribution of a particle of mass m exposed to a heat bath with the inverse temperature β (cf. (1.2)). We call the equality in (4.6) a compatibility relation between the Maxwell-Boltzmann and the quantum description of a particle.

5. An Alternative Formulation

Let the potential

$$U(x) := \begin{cases} 0 & \text{for } 0 < x < a \\ \infty & \text{elsewhere} \end{cases} \tag{5.1}$$

describe an 1-dimensional box $[0,a]$ where $a > 0$ denotes its width. The Hamiltonian $H : C^2([0,a]) \to L^2([0,a])$ describing a quantum particle of mass m within $[0,a]$ is given by

$$H\psi(x) := -\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2}\psi(x) + U(x) \cdot \psi(x).$$

The functions $\varphi_k : [0,a] \to \mathbb{R}$,

$$\varphi_k(x) = \frac{1}{d_k} \cdot \sin\left(\frac{k\pi}{a} \cdot x\right),$$

(where

$$d_k := \left(\int_0^a \sin^2\left(\frac{k\pi}{a} \cdot x\right) dx\right)^{1/2}$$

denote normalizing constants, $k = 1, 2, \ldots$), constitute an orthonormal Basis $B' = \{\varphi_k | k = 1, 2, \ldots\}$ of $L^2([0, a])$ consisting of eigenfunctions of H satisfying the Dirichlet boundary condition

$$\varphi_k(0) = \varphi_k(a) = 0 \qquad (k = 1, 2, \ldots),$$

which is known from Functional Analysis.

Again, the Gibbs operator

$$G(a, \beta) = \tau(a, \beta)^{-1} \cdot \exp(-\beta \cdot H)$$

has the matrix representation

$$G(a, \beta)_{k,l} = \tau(a, \beta)^{-1} \cdot \exp(-\beta \cdot E_k(a)) \cdot \delta_{kl} \qquad (k, l = 1, 2, \ldots)$$

where

$$\tau(a, \beta) = \mathrm{trace}\,(\exp(-\beta \cdot H)) = \sum_{k=1}^{\infty} \exp\left(-\beta \cdot \frac{\pi^2 \hbar^2 k^2}{2ma^2}\right)$$

and

$$E_k(a) = \frac{\pi^2 \cdot \hbar^2 \cdot k^2}{2m \cdot a^2}$$

denotes the eigenvalue of H associated with the eigenfunction φ_k for $k = 1, 2, \ldots$. Analogously to Section 4 we obtain in the thermodynamic limit:

$$\lim_{a \to \infty} \mathrm{trace}\left(G(a, \beta) v^2\right) = \frac{1}{m\beta}$$

where v denotes the velocity operator defined in (4.1).

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