Non-equilibrium statistical thermodynamics perturbation theory: A new approach to Maxwell molecules

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A new non-equilibrium statistical thermodynamics perturbation theory was developed which could be applied in parallel to equilibrium statistical thermodynamics perturbation theory. The present method is based on the reminiscent of Boltzmann H-theorem. The concept of the non-equilibrium statistical thermodynamics perturbation theory formalism to the non-equilibrium ensembles method has been embodied and utilized. The acquired equation can be used for molecules in fluid state to estimate the non-equilibrium internal energy in terms of non-equilibrium internal energy of the reference fluid. With grossly simplifying methodology, a closed-form equation has been deduced for the Maxwell molecules as the reference fluid for which the used pair interaction potential is proportional to the inverse power of the fourth order of separation distance.

Keywords: Non-equilibrium ensemble, Perturbation theory, Non-equilibrium statistical mechanics, Non-equilibrium partition function, Maxwell molecules

1 Introduction

Thermodynamics provides a theoretical framework for calculating the equilibrium properties of any system. If the system is not at equilibrium, kinetic theory 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 thermo physical constants such as equation of state data and transport coefficients. These values cannot be predicted by microscopic theory. Historically, this data has been supplied by experiments.

Moreover, the kinetic-thermodynamics theory of irreversible processes, non-equilibrium statistical thermodynamics, 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 present work is in continuation of previous studies on the non-equilibrium ensemble method. The non-equilibrium statistical thermodynamics perturbation theory which can play the same role in non-equilibrium statistical thermodynamics as thermodynamics perturbation theory is undertaken on equilibrium.

Later, the non-equilibrium ensemble method was probed and finally, the non-equilibrium statistical thermodynamics perturbation approach was introduced. Then, we applied our method to Maxwell molecules in the present paper.

2 Non-Equilibrium Ensemble Method

A macroscopic theory of thermodynamics, either reversible or irreversible, is useful for a large class of physical problems we encounter in natural phenomena, in general. The postulational formulation of thermodynamics has been developed by Herbert B Callen. Henceforth, the thermodynamics of reversible processes had found the sound, rigorous and well-established basis. Equilibrium thermodynamics is an axiomatic formal theory of macroscopic reversible processes which give a theoretical framework for relating diverse observable macroscopic properties to each other in a rigorous manner consistent with the laws of thermodynamics.
Moreover, a newly emerging field of irreversible thermodynamics was introduced in a manner consistent with the laws of thermodynamics\textsuperscript{24,25}. There are several approaches to molecular aspects of irreversible process\textsuperscript{24,25}. One of them is non-equilibrium statistical ensemble method\textsuperscript{11,12,16,17,26,27}. The Gibbsian ensemble theory provides molecular picture of systems consisting of an astronomically large number of constituent particles in a manner consistent with equilibrium thermodynamics\textsuperscript{27}. The aforesaid approaches are pivotal for developing the physically-based thermodynamics perturbation theory in the non-equilibrium statistical thermodynamics.

3 Non-equilibrium Statistical Thermodynamic Perturbation Theory: A General Case Study of Maxwell’s Molecules

Perturbation theory relates the properties of a real fluid described by the intermolecular potential $\phi$ to those of some reference fluid where the potential energy is $\phi_0$. For anisotropic fluids, the intermolecular potential depends on the molecular separations $r_{ij}$ as well as the relative orientations $\omega_i$, $\omega_j$, where the $\omega_i$, $\omega_j$ are the Euler’s angles. Henceforth, it is plausible to split a pair interaction potential between two anisotropic molecules as follows\textsuperscript{28}:

\[ \phi = \varepsilon_0 \phi_0 (r_{ij} / \sigma) + \lambda \delta \phi_i (r_{ij} / \sigma, \omega_i, \omega_j) \]  

... (1)

where $\phi_0$ is the isotropic part of the potential, $\lambda$ is a perturbation parameter, $\sigma$ the potential separation parameter, $\phi_i$ the anisotropic part of the potential, $\varepsilon_0$ and $\delta$ are the potential strength parameters of $\phi_0$ and $\phi$, respectively. Most thermodynamics perturbation treatments to study the properties of anisotropic fluids are based on use of a spherically symmetric reference potential. The most common choice for defining the reference potential is that of Pople\textsuperscript{28}:

\[ \phi_{ij} = \langle \phi (r_{ij} / \sigma, \omega_i, \omega_j) \rangle_{\omega_i, \omega_j} \]  

... (2)

where $\langle \rangle$ is the un-weighted angle-averaged.

So, there remains the problem of determining the non-equilibrium internal energy according to the non-equilibrium statistical ensemble approach in conjunction with the non-equilibrium partition function. The non-equilibrium ensemble method\textsuperscript{11,12,16,17,26} provides well-developed procedures for the purpose. Using these formulations, the deduced equation for non-equilibrium internal energy calculations will be\textsuperscript{11}:

\[ U^{(ne)} = q^{(1)}_{an} \int e^{-\beta G} \left( \frac{P_i^2}{2m} + \phi \right) d\Gamma = \int \left( \frac{P_i^2}{2m} + \phi \right) f^{(1)}_{ne} d\Gamma \]  

... (3)

where $q_{an}$ is the non-equilibrium partition function, $f^{(1)}_{ne} = e^{-\beta G} / q_{ne}$ is the non-equilibrium one-particle distribution function, $P_i^2/2m$ is the one-particle’s kinetic energy and $d\Gamma$ is the element of phase space volume.

Furthermore, one can study the non-equilibrium one-particle distribution function according to Mo and Starling (MS) approach\textsuperscript{29}:

\[ f^{(1)}_{ne} = f^{(1)}_{ne} (\text{ref}) - \frac{\lambda}{kT} \sum_{ij} \delta \phi_i f^{(1)}_{ne} (\text{ref}) \]  

\[ + \frac{\lambda^2 \delta^2}{2(kT)^2} f^{(1)}_{ne} (\text{ref}) \left( \sum_{ij} \phi_i \right)^2 + ... \]  

... (4)

By inserting Eq. (4) in Eq. (3), one obtains:

\[ U^{(ne)} = \int \left( \frac{P_i^2}{2m} + \phi \right) f^{(1)}_{ne} (\text{ref}) d\Gamma - \frac{\lambda}{kT} \int \left( \frac{P_i^2}{2m} + \phi \right) f^{(1)}_{ne} (\text{ref}) d\Gamma + ... \]  

... (5)

Now, we insert Eq. (1) in Eq. (5), we get:

\[ U^{(ne)} = \int \left( \frac{P_i^2}{2m} + \varepsilon_0 \phi_0 + \lambda \delta \phi_i \right) f^{(1)}_{ne} (\text{ref}) d\Gamma \]  

\[ - \frac{\lambda}{kT} \int \left( \frac{P_i^2}{2m} + \varepsilon_0 \phi_0 + \lambda \delta \phi_i \right) \delta \phi_i f^{(1)}_{ne} (\text{ref}) d\Gamma + ... \]  

... (6)

Rearrangement of the latest equation gives:

\[ U^{(ne)} = U^{(ne)}_{\text{ref}} + \lambda \delta \int \phi_i \left( 1 - \frac{U^{(ne)}_{\text{ref}}}{kT} \right) f^{(1)}_{ne} (\text{ref}) d\Gamma \]  

\[ - \frac{\lambda^2}{kT} \int (\delta \phi_i)^2 f^{(1)}_{ne} (\text{ref}) d\Gamma + ... \]  

... (7)

where

\[ U^{(ne)}_{\text{ref}} = \int \left( \frac{P_i^2}{2m} + \varepsilon_0 \phi_0 \right) f^{(1)}_{ne} (\text{ref}) d\Gamma \]  

... (8)

Henceforth, it is led to believe that:

\[ U^{(ne)} = U^{(ne)}_{\text{ref}} + \lambda \delta \int \phi_i \left( 1 - \frac{U^{(ne)}_{\text{ref}}}{kT} \right) f^{(1)}_{ne} (\text{ref}) d\Gamma \]  

... (9)
Up to so far, our proposed method is found to be exact. As it is necessary to do some modifications, we implemented Zanette and Garibotti (ZG) approach\textsuperscript{30} for Maxwell molecules\textsuperscript{31} ($\phi \propto r^{-4}$) to manipulate Eq. (9) in order to acquire appropriate equation deems to our propose. Regarding to ZG approach:

$$f_{ne}(t, v) = F(\varepsilon, t) \quad \text{\ldots (10)}$$

A non-equilibrium one-particle distribution function is obtained which is as follows\textsuperscript{30}:

$$F(\varepsilon, t) = F_0(\varepsilon) [1 + R(\varepsilon, t)] \quad \text{\ldots (11)}$$

where $F_0(\varepsilon)$ is defined as:

$$F_0(\varepsilon) = e^{\varepsilon} / \Gamma(\nu) \quad \text{\ldots (12)}$$

wherein $\Gamma(\nu)$ is the gamma function\textsuperscript{32}:

$$\Gamma(z) = (z-1)! = \int_0^\infty e^{-t}(z-1) dt \quad \text{\ldots (13)}$$

On the other hand, they used the superposition of the associated Laguerre polynomials of energy, $L_{n-1}^{\nu-1}(\varepsilon)$

$$R(\varepsilon, t) = \sum_{n=2}^{\infty} a_n(t) L_{n-1}^{\nu-1}(\varepsilon) \quad \text{\ldots (14)}$$

Meanwhile, they showed that the energy representation of the non-equilibrium one-particle distribution function is:

$$F(\varepsilon, t) = F_0(\varepsilon) \left[ 1 + \sum_{n=2}^{\infty} a_n(t) L_{n-1}^{\nu-1}(\varepsilon) \right] \quad \text{\ldots (15)}$$

By applying the energy representation of the non-equilibrium one-particle distribution function in the Eq (7), one can obtain:

$$U_{ne}^{(ne)} = U_{ref}^{ne} + \lambda \delta \int \phi_1 \left( 1 - \frac{U_{ref}^{ne}}{kT} \right)$$

$$\times \left\{ F_0(\varepsilon) \left[ 1 + \sum_{n=2}^{\infty} a_n(t) L_{n-1}^{\nu-1}(\varepsilon) \right] \right\} d\Gamma \quad \text{\ldots (16)}$$

According to the ZG approach, the relation among the coefficients of the recursion relations\textsuperscript{30} will be:

$$a_2(t) = a_2(0) \exp \left( -\frac{t}{3} \right) \quad \text{\ldots (17)}$$

$$a_n(t) = 0, n \geq 3 \quad \text{\ldots (18)}$$

Henceforth

$$U_{ne} = U_{ref}^{ne} + \lambda \delta \int \phi_1 \left( 1 - \frac{U_{ref}^{ne}}{kT} \right)$$

$$\times \left\{ F_0(\varepsilon) \left[ 1 + a_2(t) L_2^1(\varepsilon) \right] \right\} d\Gamma \quad \text{\ldots (19)}$$

where $L_2^1(\varepsilon)$ is the associated Laguerre polynomials of these coefficients.

The general form of the Laguerre polynomials\textsuperscript{32} is:

$$L_n^\nu(x) = \frac{1}{n!} e^x x^{-k} \frac{d^n}{dx^n} (e^{-x} x^{\nu k}) \quad \text{\ldots (20)}$$

By using the aforesaid compact form of the associated Laguerre polynomials and by integrating the momentum space coordinates, we have:

$$U_{ne} = U_{ref}^{ne} + \lambda \delta \int \phi_1 \left( 1 - \frac{U_{ref}^{ne}}{kT} \right) d\tilde{q}$$

$$\times \left\{ \sqrt{\frac{2}{m}} \lambda \delta \int \phi_1 \left( 1 - \frac{U_{ref}^{ne}}{kT} \right) d\tilde{q} \right\} \quad \text{\ldots (21)}$$

where $q$ is the position space coordinates of tagged particle.

For the sake of simplicity, we can write:

$$\left\{ 1 - \frac{U_{ref}^{ne}}{kT} \right\}_{\phi_1} \equiv \int \phi_1 \left( 1 - \frac{U_{ref}^{ne}}{kT} \right) d\tilde{q} \quad \text{\ldots (22)}$$

The final result is:

$$U_{ne} = U_{ref}^{ne} + \frac{16 - a_2(0) \exp \left( -\frac{t}{3} \right)}{16\Gamma \left( \frac{3}{2} \right)} \times \sqrt{\frac{2}{m}} \lambda \delta \left\{ 1 - \frac{U_{ref}^{ne}}{kT} \right\}_{\phi_1} \quad \text{\ldots (23)}$$
4 Results and Discussion

Now-a-days, the problem of deriving an analytical expression for non-equilibrium properties of fluids has been remained as an important problem in the field of non-equilibrium thermodynamics. With the admission of decomposition of the intermolecular potential, \( \phi(r) \), according to Pople,\(^{28} \) Eq. (1), and by inserting this outcome in the resultant of the non-equilibrium ensemble formalism, Eq (3), we are able to adapt MS expansion\(^{29} \) for non-equilibrium one particle distribution function, i.e., Eq. (4). Due to exactness of our results, we are able to manipulate Eq. (9) in conjunction with ZG formalism\(^{30} \). By adopting ZG formalism\(^{30} \) for energy representation of the non-equilibrium one particle distribution function, Eq. (10), we derived the closed-form for the non-equilibrium internal energy, Eq. (16), in terms of the time dependent coefficients of the recursion relation which followed by ZG approach\(^{30} \). Finally, a precise relation for the non-equilibrium internal energy, Eq. (23), in terms of relevant molecular features has been acquired. This equation has the potential to be used for further studies.

Additionally, non-equilibrium thermodynamics perturbation theory provides the properties of state on the basis of the intermolecular interaction. The unique novelty is the fact that the extension of usual thermodynamics perturbation theory has been applied to non-equilibrium statistical thermodynamics as we proved here. Albeit, the potential of Maxwell molecules treated as a pair-wise potential and is more accurately described as an effective potential but it is important to make the distinction between effective and true two-body potentials. Even though many potentials are functionally pair-wised (i.e., they only require a separation pair as inputs), they are often in reality effective potentials which should not be confused with genuinely two-body potentials\(^{33} \). Our method is restricted to the angle-averaged potentials which are independent of the relative orientations of molecules.

5 Conclusions

Non-equilibrium statistical thermodynamic perturbation theory is introduced and interesting example of this formalism is ascertained for deducing the on-equilibrium internal energy for important prototypical system. Nevertheless, the combination of the model potential used here to the non-equilibrium ensembles method reveals that the extension of the thermodynamics perturbation formalism to the non-equilibrium statistical thermodynamics is intuitively reasonable. We have selected the Maxwell molecules as the reference fluid in this case. Our used potential in conjunction to the non-equilibrium statistical thermodynamics signifies the importance of the reminiscent concept of the non-equilibrium statistical thermodynamics perturbation theory. The other choices of the reference fluid would be conspired the case of future works. So, one cannot spoil the constructed puzzle of various entities, when there is no well-organized (pre-determined) map for it.

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