Non-equilibrium ensemble method: A quantum-statistical-mechanical approach

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Received 11 February 2005; revised 27 June 2005; accepted 28 June 2005

The non-equilibrium ensembles method has been applied to Boltzmann quantum-kinetic equation. We used the quantum-kinetic equation governing the density matrix, which has been proposed by Ogul and Eren, J Chem Phys, 105 (1996) 7664. The non-equilibrium quantum-mechanical ensemble can be constructed in terms of non-equilibrium entropy, Boltzmann entropy, constrained by the quantum Boltzmann equation as a dynamical equation of motion, which has governed the time evolution of non-equilibrium density matrix. The quantum-mechanically non-equilibrium partition function has been obtained. The conjuncture with the traditional irreversible thermodynamics has been shown.

Keywords: Non-equilibrium ensemble, Non-equilibrium statistical mechanics, Non-equilibrium partition function, Non-equilibrium entropy, Time-integrated entropy, Quantum-kinetic equation

IPC Code: G06

1 Introduction

Mechanics provides a complete macroscopic description of the state of a system. When the equations of motion are combined with initial conditions and boundary conditions, the subsequent time evolution of a classical system can be predicted. Thermodynamics provides a theoretical framework for correlating the equilibrium properties of any system. If the system is not at equilibrium, fluid mechanics is capable of predicting the microscopic non-equilibrium behaviour of system. In order for these microscopic approaches to be useful their laws must be supplemented not only with a specification of appropriate boundary conditions but also with values of thermophysical constants such as equation of state and transport coefficients. These values cannot be predicted by macroscopic theory. Historically, this data has been supplied by experiments. One of the tasks of statistical mechanics is to predict these parameters from knowledge of interactions of the system's constituent molecules. This is a major purpose for statistical mechanics. Hence, properties of gases and liquids are divided into two categories: the equilibrium properties (such as equation of state, Joule-Thomson coefficient, and surface tension, etc.) and non-equilibrium properties (such as viscosity, diffusion, and thermal diffusion factor, etc.). Expression for all these bulk properties in terms of molecular properties and intermolecular forces can be obtained from statistical mechanics. These expressions, along with information about intermolecular interactions, may be used to predict the values of many physical properties for which no experimental data are available. A particularly useful result of the statistical mechanical approach is the fact that equilibrium and non-equilibrium thermodynamics can be constructed through the common link of the microscopic viewpoint (i.e. equilibrium/non-equilibrium statistical mechanics).

Equilibrium classical-statistical mechanics is relatively well developed. In the other word, equilibrium ensembles theory is, traditionally, developed from the Gibbs-Tolman principle of equal probability for the microstates of isolated systems. The basic ground rules-Gibbsian ensemble theory have been known for the best part of the previous century. The non-equilibrium statistical mechanics of dilute gases—kinetic theory—is likewise, essentially complete. The establishment of the microscopic foundation of the thermodynamics of irreversible
phenomena\textsuperscript{20} (\equiv non-equilibrium thermodynamics) is a central problem of non-equilibrium statistical mechanics\textsuperscript{17}. The statistical mechanics of Maxwell and Boltzmann is for dynamical processes in dilute monoatomic gases and is based on the evolution equation-kinetic equation for the singlet distribution function\textsuperscript{22}. Starting from the basic idea of Maxwell and Boltzmann on statistical treatment of systems of many particles, J W Gibbs synthesized a general formal theory of statistical mechanics, at least, for equilibrium phenomena\textsuperscript{18}. The molecular theory of irreversible processes, namely non-equilibrium statistical thermodynamics received conspicuous interest from scientists. There are several approaches to molecular aspects of irreversible process, which we include here not in the chronological order of their developments: (i) Correlation Function Formalism\textsuperscript{23,26} (CF); (ii) Stochastic Theory\textsuperscript{27-33}; (iii) Non-equilibrium Statistical Operator Method\textsuperscript{34} (NESO) or Non-equilibrium ensemble method\textsuperscript{35-39}; (iv) Linear/Nonlinear response theory\textsuperscript{40-41}; (v) Green-Kubo Formulas for the Transport Coefficients\textsuperscript{42}; (vi) Calculation of (Generalized) transport coefficients\textsuperscript{43,44}; (vii) Master equation Formulation\textsuperscript{45-47}; (vii) Projection Operator\textsuperscript{48}; and (viii) Regression or attenuation of fluctuation\textsuperscript{49,50}.

It should also be mentioned that the latest approach is applicable only for classical system (i.e. there is no quantum regression\textsuperscript{44}). Hence, the theoretical formulation of non-equilibrium ensemble, based on the quantum Boltzmann equation is simple in concept, namely, the description of the time dependence of the distribution of molecular states caused by collisions and the free motion between collisions, but quantum version has a number of complex technical aspects that are important for our method. However, towards the eventual goal of a fundamental and unambiguous molecular description of the irreversible processes in quantum systems, the objective of the present work is the understanding that the extension of our previous paper on classical system\textsuperscript{39} (hereafter referred to as paper I) to quantum cases appears to be intuitively reasonable. Therefore, a great deal work was done by the authors for this extension.

On the other hand, the thermodynamic theory of irreversible processes can be formulated based on the Boltzmann kinetic theory because the collision term in the Boltzmann equation satisfies a set of conditions: (i) existence of collision invariants; (ii) satisfaction of the H theorem; and (iii) invariance under canonical transformations (i.e. any transformation with the Jacobian of transformation equal to unity). The first condition guarantees the existence of the conservation laws of mass, momentum, and internal energy, whereas the second furnishes the Boltzmann entropy and its balance equation which has a positive source term namely, the H theorem.

The third condition is necessary for analytical dynamic purposes\textsuperscript{52,53}. A non-equilibrium system can be modeled as an analogue of equilibrium ensemble. A major theme of this paper is the development of a non-equilibrium system which can play the same role in non-equilibrium statistical mechanics as the Gibbsian ensembles play at equilibrium\textsuperscript{17,18}.

2 Methodology

It is possible to derive non-equilibrium distribution functions from entropy principle and Liouville’s equation\textsuperscript{37} or Boltzmann’s equation as a constraint\textsuperscript{39}.

Zubarev\textsuperscript{34} has actually pioneered in this direction. In implementing dynamics, however, he has used the three conservation laws of mass, momentum and energy, rather than the full Liouville equation. He has extremalized entropy constrained by the Fourier transform of the conservation laws of energy, momentum, and particle numbers. Since the conservation of these fundamental quantities is a consequence of the Liouville’s equation, Zubarev’s approach\textsuperscript{34} does indeed take into account a good deal of the dynamics of the problem, but not all of it. Even so, the closed form of the conservation equations is, in general, based on certain simplifying assumptions. In Zubarev’s formulation, one assumes the existence of Bogolioubov’s hierarchy of relaxation times of different orders of magnitude. MacLennan’s\textsuperscript{36} distributions are identical to those of Zubrev. His approach, however, is to consider systems in contact with an external bath and assume an entropy flow into the system characterized by a temperature field, a mass flow, etc. Eventually, Sobouti\textsuperscript{37} has proposed to consider the time integrated entropy as an action for time varying ensembles. His formulation of non-equilibrium statistical mechanics then becomes a variational formulation of non-equilibrium problem (i.e. Lagrangian formalism), common to most branches of physics\textsuperscript{54-57}. Dynamics is accounted for by using Liouville’s equation as a constraint in extremalizing the action integral. Clear distinction should be made between his maximization of entropy...
(i.e. Gibbs entropy) and the actual irreversible process in the course of time. Irreversibility and along with the time increase of the entropy, its additive property and transport phenomena could be incorporated into the formalism by replacing the Liouville's equation with Boltzmann's equation. Actually, the quantum version of the previous formalism, as mentioned in paper I, is doing by the use of time irreversible quantum Boltzmann's equation.

3 Boltzmann Equation: Quantum-Mechanical Version
In the literature, one may discern an increasing interest in the use of distribution functions in physics and quantum mechanics in phase space. There are also various studies based on the quantum generalization of classical Boltzmann's equation is well known, the six-dimensional phase space of the position and momentum coordinates, for one particle, cannot be used in quantum mechanics and forbids states with simultaneously definite coordinates and momentum in respect to Heisenberg uncertainty principle. The first quasi-probability distribution function to study quantum corrections to classical statistical mechanics was introduced by Wigner. However the Wigner function can be negative in some regions of phase space that prevents it from being interpreted as a probability density, which must be everywhere positive. So far, various works have been carried out to find alternative ways (to Wigner's) of expressing quantum wave functions or quantum operators in phase space. All the resulting wave functions and their phase-space Schroedinger equations governing the time evolution of these wave functions are equivalent to the quantum mechanical Liouville-von Neumann equation for the Wigner distribution function. Anyhow, the Ogul and Eren’s paper is intended to introduce an intuitive picture of complex non-equilibrium processes of the quantum states rather than propose a quantum correction. Ogul and Eren have considered density matrix representation. They have started from the Liouville-von Neumann equation of density matrices and derived a manifold of hierarchical equations in terms of density matrices. In their approach, the kinetic equation for one-particle density matrix is as follows:

\[ i\hbar \frac{\partial \rho^{(1)}}{\partial t} = \{K_1, \rho^{(1)}\} + Tr_{(2)}[V_{12}, \rho^{(2)}_{1,2}] \quad \ldots (1) \]

where \( K_1 \) is the one-particle kinetic energy operator, \( V_{12} \) the two-particle interaction, \( \rho^{(1)}_1 \) and \( \rho^{(1,2)}_{1,2} \) are one-particle and two-particle density operators, respectively. Here, the braces mean the commutation symbol. The physical interpretation of Eq. (1) is that time derivative of \( i\hbar \rho^{(1)}_1 \) is the sum of a flux term given by \([K_1, \rho^{(1)}_1]\) and a collision term expressed in terms of two particle interaction and two particle density matrix. In order to solve Eq. (1), one should express the two-particle density matrix \( \rho^{(2)}_{1,2} \) in terms of the one-particle density matrices, i.e. the following Stosszahlansatz, same as the chaotic assumption assumed by the Boltzmann in the classical kinetic theory

\[ \rho^{(2)}_{1,2} = \rho^{(1)}_1 \rho^{(1)}_2 A_{12} \quad \ldots (2) \]

with \( A_{12} = 1 - P_{12} \), where \( A_{12} \) is the antisymmetrization operator (in the case of fermions), \( P_{12} \) is the permutation operator. By substituting Eq. (2) in Eq. (1), one gets a time evolution for the one-particle density matrix as follows:

\[ i\hbar \frac{\partial \rho^{(1)}_1}{\partial t} = [K_1 + U_1, \rho^{(1)}_1] \quad \ldots (3) \]

where \( U_1 \) is the mean field which has the form

\[ U_1 = Tr_{(2)}V_{12}\rho^{(1)}_2 A_{12} \quad \ldots (4) \]

4 Entropy and Irreversibility of the Transport Equation
The concept of entropy originated in the nineteenth century, with applications in the field of statistical mechanics and thermodynamics. The information theory is usually considered as a creation of Shannon. During the last fifty years or so, a number of research papers, and monographs discussing and extending Shannon's original work have appeared.

On the other hand, the adequate generalization standard concept of entropy has engaged the attention of researchers in the field of statistical mechanics. The dynamical aspects of Tsallis entropy has been discussed via maximum entropy principles by Plastino and Plastino. The maximization of entropy subjects to a certain constraints has an important role in physics.
The nature of irreversibility and its connection with entropy is a challenging matter from introductory subject\textsuperscript{58} to higher topics of the physics\textsuperscript{59,74-76} and historical point of view\textsuperscript{59}. Meanwhile, equations of motions\textsuperscript{77} and its irreversibility interpretation\textsuperscript{78-83} in statistical mechanics have received conspicuous attention.

5 Non-Equilibrium Ensemble Method: An Quantum-Statistical-Mechanical Approach

The Boltzmann H-function is defined as:

\[ H(t) \equiv \text{Tr}(\rho^{(i)} \ln \rho^{(i)}) \]  \hspace{1cm} (5)

Eq. (5) gives the Boltzmann entropy if multiplied by \(-k_B\), viz:

\[ S_B(t) = -k_B \{ \text{Tr}(\rho^{(i)} \ln \rho^{(i)}) \} \]  \hspace{1cm} (6)

The concepts and procedures presented here are closely parallel to conventional Lagrangian formulations of paper I. In a time interval \((t_1, t_2)\) define the time-integrated entropy as follows:

\[ \mathcal{R}_B(t) = -k_B \int_{t_1}^{t_2} \text{Tr}(\rho^{(i)} \ln \rho^{(i)}) dt \]  \hspace{1cm} (7)

This time integration is a mathematical provision only. To find a density matrix one should maximize Eq. (7) constrained by Eq. (3) and the following equation:

\[ \rho^{(1)}_1 = N!U(N-1)!\text{Tr}(2,3,\ldots,N)\rho^{(N)}(1,2,3,\ldots,N) \]  \hspace{1cm} (8)

where \(\rho^{(1)}_1\) and \(\rho^{(N)}\) are one-particle and N-particle density operators, respectively.

With the terminology of calculus of variation\textsuperscript{54-55}, one now adds Eqs (3), (7) and (8), to form a constrained action\textsuperscript{72,84}, \(\Psi\) integral; viz:

\[ \Psi = \int_{t_1}^{t_2} \text{Tr}\Phi(t) dt \]  \hspace{1cm} (9)

where

\[ \Phi(t) = -k_B \rho^{(i)} \ln \rho^{(i)} + \beta(\rho^{(i)}_1, t) i\text{d}\rho^{(i)} / \text{d}t + [\rho^{(i)}_1, K_1 + U_1] + \alpha(t) \{ \rho^{(i)}_1 - N\text{Tr}(2,\ldots,N)\rho^{(N)}(1,2,\ldots,N) \} \]  \hspace{1cm} (10)

and \(\alpha(t)\) and \(\beta(\rho^{(i)}_1, t)\) are Lagrange multipliers. Using the Euler-Lagrange equation,

\[ \partial \Phi / \partial \rho^{(i)}_1 - d / dt(\partial \Phi / \partial \dot{\rho}^{(i)}_1) = 0 \]  \hspace{1cm} (11)

and by careful reduction of the aforesaid equation and finding the \(\dot{g}\)th element of the following equation:

\[ \Theta(\alpha(t) - k_B - k_B \ln \rho^{(i)}_1 - i\dot{\Theta}^{-1} d\beta(\rho^{(i)}_1, t) / dt + \Theta^{-1} \beta(\rho^{(i)}_1, t)([\Theta, (K_1 + \xi \Theta A_{12})] + [\Omega, \xi \Lambda A_{12}]) - \Theta \alpha(t) = 0 \]  \hspace{1cm} (12)

where \(\Theta = N\text{Tr}(2,\ldots,N)\rho_1, \xi = N\text{Tr}(2)V_{12}, \Theta = N\text{Tr}(1,\ldots,N)\rho^{(N)}, \Omega = N\text{Tr}(2,\ldots,N)\rho^{(N)}, \Lambda = N\text{Tr}(2,\ldots,N)\rho_1\) and \(\Theta_1 = |i\rangle \langle j|\). It should also be mentioned that the other symbols have their usual meaning as defined before. For the sake of brevity let:

\[ \alpha(t) - k_B \equiv k_B \ln q_{ne}(t) \]  \hspace{1cm} (13)

\[ -i\dot{d}\beta(\rho^{(i)}_1, t) / dt + \beta(\rho^{(i)}_1, t)([\Theta, (K_1 + \xi \Theta A_{12})] + [\Omega, \xi \Lambda A_{12}]) - \Theta \alpha(t) \equiv \mathcal{H}(\rho^{(i)}_1, t) \]  \hspace{1cm} (14)

By introducing the aforesaid definitions Eq. (12) becomes

\[ k_B \ln \rho^{(i)}_1 - k_B \ln q_{ne} - \mathcal{H}(\rho^{(i)}_1, t) / T = 0 \]  \hspace{1cm} (15)

Then, non-equilibrium partition function \(q_{ne}\) is defined as

\[ q_{ne} = \text{Tr}\{\exp(-\mathcal{H}(\rho^{(i)}_1, t) / k_B T)\} \]  \hspace{1cm} (16)

Rearranging of Eq. (15) gives

\[ \rho^{(i)}_1 = q_{ne}^{-1} \exp(-\mathcal{H}(\rho^{(i)}_1, t) / k_B T) \]  \hspace{1cm} (17)

6 Conjunction with Irreversible Thermodynamics

Based upon irreversible thermodynamics terminology, we have considered the well-known balance equation for entropy as follows\textsuperscript{85-87}:

\[ \rho dS / dt = -\nabla.J_S + \sigma_S \]  \hspace{1cm} (18)

Eq. (18) has the flux term, \(J_S\), and entropy production term \(\sigma_S\). First, by differentiating Eq. (6) with respect
to time, second, using hydrodynamic (≡ barycentric, material, or substantial) derivative of entropy, third insertion of Eq. (17) in it and finally, comparing with the Eq. (18), one can find the following relation:

$$S_B = \rho \nabla \rho + \sqrt{\rho} \nabla \frac{\rho}{\sqrt{\rho}} \ldots (19)$$

$$\sigma_s = -i\rho \{k_B \text{Tr} \left[ (ih/2m) \nabla \rho_i^{(1)} + [\nabla, \rho_i^{(1)}] \right] \} \ldots (20)$$

where $\rho = \rho(r,t)$ is density and the other symbols have their usual meanings.

7 Results and Discussion

It is proposed to consider the entropy as a function which has been maximized under constraints $L_2-L_3$. Hence, the present formulation of non-equilibrium statistical mechanics then becomes a Lagrangian formalism. Dynamics is accounted for by using quantum version of Boltzmann kinetic equation as a constraint extremizing the time integrated entropy. There is no distinction between this maximization of the entropy and its increase in actual irreversible processes in course of time. Irreversibility has been considered in the present paper. Alternatively, irreversibility, along with the time increase of the entropy and the transport phenomena which have been considered here, could be alternatively incorporated in the formalism in a number of way: by introducing non-conservative terms in the time reversal equation such as Liouville's equation or application of BBGKY hierarchy, by replacing the other alternatives of dynamical equations such as Fokker-Planck or master equation type, by letting the system in contact with external reservoirs, by coarse-graining the distributions in time or space. These aspects would be the scope of future work.

8 Conclusion

In the paper I, we presented the basics of the classical non-equilibrium ensemble theory in order to be able to derive the macroscopic quantity of non-equilibrium thermodynamics starting from an N-body system satisfying classical Boltzmann equation. Such derivation is certainly satisfactory for gases at high enough temperatures and low enough densities where the details of particle statistics and the exact nature of particle dynamics do not play a decisive role. If statistics and dynamics, however, are important, a satisfactory derivation of macroscopic balance equations has to start from the quantum mechanical N-body problem such as the case which has been considered here. Since, the quantum mechanics is a richer dynamical theory than classical mechanics, then the basis of present approach is quite sound and the method is rigorous. Hence, we have considered the statistical ensemble formalism which provides microscopic (quantum mechanical) foundations to the thermodynamics of irreversible processes. By combining the theory of irreversible thermodynamics and the results of the quantum description of kinetic theory of irreversible processes, i.e. quantum Boltzmann equation, for a dilute gas, a non-equilibrium ensemble method has been formulated for dilute quantum gases as parallel extension to the Gibbs ensemble method in equilibrium statistical mechanics. This method is distinct from those of McLennan, Zubarev and Sobouti. The main distinguishing feature is, the use of an irreversible kinetic equation (i.e., the quantum Boltzmann-kinetic equation) instead of the time reversal invariant Liouville equation (ref. 89-90). In the present work, the microscopic derivation of the entropy flux and entropy production have been demonstrated.

Acknowledgement

Authors would like to thank the University authorities for partly providing the necessary facilities to carry out the work. The authors feel indebted to Prof A Maghari for his stimulating suggestions and comments, important criticisms, skillful technical assistance, useful discussions and sharing of information. Also, we would like to acknowledge helpful conversations with Prof Y Sobouti.

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