

THE QUANTUM STATISTICAL MECHANICAL THEORY OF TRANSPORT PROCESSES

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ABSTRACT : *A new derivation of the quantum Boltzmann transport equation for the Fermion system from the quantum time evolution equation for the Wigner distribution function is presented. The method exhibits the origin of the time- irreversibility of the Boltzmann equation. In the present work, the spin dependent and indistinguishability of particles are also considered.*

KEY WORDS : *Boltzmann Equation, Reduced Distribution Function, Wigner Function.*

INTRODUCTION :

Approximately one hundred years ago, *L. Boltzmann* [1] derived his transport equation for dilute gases from physical arguments. The Boltzmann equation is accepted today as a means of providing a completely adequate description of the behaviour of dilute gases. The resulting solutions of the Boltzmann transport equation by the Chapman- Enskog perturbation method [2] involve a set of integrals called "collision integrals", which are used to obtain expressions for the fluxes and the transport coefficients.

Many authors have described methods of deducing the classical Boltzmann equation from the Liouville equation [3-9], and some others proposed the quantum- mechanical Boltzmann equation by using the von Neumann equation [10-12]. In fact, it is well known that the uncertainty principle makes the concept of phase space in quantum mechanics a problematic one. As a result, because a particle can not simultaneously have a well defined position and momentum, the concept of a probability distri-

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bution function which is defined over the phase space of the system can not be defined for a quantum mechanical particle. On the other hand, at low enough temperatures, the de Broglie wave length of the lighter particles, such as H, He and electron gas in a superconductor becomes comparable to that of their interaction range and indistinguishability of particles must be taken into account. In quantum statistical mechanics a density matrix method can be developed and the quantum Boltzmann equation can be obtained from the quantum Liouville equation. However, a quantum Boltzmann equation can be derived in terms of the Wigner representation which will be introduced in the next section.

In this paper, the quantum Boltzmann equation for a dilute quantum gas described by the Wigner reduced distribution function is derived. In the present work, the spin dependence and Pauli principle are considered and the origin of the time irreversibility of the Boltzmann equation is directly exhibited.

The Wigner Distribution Function :

In this section we give a brief review of the Wigner function, which was Proposed by Wigner in 1932 [13]. The Wigner function ρ_w , can be considered as a quantum-mechanical phase space distribution function and it is defined as a Fourier transform of the density matrix ρ :

$$\rho_w(q, p, t) = \left(\frac{1}{\pi \hbar}\right)^{3N} \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \exp(2i p \cdot R / \hbar) \langle q - R | \hat{\rho}(t) | q + R \rangle dR \quad (1)$$

where \hbar is Planck's constant divided by 2π and $\{q, p\}$ are the phase space coordinates of all particles. The matrix element of ρ is defined as :

$$\langle q - R | \hat{\rho}(t) | q + R \rangle = \psi^*(q + R, t) \psi(q - R, t) \quad (2)$$

for a pure state, and as :

$$\langle q - R | \hat{\rho}(t) | q + R \rangle = \sum_{\lambda} \Omega_{\lambda} \psi_{\lambda}^*(q + R, t) \psi_{\lambda}(q - R, t) \quad (3)$$

for a mixed state, where ψ_{λ} is the wave function and W_{λ} is the Probability of the system being in the state ψ_{λ} .

The N- Particle Wigner distribution function is normalized by :

$$\int \rho_w(q, p, t) d\tau = N! \quad (4)$$

where $d\tau = \prod d\tau_i = \prod d^3 q_i d^3 p_i$. Here we introduce S- Particle Wigner functions defined by :

$$\rho_w^{(S)}(q_1 \dots q_S; p_1 \dots p_S, t) = \frac{1}{(N-S)!} \int \rho_w(q, p, t) d\tau_{S+1} \dots d\tau_N \quad (5)$$

where V is the volume of the container. A special case of the Wigner function is the one-particle projection of ρ_w , defined by :

$$\rho_w^{(1)}(q, p, t) = \frac{1}{(N-1)!} \int \rho_w(q, p, t) d\tau_2 \dots d\tau_N \quad (6)$$

The expectation value of an observable $A(q, p)$ becomes :

$$\langle \hat{A} \rangle = \int \int dq dp A(q, p) \rho_w(q, p, t) \quad (7)$$

which is analogous to the classical expression for the average value, where the dynamical function $A(q, p, t)$ is a classical function. In other words, the Wigner function can be used to express quantum mechanical expectation values of observables in a form which is very similar to that of classical averages [14], i.e., by integrating the product of the observable and the Wigner function over the entire phase space.

The time evolution equation for $\rho_w(q, p, t)$ can be obtained by starting the time-dependent Schrodinger equation. It can be shown that the time evolution of ρ_w for N-Particle system is [14]:

$$\partial_t \rho_w = \{H, \rho_w\} - \frac{\hbar^2}{4} \sum_{lmn} \Delta^{-1}(lmn) \frac{\partial^3 V}{\partial q_l \partial q_m \partial q_n} \rho_w + O(\hbar^4) + \dots \quad (8)$$

where H is the N - Particle Hamiltonian, $\{ \dots \}$ denotes a Poisson bracket, V is the potential energy of the system, and $\Delta(lmn) = 1$ if $l \neq m \neq n$, $\Delta(lmn) = 2$ if two indices are equal and $\Delta(lmn) = 3$ if three indices are equal. It is evident that in the limit $\hbar \rightarrow 0$, Eq. (8) reduces to the corresponding Liouville equation, that is :

$$\partial_t \rho_w = \{H, \rho_w\} \quad (9)$$

The \hbar^2 term gives the quantum correction and is considered in this work, but the fourth and higher order terms of \hbar^2 are neglected. From Eq. (8) it is clear that the equation of motion is the same as the classical equation of motion, when the potential function has no third and higher derivatives as, for example, in the case of a force free problem, a uniform field or a system of harmonic oscillators.

Derivation of the Quantum Boltzmann Equation :

For the N - Fermion system, consisting of a dilute spin- polarized gas, the Wigner distribution function must be antisymmetric with respect to the permutation of identical particles. The approximate Wigner function can be defined as :

$$\begin{aligned} \rho_w(s | q, l, t) \\ = \frac{N!}{V^N} \sum_P (-1)^{PP} \{ \phi_{s_1}^{(1)}(1, t) \phi_{s_2}^{(2)}(2, t) \dots \phi_{s_N}^{(N)}(N, t) \} \end{aligned} \quad (10)$$

where V^{-N} is normalization factor, \hat{P} is permutation operator which exchange the indices S_i and $\phi_{s_i}^{(i)}(i, t)$ is the single particle projection of particle j at the phase point (q_i, p_i) , which can be normalized by :

$$\sum_{i=1}^N \int \phi_{s_i}(i, t) d\tau_i = V \quad (11)$$

It can be noticed that the Wigner function includes the description of the correlated behaviour of the quantum mechanical particles

making up the system. However, at a given time, a situation may arise where the particles are statistically uncorrelated. Of course, there was an unrecognized difficulty for particles with intrinsic spin angular momentum, where in such a case there is an intrinsic quantum correlation due to the Pauli principle. In fact, we can say that the uncorrelated assumption included in Eq.(10) fails to be true, because of the existence of identical spin rotation effects and spin-spin interactions. However, in this paper the spin correlation effects are not considered and will be studied later. We may choose the initial condition of Eq. (10) as :

$$\rho_w(s | q, p, \circ) = \frac{N!}{V^N} \sum_P (-1)^P \hat{P} \prod_i \phi_{s_i}(i, \circ) \quad (12)$$

Let us now consider a time interval Δt which is much longer than the duration of one collision, but much shorter than the mean free time of a typical particle between successive collisions. If the gas is sufficiently dilute, the function $\phi(1, \Delta t)$ must be chosen in such a way that Eq. (10) represents the best approximation to the true Wigner function ρ_w at time Δt . This approximation is similar to the famous stochanzahl hypothesis introduced by Boltzmann, which fundamentally postulates the absence of correlations of two particles impinging on each other, that is :

$$\rho_w^{(2)}(1, 2, t) = \rho_w^{(1)}(1, t) \rho_w^{(1)}(2, t) \quad (13)$$

As a result the best function $\phi(i, \Delta t)$ can be chosen in such a way that the single- particle projection of the approximate ρ_w is equal to the one- particle projection of the exact ρ_w at $t = \Delta t$, so that :

$$\begin{aligned} \rho_w^{(1)}(s_1 | q_1, p_1, \Delta t) \\ = \frac{1}{(N-1)!} \sum_{\{s_i\}_{2-N}} \int \frac{N!}{V^N} \sum_P (-1)^P \hat{P} \\ \prod_i \phi_{s_i}(i, \Delta t) d\tau_2 \dots d\tau_N = \frac{N}{V} \phi_{s_1}^{(1)}(1, \Delta t) \end{aligned} \quad (14)$$

In a similar way, the two particle projection can be written as :

$$\rho_w^{(2)}(s_1 s_2 | 1, 2, \Delta t) = \frac{N(N-1)}{V^2} \sum_{\{m_i\}_{2..N}} \int d\tau_3 \dots d\tau_N [\sum_i (-1)^P \hat{P} \phi_{s_1}^{(1)}(1, \Delta t) \dots \phi_{s_N}^{(N)}(N, \Delta t)]$$

$$= \frac{N(N-1)}{V^2} \sum_P (-1)^P \hat{P} [\phi_{s_1}^{(1)}(1, \Delta t) \phi_{s_2}^{(2)}(2, \Delta t) \dots \phi_{s_N}^{(N)}(N, \Delta t)] \quad (15)$$

By making approximations suitable to a dilute gas in the evaluation of (14) and (15), it is possible to deduce a value for the change:

$$\Delta\phi = \phi_{s_i}(i, \Delta t) - \phi_{s_i}(i, \circ) \quad (16)$$

which can then be approximated as :

$$\frac{\partial \rho_w^{(1)}}{\partial t} = \frac{N}{V} \frac{\Delta\phi}{\Delta t} = \frac{N}{V} \cdot \frac{1}{\Delta t} \sum_{\{m_i\}_{2..N}} \int d\tau_2 \dots d\tau_N \left\{ \sum_P (-1)^P \hat{P} [\phi_{s_1}(1) \dots \phi_{s_N}(N)] - \sum_P (-1)^P \hat{P} [\phi_{s_1}(1, \circ) \dots \phi_{s_N}(N, \circ)] \right\} \quad (17)$$

If $\{p'_1, \dots, p'_N, q'_1, \dots, q'_N\}$ and $\{p_1, \dots, p_N, q_1, \dots, q_N\}$ are assumed as the initial configuration at $t = 0$ and final configuration at $t = \Delta t$, respectively, then under the action of the Hamiltonian, H , the Wigner function can be written as:

$$\rho_w(q, p, \Delta t) = \rho_w(q', p', \circ) \quad (18)$$

Therefore :

$$\Delta\phi = \frac{1}{V^{N-1}} \sum_{\{m_i\}_{2..N}} \int d\tau_2 \dots d\tau_N \left\{ \sum_P (-1)^P \hat{P} [\phi_{s_1}(1', \circ) \dots \phi_{s_N}(N', \circ)] - \sum_P (-1)^P \hat{P} [\phi_{s_1}(1, \circ) \dots \phi_{s_N}(N, \circ)] \right\} \quad (19)$$

where $\phi_{s_i}(i', \circ)$ and $\phi_{s_i}(i, \circ)$ are the precollisional and post collisional single-particle distribution functions at $t=0$, respectively. This equation is exact differential, and its evaluation yields the best possible $\Delta\phi$. By using the Liouville theorem, which expresses for an isolated system is expressed as :

$$d\tau_2 \dots d\tau_N = d\tau'_2 \dots d\tau'_N \quad (20)$$

Eq. (19) can be rewritten as :

$$\Delta\phi = \frac{1}{V^{N-1}} \sum_{\{m_i\}_{2..N}} \sum_P (-1)^P \hat{P} [\phi_{s_1}(1', \circ) - \phi_{s_1}(1, \circ)] \int dq_2 dq_3 \dots dq_N \int [\phi_{s_2}(2, \circ) \phi_{s_3}(3, \circ) \dots \phi_{s_N}(N, \circ)] dp_2 dp_3 \dots dp_N \quad (21)$$

The multiple integral over the coordinates may be broken up as follows [9] :

$$\int d^3q_2 d^3q_3 \dots d^3q_N = \int_{V-\Delta V_2} d^3q_2 \int_{V-\Delta V_3} d^3q_3 \dots$$

$$\int_{V-\Delta V_N} d^3q_N + \int_{\Delta V_2} d^3q_2 \int_{V-\Delta V_3} d^3q_3 \dots \int_{V-\Delta V_N} d^3q_N +$$

$$\text{Permutations} + \int_{\Delta V_2} d^3q_2 \int_{\Delta V_3} d^3q_3 \int_{V-\Delta V_4} d^3q_4 \dots$$

$$\int_{V-\Delta V_N} d^3q_N + \text{Permutations} + \text{Configurational Permutations} \quad (22)$$

The first term on the right-hand side gives the contribution of configurations in which none of the particles 2, 3, ..., N collide with particle 1 during the time interval Δt . The second line contains (N-1) terms altogether, and configuration permutation represent (1,3), (1,4), ..., collisions. The third line contains $\frac{1}{4}(N-1)(N-2)$ terms, each representing a ternary collision, and so on.

In a dilute gas, when the ternary and higher-order collisions are neglected, we can write:

$$\Delta\phi \approx \Delta\phi^{(1)} + \Delta\phi^{(2)} \quad (23)$$

where the superscripts represent the order of the collisions involved.

Calculation of $\Delta\phi^{(1)}$ and $\Delta\phi^{(2)}$

Using Eqs. (21), (22) and the definition of $\Delta\phi^{(1)}$, we have :

$$\Delta\phi^{(1)} = \frac{1}{V^{N-1}} [\phi_{s_1}(1', \circ) - \phi_{s_1}(1, \circ)] \prod_{i=2}^N \int dp_i \int_{V-\Delta V_i} dq_i \phi_{s_i}(1, \circ) \quad (24)$$

which is similar to the classical form. A simple calculation yields :

$$\Delta\phi^{(1)} \approx [\phi_{s_1}(1', \circ) - \phi_{s_1}(1, \circ)] \left[1 - \frac{\Delta V}{N} n(q_1)\right]^{N-1} \quad (25)$$

where ΔV is a suitable average of the excluded volume $\Delta V_1(q_1, p_1, p_1)$ over the momenta p_i and $n(q_1)$ in the number density, i.e.,

$$n(q_1) = \frac{N}{V} \int dp_1 \phi(1, \circ) \quad (26)$$

Using the identity :

$$\lim_{N \rightarrow \infty} \left(1 - \frac{Q}{N}\right)^N = \exp(-Q) \quad (27)$$

and assuming the particle 1 does not collide during time t , i.e.,

$$r'_1 = r_1 - \frac{\Delta t}{m} p_1, \quad p'_1 = p_1 \quad (28)$$

Eq. (25) becomes :

$$\frac{\Delta\phi^{(1)}(1, t)}{\Delta t} = -\frac{p_1}{m} \cdot \nabla\phi(1, \circ) \quad (29)$$

Let us now evaluate $\Delta\phi^{(2)}$, the contribution of binary collisions of particle 1 with one other particle. This contribution consists of $(N-1)$ terms. Straight forward combination of Eq. (19) with (22) gives :

$$\Delta\phi^{(2)} = \frac{N-1}{V} \sum_{s_2} \int_{\Delta V_2} \{ |\phi(1', \circ) \phi(2', \circ)| - |\phi(1, \circ) \phi(2, \circ)| \} d\tau_2 \quad (30)$$

where $|\dots|$ denotes a determinant. Substitution of Eqs. (29), (30), (14) into (17) then gives the result :

$$\frac{\partial\rho_w^{(1)}}{\partial t} = \{H_1, \rho_w^{(1)}\} + J_c(|\rho_w^{(1)}|, |\rho_w^{(1)}|) \quad (31)$$

where H_1 is the one particle Hamiltonian and :

$$J_c(|\rho_w^{(1)}|, |\rho_w^{(1)}|) = \frac{V}{N} \cdot \frac{1}{\Delta t} \sum_{s_2} \int_{\Delta V_2} \{ |\rho_w^{(1)}(s|1') \rho_w^{(1)}(s|2')| - |\rho_w^{(1)}(s|1) \rho_w^{(1)}(s|2)| \} d\tau_2 \quad (32)$$

Eq. (31) is the famous Boltzmann equation for spin dependent Wigner distribution functions. The first term on the right hand side of Eq. (31) is a drift term and the second term is a collision term, which describes the effect of binary collisions.

It can be understood that the origin of the time-irreversibility of the Boltzmann equation is related to the replacement of the exact N -Particle Wigner function by approximate form (10), since the information about the state of the system at $t=\Delta t$ may be lost.

Finally, an attempt is made to explain, the quantum correction due to the wave property of particles on the Boltzmann transport equation. By taking the integration of Eq. (8) over all particles but one, and considering the evaluation of Eq. (31), we obtain :

$$\begin{aligned} \partial_t \rho_w^{(1)} = & \{H_1, \rho_w^{(1)}\} + J_c(|\rho_w^{(1)}|, |\rho_w^{(1)}|) - \frac{\hbar^2}{4V} \\ & \sum_{lmn} \Delta^{-1}(lmn) \int \frac{\partial\rho_w^{(1)}(l)}{\partial p_l} \frac{\partial\rho_w^{(1)}(m)}{\partial p_m} \frac{\partial\rho_w^{(1)}(n)}{\partial p_n} \\ & \prod_{j=1}^N \rho_w^{(1)}(\partial) \frac{\partial^3 V}{\partial q_1 \partial q_m \partial q_n} d\tau_2 \dots d\tau_N + O(\hbar^4) + \dots \end{aligned} \quad (33)$$

This equation is the quantum Boltzmann equation for a fermion system. The first term on the right-hand side represents the change in $\rho_w^{(1)}$ due to the collisionless motion of the molecules, called a drift term. The second term represents the change of $\rho_w^{(1)}$ due to the binary collisions, and the third term is the first-order quantum correction term. The fourth and other terms are the higher-order quantum correction terms, which is usually neglected.

CONCLUSIONS :

A quantum Boltzmann equation for the spin-polarized system has been derived for the Wigner distribution function for a dilute quantum gas without internal states. This is Eq. (33). This equation reduces to the classical form at high temperatures for spin independent particles. At low enough temperatures, the term \hbar^2 in Eq. (33) must be taken into account and

the Pauli principle must be considered. The present method directly exhibits the origin of time irreversibility of the Boltzmann equation. It is shown that the time- irreversibility may be related to the replacement of the exact Wigner function by an approximate function [10].

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