# Studies in Dynamics

Thesis by

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# Summary

In this thesis, three parts of my work are reported. The first part of the work was done with Prof. Rudy Marcus, the second and third parts of the work were done with Prof. Bill Goddard. Here I would like to summarize the results from each part briefly.

In the first part, we propose doing Scanning Tunneling Microscopy(STM) current calculations with a new model in the spheroidal coordinate system. The tip is modeled as a hyperboloid. The electrostatic potential part of this model is solved exactly. The free electron model of the whole system is also solved exactly.

In the second part, we found that the Nosè Canonical Molecular Dynamics, the most commonly used CMD method, leads to the wrong heat capacity for the system and hence is inconsistent with the thermodynamics. To solve this problem, we propose Two Nosè variable Dynamics by changing the dimensionality of the Nose variable s and its conjugate $p_s$ from one- to two-dimension.

In the third part, The exact expression for the quantum statistical partition function in the canonical ensemble is given. The physical interpretation of each term for N-particle system is discussed. The new formula is applied to the weakly degenerate quantum ideal case. By analyzing each term in the expansion, it is possible that this canonical partition function can be applied to cases where both quantum correlation effects and particle interactions are important.

# Acknowledgements

Here I would like to express my sincere gratitude to my advisor Prof. Rudy Marcus for his encouragement and guidance. His viewpoint on basic issues and his broad perspective on chemistry and physics have a major impact on my way of thinking. Learning and discussing science with him is a great pleasure. I would like to have more opportunities to stay in his group and learn from him. Not only is he a great scientist, but also a great human being who cares his students so much in every aspects. There are simply no words I can find out to express my sincere appreciation to him. He runs a terrific research group in which I enjoyed a lot to stay. Especially I would like to thank Xueyu Song, one of my best friends, for his numerous help not only in science but also in real life.

I would also like to thank Prof. Bill Goddard for his academic guidance and support during my first two-year residence at Caltech. He is another great scientist who gives his students a lot of freedom to solve the problems that confuse them. In the mean time, whenever we are confused and would like to discuss with him, he is always available and his suggestions are valuable and helpful. I enjoyed that very much during the period I was working hard under his guidance. His scientific interests are very broad and his

insights toward scientific problems are very deep. Due to the broad ranges of research going on in his group, I learned a lot during the time I stayed in his group. I would like to express my special thanks to Prof. Zhen-Gang Wang, who has helped me a lot not only on the scientific research but also others. Also it is my great pleasure to mention my appreciation to my thesis committee.

Last but certainly not the least, I would like to thank my whole family. Without them nothing would be possible.

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# I. A STM model in the spheroidal coordinate system

## Abstract

Scanning Tunneling Microscopy (STM) provides a real-space view of the atomic structure and electronic states of the solid and of the adsorbate. It has had a great impact on the developement of the surface science and the materials science. Some theoretical work has been done to try to interpret the imaging process using semi-infinite and spherical models. In this report, we propose doing STM current calculations in the spheroidal coordinate system, which features the tip as the hyperboloid. This model is still mathematically-solvable. Intuitively we feel this model might be more realistic due to it symmetry.

## 1 Introduction

The invention of the Scanning Tunneling Microscope(STM) has revolutionized the surface science[1,2,3]. For the first time, individual atoms on the surface become directly perceptible. Not only the topographical information is provided by STM but also a rich body of information on the electronic states and energy spectra can be obtained by varying the bias voltage between the tip and the sample. This method is providing us an increasingly large amount of information on the details of the electronic states of various surfaces. To date, the most widely used theoretical approach for the interpretation of STM images is that of Tersoff and Hamann [4,5], which is based on the transfer Hamiltonian theory due to Bardeen [6]. In the limit of the small bias voltage, low temperature, and an s-wave modeled tip, the transfer Hamiltonian approach gives the direct proportionality between the STM current and the local density of states (LDOS) at the effective center of curvature of the tip and at the Fermi energy. The interpretation of the STM current is then straightforward: it represents the contour of the constant Fermi level LDOS of the unperturbed sample surface.

There have been different ways to model the tip [4,5,7]. However, we should take the geometry into consideration, and so try to go further beyond the semi-infinite chain and the spherical model. We believe that a natural and more realistic model is a hyperboloidal model for the tip which is also mathematically-solvable one. In this report, first we model the tip with a hyperboloid and the sample surface with a plane, apply the bias voltage between the tip and the sample surface and solve the electrostatic potential problem in the spheroidal coordinate with the physical boundary conditions; Second we will solve the free-electron model in this spheroidal coordinate system as the unperturbed sytem. Later we will add the adsorbate on the surface and calculate the dipole moment contribution from the field-polarized adsorbate to the potential. Finally, we will use the time-independent perturbation theory and solve the Schrödinger equation to calculate the contribution of the adsorbate to the matrix element and to the tunneling current. It is hoped that this will give us a good guidance on explaining the various experimental phenomena of STM due to the adsorbate.

## 2 The calculation of the electrostatic potential

As noted above, to describe the Scanning Tunneling Microscopy more realistically, we propose the following model. The tip is modelled as a hyperboloid and the sample surface is as usual a planar surface. Mathematically we know that the spheroidal coordinate will give us a convenient description of this model. Hence, we first solve for the electrostatic potential in the spheroidal coordinate system [8,9].

Figure 1. shows the spheroidal coordinate system. Utilizing the symmetry , the point charge $q$ of current is placed along the z-axis. Now we have a model which has a point charge $q$ moving between the hyperboloidal tip and the planar sample surface under the bias voltage $V_0$. (Contributions of charges "off-axis" would be treated by pertubation theory.)

To simplify the calculation of the potential for this model, we separate the potential into two parts: one is due to the bias voltage $V_0$, the other part is due to the image and multi-image effects of the point charge under the boundary conditions for the electric potential being zero on both the tip and the sample surface. It is the image term which is calculated using the point charge and described above. We graphically show the idea in Figure 2.

First, we calculate the potential which is due to the bias voltage $V_0$. To begin the analysis, the prolate-spheroidal coordinate system is given by [8,9],

$$\begin{aligned} x &= c\sinh\alpha\sin\beta\cos\phi \\ y &= c\sinh\alpha\sin\beta\sin\phi \\ z &= c\cosh\alpha\cos\beta \end{aligned} \tag{1}$$

where $c$ is the one half of the distance between the hyperboli foci; $\beta$ corresponds to the hyperboloid surfaces and $\alpha$ corresponds to the prolate-spheroidal surfaces. Starting with the above set of equations, we introduce the transformations $\xi = \cosh\alpha$, $\eta = \cos\beta$ and obtain another set of equations which will be useful later on

$$\begin{aligned} x &= c\sqrt{\xi^2 - 1}\sqrt{1-\eta^2}\cos\phi \\ y &= c\sqrt{\xi^2 - 1}\sqrt{1-\eta^2}\sin\phi \\ z &= c\xi\eta \end{aligned} \tag{2}$$

The region of the physical interest is : $\xi$=[1,$\infty$],$\eta$=[$\eta_0$, 0] , $\phi$=[-$\pi$, $\pi$]. Here, $\eta_0$ corresponds to the hyperboloid surface associated with the tip and $\eta$=0 corresponds to the planar sample surface. In this coordinate system, the Laplacian operator is

$$\nabla^2 = \frac{1}{c^2\{\sinh^2\alpha + \sin^2\beta\}}\{\frac{1}{\sinh\alpha}\frac{\partial}{\partial\alpha}\sinh\alpha\frac{\partial}{\partial\alpha}+\frac{1}{\sin\beta}\frac{\partial}{\partial\beta}\sin\beta\frac{\partial}{\partial\beta}+\{\frac{1}{\sinh^2\alpha}+\frac{1}{\sin^2\beta}\}\frac{\partial^2}{\partial\phi^2}\} \tag{3}$$

Next, we calculate the part of the potential which arises from the bias voltage. Because that potential is only dependent on $\beta$, we reduce the Laplace equation to the following one-variable ordinary differential equation

$$\frac{1}{\sin\beta}\frac{d}{d\beta}\sin\beta\frac{d}{d\beta}\Phi_1 = 0 \tag{4}$$

The solution is given by [11]

$$\Phi_1(\eta) = V_0\frac{\ln\frac{1+\eta}{1-\eta}}{\ln\frac{1+\eta_0}{1-\eta_0}} \quad . \tag{5}$$

Next, we consider calculating the electric potential which arises only from the image and multi-image effects with the boundary condition that the resulting potential is zero at both the tip and sample surface. We denote the potential due to the image and multi-image effects by $\Phi_2$. Poisson equation is

$$\nabla^2\Phi_2(\vec{\mathbf{r}},\vec{\mathbf{r_e}}) = -4\pi q\delta(\vec{\mathbf{r}}-\vec{\mathbf{r_e}}) \tag{6}$$

where $\vec{\mathbf{r_e}}$ denotes the coordinate for the point charge $q$. Realizing that $\Phi_2$ is the Green's function $G(\vec{\mathbf{r}},\vec{\mathbf{r_e}})$ which represents the exact potential at the point $\vec{\mathbf{r}}$ in the presence of the charge $q$ at $\vec{\mathbf{r_e}}$, we can write the following

$$\Phi_2(\vec{\mathbf{r}},\vec{\mathbf{r_e}}) = G(\vec{\mathbf{r}},\vec{\mathbf{r_e}}) = \frac{q}{|\vec{\mathbf{r}}-\vec{\mathbf{r_e}}|} + \Phi_3(\vec{\mathbf{r}},\vec{\mathbf{r_e}}) \tag{7}$$

where $\Phi_3(\vec{\mathbf{r}}, \vec{\mathbf{r_e}})$ satisfies

$$\nabla^2 \Phi_3(\vec{\mathbf{r}}, \vec{\mathbf{r_e}}) = 0 \tag{8}$$

By separating the variables in the spheroidal coordinate system, we obtain the following set of equations,

$$\Phi_3(\vec{\mathbf{r}}, \vec{\mathbf{r_e}}) = A(\alpha)B(\beta)\Psi(\psi) \tag{9}$$

$$\frac{\partial^2 \Psi}{\partial \psi^2} + m^2 \Psi = 0 \tag{10}$$

$$\frac{1}{\sinh\alpha}\frac{\partial}{\partial\alpha}\sinh\alpha\frac{\partial}{\partial\alpha}A - \frac{m^2}{\sinh^2\alpha}A = \nu(\nu+1)A \tag{11}$$

$$-\frac{1}{\sin\beta}\frac{\partial}{\partial\beta}\sin\beta\frac{\partial}{\partial\beta}B + \frac{m^2}{\sin^2\beta}B = \nu(\nu+1)B \tag{12}$$

Due to the symmetry of the electric potential,$\Psi$ is a constant and so we can reduce the above set of equations to the following two Legendre equations without losing generality, (where $\xi = \cosh$ and $\eta = \cos\beta$)

$$\Phi_3 = A(\xi)B(\eta) \tag{13}$$

$$\frac{d}{d\xi}(\xi^2 - 1)\frac{d}{d\xi}A - \nu(\nu+1)A = 0 \tag{14}$$

$$\frac{d}{d\eta}(1 - \eta^2)\frac{d}{d\eta}B + \nu(\nu+1)B = 0 \tag{15}$$

Since $\Phi_3$ must converge when $\xi$ goes to infinity, we find that $\nu$ has to be $-\frac{1}{2} \pm \imath\tau$ $(\tau \geq 0)$ by using the integral representation for $P_\nu(\xi)$ [9],

$$P_\nu(\xi) = \frac{2}{\pi}\int_0^\alpha \frac{\cosh(\nu + \frac{1}{2})\theta}{\sqrt{2\xi - 2\cosh\theta}}d\theta \tag{16}$$

A brief explanation is given in the following. First, if $\nu$ were real, the integral would diverge(become infinite). Second, to make the formula converge, the $\frac{1}{2}$ in the numerator of the intergrand has to be cancelled by the real part from the complex $\nu$, namely, $\nu$ has to be $-\frac{1}{2}\pm\imath\tau$. From now on, we introduce $K_\tau(\xi) = P_{-\frac{1}{2}+\imath\tau}(\xi)$. $K_\tau(\xi)$ is called the conical function. The Legendre function of the second kind $Q_\nu(\xi)$ diverges when $\alpha$ approaches $0^+$, and hence we discard that term. Thereby, we do not have a term $K_\tau(-\xi)$. ($K_\tau(-\xi)$ is a linear combination of $Q_{-\frac{1}{2}+\imath\tau}(\xi)$ and $K_\tau(\xi)$.)

We consider next the solution of the $\eta$ equation, Eq.(15). For mathematical convenience, comparing Eqs. (14) and (15) we see that the general solution for the $\eta$ equation is $C_\tau P_{-\frac{1}{2}+\imath\tau}(\eta) + D_\tau Q_{-\frac{1}{2}+\imath\tau}(\eta)$. We can reconvert the latter as $A_\tau K_\tau(\eta) + B_\tau K_\tau(-\eta)$[8]. Hence the general solution for this electrostatic potential is

$$\Phi_3 = \int_0^\infty [A_\tau K_\tau(\eta) + B_\tau K_\tau(-\eta)] K_\tau(\xi) d\tau \tag{17}$$

To determine the coefficients $A_\tau$ and $B_\tau$, we note that at $\eta = \eta_0$ and $\eta = 0$ the electrostatic potential $\Phi_2 = 0$ and hence from Eq.(7) $\Phi_3$ is $-\frac{q}{|\vec{r}-\vec{r_c}|}$($\vec{r_c}$ is the coordinate for the point charge, $\vec{r}$ is the coordinate describing the tip or the surface.). The Green's function in the prolate spheroidal coordinate is [10]

$$-\frac{q}{|\vec{r}-\vec{r_c}|} = -\frac{q\pi}{c}\int_0^\infty \frac{\tau\tanh(\pi\tau)}{\cosh(\pi\tau)} K_\tau(\pm\eta_c) K_\tau(\mp\eta) K_\tau(\xi) d\tau \tag{18}$$

where the upper and lower signs correspond to $\eta < \eta_c$ and $\eta > \eta_c$, respectively. By equating Eq. (17) and Eq. (18) for both $\eta = \eta_0 > \eta_c$ and $\eta = 0 < \eta_c$ cases, we obtain

$$A_\tau = \frac{q\pi}{c}\frac{\tau\tanh(\pi\tau)}{\cosh(\pi\tau)}\frac{K_\tau(\eta_0)K_\tau(-\eta_c) - K_\tau(\eta_0)K_\tau(\eta_c)}{K_\tau(\eta_0 - K_\tau(-\eta_0)} \tag{19}$$

$$B_\tau = \frac{q\pi}{c}\frac{\tau\tanh(\pi\tau)}{\cosh(\pi\tau)}\frac{K_\tau(\eta_0)K_\tau(-\eta_c) - K_\tau(\eta_0)K_\tau(\eta_c)}{K_\tau(\eta_0) - K_\tau(-\eta_0)} \tag{20}$$

Now we have solved the electrostatic potential $\Phi$ given by $\Phi_1 + \Phi_2$ for this hyperboloidal model of STM *exactly*. We summarize here

$$\Phi = \Phi_1 + \Phi_2 \tag{21}$$

$$\Phi_1 = V_0 \frac{\ln \frac{1+\eta}{1-\eta}}{\ln \frac{1+\eta_0}{1-\eta_0}} \tag{22}$$

$$\Phi_2 = \frac{q}{|\vec{r} - \vec{r_c}|} + \Phi_3 \tag{23}$$

$$\Phi_3 = \int_0^\infty (A_\tau K_\tau(\eta) + B_\tau K_\tau(-\eta)) K_\tau(\xi) d\tau \tag{24}$$

$$A_\tau = \frac{q\pi}{c} \frac{\tau \tanh(\pi\tau)}{\cosh(\pi\tau)} \frac{K_\tau(\eta_c)K_\tau(-\eta_0) - K_\tau(-\eta_c)K_\tau(\eta_0)}{K_\tau(\eta_0) - K_\tau(-\eta_0)} \tag{25}$$

$$B_\tau = \frac{q\pi}{c} \frac{\tau \tanh(\pi\tau)}{\cosh(\pi\tau)} \frac{K_\tau(\eta_0)K_\tau(-\eta_c) - K_\tau(\eta_0)K_\tau(\eta_c)}{K_\tau(\eta_0) - K_\tau(-\eta_0)} \tag{26}$$

## 3 Free-electron Model in the spheroidal coordinate system

Here, we solve the free electron model in the spheroidal coordinate. The Schröndinger equation for the free electron model in the spheroidal coordinate is,

$$(\nabla^2 + k^2)\Psi = 0 \tag{27}$$

where

$$\nabla^2 = \frac{1}{c^2(\sinh^2\alpha + \sin^2\beta)} \{ \frac{1}{\sinh\alpha} \frac{\partial}{\partial\alpha} \sinh\alpha \frac{\partial}{\partial\alpha} + \frac{1}{\sin\beta} \frac{\partial}{\partial\beta} \sin\beta \frac{\partial}{al\beta} + (\frac{1}{\sinh^2\alpha} + \frac{1}{\sin^2\beta}) \frac{\partial^2}{\partial\varphi^2} \}$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

By separating variables, we reach the following set of equations

$$\Psi = A(\alpha)B(\beta)\Phi(\varphi) \tag{28}$$

$$\xi = \cosh\alpha$$

$$\eta = \cos\beta$$

$$\frac{d}{d\xi}(\xi^2-1)\frac{dA}{d\xi} - \frac{\mu^2}{\xi^2-1}A = \nu(\nu+1)A \tag{29}$$

$$\frac{d}{d\eta}(\eta^2-1)\frac{dB}{d\eta} - \frac{\mu^2}{\eta^2-1}B = \nu(\nu+1)B \tag{30}$$

$$\frac{d^2\Phi}{d\varphi^2} + (k^2c^2+\mu^2)\Phi = 0 \tag{31}$$

where $\mu$ and $\nu$ are the parameters for the associated Legendre equations.

From Eq.(30), we obtain the energy eigenvalues for the tip and the sample by using the condition that $\Phi(\varphi+2\pi) = \Phi(\varphi)$.

$$E_n = \frac{n^2-\mu^2}{2mc^2}\hbar^2 \tag{32}$$

where $n$ is an non-negative integer which describes the energy level of the system. The wavefunction is

$$\Psi = A(\xi)B(\eta)\Phi(\varphi) \tag{33}$$

$$A(\xi) = a_1 K^\mu_\tau(\xi) \tag{34}$$

$$B(\eta) = b_1 K^\mu_\tau(\eta) + b_2 K^\mu_\tau(-\eta) \tag{35}$$

$$\Phi(\varphi) = c_1 \exp(\imath n\varphi) + c_2 \exp(-\imath n\varphi) \tag{36}$$

with $\nu = -\frac{1}{2} + \imath\tau$ and $K^\mu_\tau(\lambda) = P^\mu_\nu(\lambda) = P^\mu_{-\frac{1}{2}+\imath\tau}(\lambda)$.($K^\mu_\tau(-\eta)$ is a linear combination of $Q^\mu_{-\frac{1}{2}+\imath\tau}(\eta)$ and $K^\mu_\tau(\eta)$.)

The coefficients in the wavefunction can be obtained from the normalization of each part of the wavefunction. For the tip and the sample, we have a fixed $\eta$ value for each of them. That means the $\eta$ part of the wavefunction can be treated as a constant. Hence, we only need to find out the coefficients for the $\xi$ and $\varphi$ part. We obtain

$$a_1 = \sqrt{(-1)^{\mu} \frac{\coth(\pi\tau)}{\tau} \frac{\Gamma(\imath\tau + \frac{1}{2} + \mu)}{\Gamma(\imath\tau + \frac{1}{2} - \mu)}} \tag{37}$$

$$c_1 = c_2 = \frac{1}{2\sqrt{\pi}} \tag{38}$$

# 4 Summary

We have shown briefly the work has been done in the past few months. This is only the beginning stage of the work. There still is much work to be done in the future. The next thing is we need to place the adsorbate on the substrate and calculate the perturbation due to the dipole moment of the adsorbate. From there, we can begin with the real-time calculations and see how the model works for the real systems.

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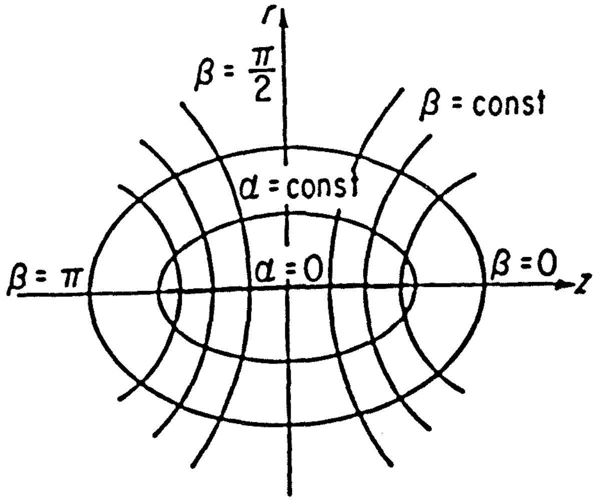

FIGURE 1

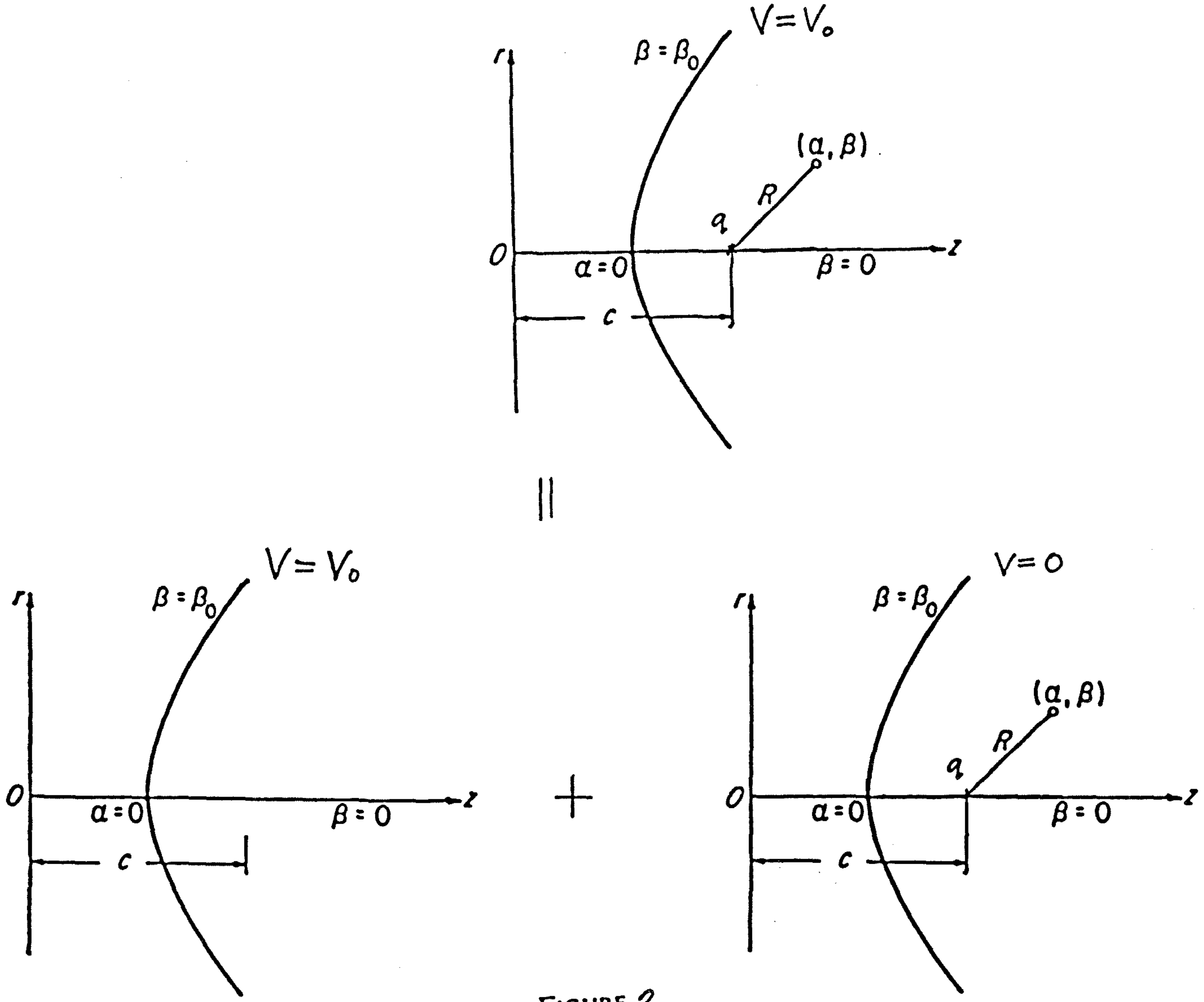

FIGURE 2

## II. Canonical Molecular Dynamics with Two Nosè Variables

### Abstract

A new era in molecular dynamics (MD) was initiated by S. Nosè in 1984 who showed how to modify the Lagrangian to obtain a new equation of motion with the property that the states sampled by the trajectories lead to a Boltzmann distribution of state

$$\mathcal{P}(p,q) = Ae^{-\beta E} \tag{1}$$

Such canonical molecular dynamics (CMD) methods have rapidly become the standard for modern MD. However, Nosè CMD leads to a temperature dependence of $A$ and hence an incorrect heat capacity. In order to make Nosè more fully consistent with thermodynamics we change the dimensionality of the heat bath variable $s$ and its conjugate momentum $p_s$ from one- to two-dimensions. This leads to a modified CMD which is consistent with the heat capacity. Part II and III were performed under the guidance of Professor. W. Goddard.

## 1.0 Introduction

Molecular dynamics (MD) computer simulations have become a very important tool for modern materials research. In the 1980's a revolution occured in which the standard Newtonian dynamics was extended to include the effects of a temperature bath (Nosè or NVT molecular dynamics), a pressure bath (Andersen-Rahman-Parrinello or NPH dynamics), or both (Gibbs or NPT dynamics). In principle, these various types of canonical molecular dynamics (CMD) lead to the standard distributions functions of thermodynamics, allowing us to use thermodynamics relationships in predicting properties from the calculated dynamical distributions. Here we will focus on the Nosè (NVT) and Gibbs (NPT) dynamics.

Nosè in 1984 extended the application of molecular dynamics from the microcanonical ensemble to the canonical ensemble by introducing a pair of additional variables ($s$ and $p_s$). Later, Hoover modified this formulation by transforming the virtual time coordinate of Nosè to real time, changing the equations of motion such that the conjugate pair ($s$ and $p_s$) is replaced by a single variable $\zeta = p_s/s$. We show that in either case the Nosè formulation leads to a heat capacity differing slightly from the correct value for a canonical ensemble. We show how to remove this problem by adding one additional Nosè degree of freedom.

Section 2 reviews the Nosè and the Hoover formulations. Section 3 points out the difficulty with these formulations, and Section 4 shows how to modify the formulation to eliminate the problem. Section 5 presents the new formulation. Finally, Section 6 compares the new formulation with the standard Nosè-Hoover formulations and discusses applications.

## 2.0 The Nosè and Hoover Formulations of Canonical Molecular Dynamics

In 1984, Nosè proposed a new molecular dynamics which extended the description from that of a microcanonical system to a canonical system. This has greatly extended the domain for applications of molecular dynamics simulations methods. Most experiments are carried out under conditions in which the system is in a constant temperature bath, leading to fluctuations in the energy of the system corresponding to a canonical ensemble. This contrasts with the description of Newtonian mechanics which conserves the total energy of the system, leading to a microcanonical ensemble. To do this Nosè introduced an additional variable $s$ and its conjugate momentum $p_s$. These two variables describe the heat bath and the energy exchange between the system and the heat bath. The variable $s$ is a time scaling variable. When the system is hotter (colder) than the heat bath, $s$ increases (decreases), slowing (accelerating) the velocities and thereby cooling (heating) the system. We denote the physical system coupled with the heat bath as the extended system. The extended system is considered as isolated, so that the total Hamiltonian is conserved, leading to a microcanonical ensemble. Thus we use Newtonian mechanics to solve the equations of motion.

In terms of these two additional variables, ($s$ and $p_s$) Nosè introduced the virtual variables $\bar{\mathbf{q}}$, $\bar{\mathbf{p}}$ and $\bar{t}$ for the $3N$ coordinates and momenta and the time. These are to be related to the real variables ($q$, $p$, $t$) as follows:

$$q = \bar{q} \tag{1}$$

$$p = \frac{\bar{p}}{s} \tag{2}$$

$$t = \int^{\bar{t}} \frac{d\bar{t}}{s} \tag{3}$$

The Hamiltonian of the extended system is postulated as,

$$H_s = H_0 + \frac{p_s^2}{2Q} + gk_BT \ln s \tag{4}$$

where

$$H_0 = \sum_i \frac{\bar{p}_i^2}{2m_i s^2} + \phi(\bar{q})$$

and the Lagrangian is correspondingly supposed to be

$$L_s = \sum_i \frac{1}{2} m_i s^2 \bar{v}_i^2 - \phi(\bar{q}) + \frac{1}{2} Q \dot{s}^2 - g k_B T \ln s \tag{5}$$

where $\phi$ is the multibody potential energy of the physical system.

Then it is assumed that Hamiltonian formalism works in the virtual time with the virtual variables, namely,

$$\frac{d\bar{q}_i}{d\bar{t}} = \frac{\partial H}{\partial \bar{p}_i} = \frac{\bar{p}_i}{m_i s^2} \tag{6}$$

$$\frac{d\bar{p}_i}{d\bar{t}} = -\frac{\partial H}{\partial \bar{q}_i} = -\frac{\partial \phi}{\partial \bar{q}_i} = F_i \tag{7}$$

$$\frac{ds}{d\bar{t}} = \frac{\partial H}{\partial p_s} = \frac{p_s}{Q} \tag{8}$$

$$\frac{dp_s}{d\bar{t}} = -\frac{\partial H}{\partial s} = \frac{\left(\sum_i \frac{\bar{p}_i^2}{m_i s^2} - g k_B T\right)}{s} \tag{9}$$

Thus

$$\frac{dH}{dt} = \sum_i \left( \frac{\partial H}{\partial \bar{p}_i} \frac{d\bar{p}_i}{d\bar{t}} + \frac{\partial H}{\partial \bar{q}_i} \frac{d\bar{q}_i}{d\bar{t}} \right) + \frac{\partial H}{\partial p_s} \frac{dp_s}{d\bar{t}} + \frac{\partial H}{\partial s} \frac{ds}{d\bar{t}} = 0$$

so that the total Hamiltonian is conserved. Similarly in the Lagrangian form we obtain

$$\frac{d^2\bar{q}_i}{d\bar{t}^2} = -\frac{1}{m_i s^2} \frac{\partial \phi}{\partial \bar{q}_i} - \frac{2}{s} \frac{ds}{d\bar{t}} \frac{d\bar{q}_i}{d\bar{t}} \tag{10}$$

and

$$\frac{d}{d\bar{t}} \left( Q \frac{ds}{d\bar{t}} \right) = \frac{\sum_i \frac{\bar{p}_i^2}{m_i s^2} - g k_B T}{s} \tag{11}$$

Since $H$ is conserved the partition function for the $3N+1$ coordinates is

$$Z_{3N+1} = \frac{1}{N! h^{(3N+1)}} \int dp_s d_s \prod_{i=1}^{3N} dp_i dq_i \delta \left( H_s - E_s \right) \tag{12}$$

Substituting (4) into (12) leads to

$$Z_{3N+1} = \int dp_s \int ds \int \prod_{i=1}^{3N} d\bar{p}_i d\bar{q}_i \delta \left[ H_0 \left( \frac{p}{s}, q \right) + \frac{p_s^2}{2Q} + g k_B T \ln s - E_s \right] \tag{13}$$

Integrating over $p_s$ and $s$ and using the mathematical properties of the Dirac $\delta$-function, the expression (13) leads to

$$Z = C \int \prod_{i=1}^{3N} dp_i dq_i \exp\left[\frac{-H_0\left(p, q\right)}{k_B T}\right] \tag{14}$$

Thus we obtain the standard canonical partition function if the parameter $g$ is set to

$$g = 3N + 1 \tag{15}$$

The above description is a brief review of the Nosè dynamics. Now we consider how Hoover changed the formulation from the virtual time to the real time. With the equations (6)-(9) Hoover substituted the differential form of (3) $dt = d\bar{t}/s$, changing from Nosè time $\bar{t}$ back to the real time, $t$. This leads to the following equations in the real time

$$\frac{d\bar{q}_i}{dt} = \frac{\bar{p}_i}{m_i s} \tag{16}$$

$$\frac{d\bar{p}_i}{dt} = sF_i(\bar{q}) \tag{17}$$

$$\frac{ds}{dt} = \frac{sp_s}{Q} \tag{18}$$

$$\frac{dp_s}{dt} = \sum_i \frac{\bar{p}_i^2}{m_i s^2} - gk_B T \tag{19}$$

Then Hoover redefined quantities as follows:

$$p_i = \frac{1}{s}\bar{p}_i \tag{20}$$

$$q_i = \bar{q}_i \tag{21}$$

$$\zeta = \frac{1}{s}\frac{ds}{dt} \tag{22}$$

so that the new $p$ is back to the real world momentum, he also replaced the Nosé parameter $g = 3N + 1$ in the $\zeta$ equation by $g = 3N$ and reached the following equations

$$\frac{dq_i}{dt} = \frac{p_i}{m_i} \tag{23}$$

$$\frac{dp}{dt} = F_i(q) - \zeta p \tag{24}$$

$$\dot{\zeta} = \frac{\sum_i \frac{p_i^2}{m_i} - (3N)k_B T}{Q} \tag{25}$$

In the Hoover formulation, the dynamical equation (24) has a momentum dependent force corresponding to a thermodynamic friction, $\zeta$. This is due to the energy transfer from the $N$ particles to the Nosè coordinates. The Nosè formulation and the Hoover formulation are essentially equivalent. The only difference is that the Nosè formulation is in virtual time and the Hoover formulation uses real time. From practical point of view, the Hoover formulation is more convenient than the Nosè formulation, because it is easier to carry out fast Fourier transforms over the time coordinate to obtain properties.

### 3.0 A Problem with the Nosè and Hoover Formulations

A problem with the Nosè formulation is that it leads to a heat capacity that is $k_B/2$ less than that from standard canonical partition function. To see this consider the derivation from (13) to (14) in more detail.

$$\begin{aligned} Z &= C \int d\bar{p}d\bar{q}dp_s d_s \cdot \delta\left(\sum_i \frac{\bar{p}_i^2}{2m_i s^2} + \phi(\bar{q}) + \frac{p_s^2}{2Q} + gk_B T \ln s - E\right) \\ &= C \int dpdqdp_s d_s \cdot s^{3N} \cdot \delta \frac{(s - s_0)}{f'(s_0)} \end{aligned} \tag{26}$$

where

$$s_0 = \exp\left\{ -\frac{\left(H_0 + \frac{p_s^2}{2Q} - E\right)}{gk_B T} \right\} \tag{27}$$

and

$$H_0 = \sum \frac{\bar{p}_i^2}{2m_i s^2} + Q(q) \tag{28}$$

and

$$f'(s_0) = \frac{gk_B T}{s_0} \tag{29}$$

$$Z = C \cdot \frac{1}{gk_BT} \int dpdqdp_s \cdot \exp\left\{ -\frac{(3N+1)\left(H_0 + \frac{p_s^2}{2Q} - E\right)}{gk_BT} \right\} \tag{30}$$

To satisfy canonical distribution, we need to use $g = 3N + 1$

$$\begin{aligned} Z &= C \cdot \frac{1}{(3N+1)} \cdot \beta \cdot \left(\frac{2Q}{\beta}\right)^{1/2} \cdot \frac{1}{2}\sqrt{\pi} \cdot e^{\beta E} \int dpdqe^{-\beta H_0} \\ &= C' \cdot e^{\beta E} \cdot \beta^{1/2} \cdot Z_{can} \end{aligned} \tag{29}$$

where

$$C' = \frac{Q^{\frac{1}{2}}C}{(3N+1)}\sqrt{\frac{\pi}{2}} \tag{30}$$

¿From thermodynamics we have

$$-\beta A_{nose} = \ln Z \tag{31}$$

$$C_{v,nose} = -T\left(\frac{\partial^2 A_{nose}}{\partial T^2}\right)_v \tag{32}$$

This leads to

$$C_{v,nose} = C_{v,can} - \frac{1}{2}k_B \tag{33}$$

That is, the specific heat is too small by $\frac{1}{2}k_B$. In the next section we will consider how to solve this problem.

Considering the Hoover formulation, we see that $g = 3N+1$ should be retained rather than using $g = 3N$.

## 4.0 Reformulation of the Canonical Molecular Dynamics

We start by considering two Nosè variables $s_1$ and $s_2$ in the virtual time. The virtual variables (coordinates $\bar{q}$, momentum $\bar{p}$, time $\bar{t}$) and real variables (coordinates $q$, momentum $p$, time $t$) are related by

$$\bar{q} = q \tag{33}$$

$$\frac{\bar{p}}{s} = p \tag{34}$$

$$\frac{d\bar{t}}{s} = dt \tag{35}$$

The Hamiltonian of the extended system of the particles and the variables $s_1$ and $s_2$ in terms of the virtual variables are postulated as

$$H_{2_s} = \sum_{i=1}^{3N} \frac{\bar{p}_i^2}{2m_i s^2} + \phi(\bar{q}) + \frac{p_{s_1}^2}{2Q_1} + \frac{p_{s_2}^2}{2Q_2} + \frac{1}{2} g k_B T \ln\left(s_1^2 + s_2^2\right) \tag{36}$$

where

$$s^2 = s_1^2 + s_2^2 \tag{37}$$

This leads to

$$\frac{d\bar{q}_i}{d\bar{t}} = \frac{\partial H}{\partial \bar{p}_i} = \frac{\bar{p}_i}{m_i s^2} \tag{38}$$

$$\frac{d\bar{p}_i}{d\bar{t}} = -\frac{\partial H}{\partial \bar{q}_i} = -\frac{\partial \phi}{\partial \bar{q}_i} \tag{39}$$

$$\frac{ds_1}{d\bar{t}} = \frac{p_{s_1}}{Q_1}, \qquad \frac{ds_2}{d\bar{t}} = \frac{p_{s_2}}{Q_2}. \tag{40}$$

$$\frac{dp_{s_1}}{dt} = -\frac{\partial H}{\partial s_1} = \frac{s_1}{s^2}\left[\sum_i \frac{\bar{p}_i^2}{m_i s^2} - g k_B T\right] = \frac{2s_1}{s^2}\left[KE - \frac{g}{2}\cdot k_B T\right] \tag{41}$$

$$\frac{dp_{s_2}}{dt} = -\frac{\partial H}{\partial s_2} = \frac{s_2}{s^2}\left[\sum_i \frac{\bar{p}_i^2}{m_i s^2} - g k_B T\right] = \frac{2s_2}{s^2}\left[KE - \frac{g}{2}\cdot k_B T\right] \tag{42}$$

where

$$KE = \sum_i \frac{1}{2}\frac{\bar{p}_i^2}{m_i s^2}$$

In the Lagarangian formulation, these are

$$L = \frac{1}{2}\sum_i s^2 m_i \bar{v}_i^2 - \phi(\bar{q}) + \frac{1}{2}Q_1 \dot{s}_1^2 + \frac{1}{2}Q_2 \dot{s}_2^2 - \frac{1}{2} g k_B T \ln\left(s_1^2 + s_2^2\right) \tag{43}$$

$$\frac{d}{d\bar{t}}\left(m_i s^2 \frac{d\bar{q}_i}{d\bar{t}}\right) = -\frac{\partial \phi}{\partial \bar{q}_i} \tag{44}$$

$$Q_1 \ddot{s}_1 = \frac{2s_1}{s^2}\left[\frac{1}{2}\sum_i s^2 m_i \bar{v}_i^2 - \frac{1}{2} g k_B T\right] = \frac{2s_1}{s^2}\left[KE - \frac{1}{2} g k_B T\right] \tag{45}$$

$$Q_2 \ddot{s}_2 = \frac{2s_2}{s^2}\left[\frac{1}{2}\sum_i s^2 m_i \bar{v}_i^2 - \frac{1}{2} g k_B T\right] = \frac{2s_2}{s^2}\left[KE - \frac{1}{2} g k_B T\right] \tag{46}$$

These equations are in the virtual time domain.

Now we consider the dynamics in the real time domain.

$$\frac{d\bar{q}_i}{dt} = \frac{\bar{p}_i}{m_i s} \tag{47}$$

$$\frac{d\bar{p}_i}{dt} = sF_i \tag{48}$$

$$\frac{ds_1}{dt} = s\frac{p_{s_1}}{Q_1}, \qquad \frac{ds_2}{dt} = s\frac{p_{s_2}}{Q_2} \tag{49}$$

$$\frac{dp_{s_1}}{dt} = 2\frac{s_1}{s}\left[KE - \frac{g}{2} k_B T\right] \tag{50}$$

$$\frac{dp_{s_2}}{dt} = 2\frac{s_2}{s}\left[KE - \frac{g}{2} k_B T\right] \tag{51}$$

Now we have the set of the dynamic equations in the real variables.

$$\dot{p}_i = -\frac{\partial \phi}{\partial q_i} - \zeta p_i$$

$$\dot{q}_i = \frac{p_i}{m_i}$$

$$\zeta = \frac{\dot{s}}{s}$$

$$s = \sqrt{s_1^2 + s_2^2}$$

$$\ddot{s}_1 = \zeta \dot{s}_1 + \alpha s_1$$

$$\ddot{s}_2 = \zeta \dot{s}_2 + \beta s_2$$

$$\alpha = 2\left[KE - \frac{1}{2} g k_B T\right] / Q_1$$

$$\beta = 2\left[KE - \frac{1}{2} g k_B T\right] / Q_2$$

$$KE = \sum_i \frac{1}{2} m_i s^2 \bar{v}_i^2 = \sum_i \frac{p_i^2}{2m_i}$$

$$g = 3N + 2$$

## 5.0 Discussions and Comparisons with the Nosè and Hoover Formulations

In the new formulation, both the $s$ variable and its conjugate momentum $p_s$ have two degrees of freedom. This leads to a heat capacity which is the same for the canonical ensemble. If we assumed that s has three degrees of freedom, we would obtain the heat capacity of $C_{v,nose} = C_{v,can} + k_B/2$ and a $g$ parameter of $g = 3N + 3$. Thus considering $s$ as $1 - D$, $2 - D$, or $3 - D$ leads to Table 1.

Considering a $2 - D$ Nosè variable leads to the Nosè masses $Q_1$ and $Q_2$ which presumably should be allowed to be different. There is a great deal of work left to be done. The big question is whether the new formulation changes any results.

## References

1. S. Nosè, J. Chem. Phys. **81**, 511 (1984).
2. W. G. Hoover, Phys. Rev. **31**, 1695 (1985).

**Table 1.** Relation between Nosè variable and heat capacity.

| Dimensions for the Nosè Variables | 1 | 2 | 3 |
|---|---|---|---|
| $g$ | $3N+1$ | $3N+2$ | $3N+3$ |
| $C_{v,nose} - C_{v,can}$ | $-k_B/2$ | $0$ | $k_B/2$ |

## III. Quantum Statistics in Canonical Ensembles Of Identical Particles

### Abstract

The exact expression for the quantum statistical partition function in the canonical ensemble is given in this report. The physical sense of the new expression is discussed. The new formula is applied to the weakly degenerate quantum ideal case to calculate its thermodynamic properties. It is analyzed in terms of the nature of the coherent correlations among the quantum particles, to obtain the origins of quantum correlation effects both mathematically and physically. This method produces the same virial coefficients as previously derived in the infinite $N$ limit from the grand canonical emsemble, but also leads to the value for the finite clusters. Details of these derivations of the quantum canonical partition function are given. The expressions are applied only for the mean field case. It is also possible that this canonical partition function can be applied to cases where both quantum correlation effects and particle interactions are important.

## 1.0 Introduction

For collections of identical particles, it is necessary to properly correct the quantum statistics for the boson or fermion character of the particles. Usually such corrections are derived from considerations of the grand canonical ensemble and are valid only in the large $N$ limit. We are interested in the properties of clusters of identical particles. We present a new derivations of the quantum statistics for finite canonical ensembles. Using the recursion formulae of Borrmann and Franke,[1] we derive analytical formulae for the canonical partition function. This canonical partition function is analyzed in terms of the physical origins for each term of the quantum corrections. The quantum statistics is expressed in terms of classical Boltzmann statistics plus additional terms where the difference between Bose-Einstein statistics and Fermi-Dirac statistics shows up in the form of signs for each many-body correction. These canonical partition functions should be useful for considering nucleation of identical particles.

In Section 2 we present the exact expression for the quantum statistical partition function in the canonical ensemble and discuss the physical sense of the new expression. In Section 3 we consider the weakly degenerate quantum ideal case and apply the canonical partition function to calculate thermodynamic properties. This is analyzed in terms of the nature of the coherent correlations among the quantum particles, to obtain the origins of quantum correlation effects both mathematically and physically. This produces the same virial coefficients as previously derived in the infinite $N$ limit from the grand canonical ensemble, but also leads to values for finite clusters. Details of these derivations of the quantum canonical partition function are given. The expressions are applied only for the mean field case. It is also possible tha this canonical partition function can also be applied to cases where both quantum correlation effects and particle interactions are important.

## 2.0 Exact Formula for the Canonical Partition Function

Recently Borrmann and Franke[1] derived the exact recursion formula for the canonical quantum statistical partition function for quantum systems of $N$ independent particles.

The results is

$$Q(N) = \frac{1}{N} \sum_{K=1}^{N} (\pm 1)^{K+1} q_K Q(N-K) \tag{1}$$

where

$$Q(0) = 1 \tag{2}$$

and

$$q_K = \sum_j e^{-K\beta\epsilon_j} \tag{3}$$

is the single-particle Boltzmann partition function with the original energy levels, $\epsilon_K$, $K$-times amplified. The upper and lower signs represent Bose-Einstein and Fermi-Dirac statistics, respectively. Thus the partition function of the quantum systems having $(K+1)$ particles is obtained directly from the canonical partition functions for quantum systems having 2 to K particles. However it would be useful to have a unified formula with which to compare the different statistics and to relate them to the classical case. That is, we would like a formula in which both Bose-Einstein and Fermi-Dirac statistics go to the same classical Boltzmann statistics as the quantum correlation effects become negligible. The first difference between the two quantum statistics appears in the second order which is plausible since two-body quantum correlations have opposite signs and the same absolute value for the two statistics.

We consider here that $N$ particles can be distributed over the available energy state $\{\epsilon_j\}$ in a number of ways. Thus we could put all $N$ particles together in one state; this would be denoted as $P = 1$, $K_1 = N$, $l_1 = 1$. Or we could have every particle in a different state; this would be denoted as $P = 0$, $K = 0$. Or we could have $M$ particles together in one state and $N - M$ particle in another; this would be denoted as $P = 2$, $K_1 = M$, $K_2 = N - M$, $l_1 = 1$, and $l_2 = 1$ (assuming $M > N/2$). Or we could have two particles in one state, two particles in another state, and all others singly compared; this would be denoted as $P = 1$, $K_1 = 2$, $l_1 = 2$. For the general case we partition the $N$ particles into classes as follows. The multiple occupations numbers $K_i$ are defined as

$$K_1 \geq K_2 \geq \cdots K_i \geq \cdots K_P \geq 2 \tag{4}$$

and the number of times each occurs is defined as

$$L_i = 1, 2, \cdots \tag{5}$$

The total number of particles in multiple occupations is then

$$S = \sum_{i=1}^{P} K_i L_i \tag{6}$$

This leads to

$$N \geq S \geq 2 \tag{7}$$

The total class number $K$ is defined as

$$K = 1 + \sum_{i=1}^{P} (K_i - 1)\, L_i \tag{8}$$

which corresponds to 1 plus the excess populations (over 1) summed over all states. This leads to

$$N \geq K \geq K_1 \geq 2 \tag{9}$$

As derived in Appendix A, the partition function for $N$ particles can be written as

$$Q(N) = \frac{1}{N!} q^N \left( 1 + \sum_{K=2}^{N} (\pm 1)^{K+1} X_K(N) \right) \tag{10$a$}$$

where

$$Q^{Cl}(N) = \frac{1}{N!} q^N \tag{10$b$}$$

is the classical partition function. The quantum corrections are

$$X_2(N) = \frac{N(N-1)}{2} b_2 \tag{10$c$}$$

$$b_2 = \frac{q_2}{q^2} \tag{10$d$}$$

$$X_3(N) = \frac{N(N-1)(N-2)}{3} b_3 + \frac{N(N-1)(N-2)(N-3)}{8} b_2^2 \tag{10$e$}$$

$$b_3 = \frac{q_3}{q^3} \tag{10f}$$

and the general case is

$$X_K(N) = f_K(N)b_K + f_{K-1,2}(N)b_{K-1}b_2 + \cdots + f_{K_1^{L1},K_2^{L2},\ldots,K_i^{Li},\ldots,K_P^{LP}}(N) \prod_{i=1}^{P} b_{K_i}^{Li} + \cdots \tag{11}$$

where the coefficient in the general term is

$$f_{K_1^{L1},K_2^{L2},\ldots,K_i^{Li},\ldots,K_P^{LFP}}(N) = \frac{N!}{(N-S)!} \frac{1}{\prod_{i=1}^{P} L_i! K_i^{Li}} \tag{12}$$

$$b_{Ki}^{Li} = \left(\frac{q_{K_i}}{q^{K_i}}\right)^{Li} \tag{13}$$

[$S$ is given by (6)]. The terminal term is

$$X_N(N) = f_N(N)b_N$$

with

$$f_N(N) = (N-1)!$$

Thus for any $N$, the partition function $Q(N)$ is analytically expressed in terms of $X_K(N)$, the summation of $K-$order quantum effects. Each term in (11) has an $f$ coefficient, which combines all combinational factors.

The coëfficient in (12) is a product of two factors:

$$\frac{N!}{S!(N-S)!}$$

is the number of ways for picking $S$ particles from the total of $N$ while

$$\frac{S!}{\prod_{i=1}^{P} K_i^{L_i}}$$

corrects for the number of equivalent ways of grouping these particles specifically into $(l_i \times K_i)$ sets and

$$\prod_{i=1}^{P} l_i!$$

corrects for the indistinguishibility among the groups with the same number of particles.

¿From the above conditions, we see that we can organize the $f$ coefficients for any $X_K(N)$ in the following way:

*(i.)* the first term has all $K$ particles in one state leading to $f_K(N)b_K$

*(ii.)* The second term has all $K-1$ particles in one state plus 2 in another leading to the term $f_{K-1,2}(N)b_{K-1}b_2$

*(iii.)* the third term has $K-2$ in one state with 3 in a second while the fourth has $K-2$ in one state and 2 in each of 2 others.

*(iv.)* This process continues as illustrated in Table 1.

Now we discuss the leading terms in (10)

*i.* the first term represents classical statistics. There are no quantum correlations since every particle is in a different state.

*ii.* The second term $X_2(N) = \frac{1}{2}N(N-1)b_2$ is the two-body quantum correlation;

*iii.* The third term $X_3(N)$ has two terms: $\frac{1}{3}N(N-1)(N-2)b_3$ is the three-body correlation, while $\frac{1}{8}N(N-1)(N-2)(N-3)b_2^2$ is the quantum correlation between two groups, each already having two-body quantum correlations. These two terms are grouped into $X_3(N)$ because both are $1/q^2$ order (if we assume that $q_K$ is about the same order as $q$ as shown later for the case of an ideal quantum gas case).

*iv.* Similarly, $X_4(N)$ has three terms, all of which have order of $1/q^3$.

## 3.0 Application to the Quantum Ideal Gas

Here we apply the above results to the calculation of the thermodynamic properties and the virial coefficients for the quantum ideal gas. Consider the canonical partition function $Q(N)$ in (10) truncated at $X_3$, namely up to the third order correlation.

$$\begin{aligned}Q(N) &= \frac{1}{N!}q^N\left[1 \pm X_2(N) + X_3(N)\right]\\ &= \frac{1}{N!}q^N\left[1 \pm \frac{1}{2}N(N-1)b_2 + \frac{1}{3}N(N-1)(N-2)b_3 + \frac{1}{8}N(N-1)(N-2)(N-3)b_2^2\right]\end{aligned}$$

we can write the single particle partition function as

$$q = \frac{V}{\Lambda^3},$$

where

$$\Lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}$$

In addition we obtain

$$q_2 = \frac{1}{2^{3/2}} q$$

$$q_3 = \frac{1}{3^{3/2}} q$$

In the ideal gas limit we can assume

$$X_3(N) << X_2(N) << 1$$

hence

$$\begin{aligned} lnQ(N) &= ln\left[\frac{1}{N!}q^N\right] + ln\left[1 \pm X_2(N) + X_3(N)\right] \\ &= ln\left[\frac{1}{N!}q^N\right] + ln\left[1 \pm X_2(N)\right] + ln\left[1 + \frac{X_3(N)}{1 \pm X_2(N)}\right] \\ &= ln\left[\frac{1}{N!}q^N\right] \pm X_2(N) + X_3(N) - \left[X_2(N)\right]^2 + 0(\Lambda^9) \\ &= ln\left[\frac{1}{N!}q^N\right] \pm \frac{N(N-1)}{2^{5/2}}\frac{\Lambda^3}{V} + N(N-1)\left[\frac{N-2}{3^{5/2}} - \frac{N-\frac{3}{2}}{16}\right]\left(\frac{\Lambda^3}{V}\right)^2 + 0(\Lambda^9) \end{aligned}$$

The free energy becomes

$$F = -k_B T \ln Q(N)$$

$$F = F^{class} \mp \frac{N(N-1)}{2^{5/2}}\frac{\Lambda^3}{V} k_B T - \left(\frac{N-2}{3^{5/2}} - \frac{N-\frac{3}{2}}{16}\right) N(N-1)\left(\frac{\Lambda^3}{V}\right)^2 k_B T$$

where

$$F^{class} = -k_B T \ln\left[\frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N\right]$$

The energy becomes

$$E = -\frac{\partial \ln Q(N)}{\partial \beta}$$

$$= E^{class} \mp \frac{3}{2^{7/2}} N(N-1)\frac{\Lambda^3}{V} k_B T - 3\left(\frac{N-2}{3^{5/2}} - \frac{N-\frac{3}{2}}{16}\right) N(N-1)\left(\frac{\Lambda^3}{V}\right)^2 k_B T$$

where

$$E^{class} = \frac{3}{2}Nk_BT$$

The entropy becomes

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$

$$= S^{class} \pm \frac{N(N-1)}{2^{7/2}}\frac{\Lambda^3}{V}k_B - 2\left(\frac{N-2}{3^{5/2}} - \frac{N-\frac{3}{2}}{16}\right)N(N-1)\left(\frac{\Lambda^3}{V}\right)^2 k_B$$

where

$$S^{class} = k_B \ln\left[\frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N\right] + \frac{3}{2}Nk_B$$

The heat capacity becomes

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = C_V^{class} \pm \frac{3}{2^{9/2}}N(N-1)\frac{\Lambda^3}{V}k_B + 6\left(\frac{N-2}{3^{5/2}} - \frac{N-\frac{3}{2}}{16}\right)N(N-1)\left(\frac{\Lambda^3}{V}\right)^2 k_B$$

where

$$C_V^{class} = \frac{3}{2}Nk_B$$

Thus the equation of state is

$$P = P^{class} \mp \frac{1}{2^{5/2}}N(N-1)\frac{\Lambda^3}{V^2}k_BT - 2\left(\frac{N-2}{3^{5/2}} - \frac{N-\frac{3}{2}}{16}\right)N(N-1)\frac{\Lambda^6}{V^3}k_BT$$

$$= P^{class} + B_2(T)\frac{N(N-1)k_BT}{V^2} + B_3(T)\frac{N(N-1)}{V^3}k_BT$$

where

$$P^{class} = \rho k_BT,$$

$\rho$ is the density, and

$$B_2(T) = \mp\frac{1}{2^{5/2}}\Lambda^3$$

$$B_3(T) = \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)\Lambda^6$$

are the corresponding second and third virial coefficients. These final results are just as derived from the grand canonical ensemble.[3] However we believe that the physical origins are clearer, this procedure allows any order virial coefficients to be calculated exactly by keeping higher order terms.

## References

1. P. Borrmann, G. Franke, J. Chem. Phys. 98, 2484 - 2445 (1993).
2. R. P. Feynman, Statistical Mechanics, W. A. Benjamin editor (Reading, Massachusetts, 1972).
3. D. A. McQuarrie, Statistical Mechanics, (Harper and Row, 1976).

## Appendix

Here we present additional details for deriving the canonical quantum statistical partition function. The basic tool is mathematical induction on the basis of the intuitive guess of the result. It works straightforward and elegantly. The Borrmann-Franke formula,[1]

$$Q(N) = \frac{1}{N} \sum_{K=1}^{N} (\pm 1)^{K+1} q_K Q(N-K) \qquad (A-1)$$

$$q_K = \sum_j e^{-K\beta\epsilon_j} \qquad (A-2)$$

expresses the partition function for $N$ particles into terms of a sum of partition functions of fewer particles. We want to derive the expression

$$Q(N) = \frac{1}{N!} q^N \left[ 1 + \sum_{K=2}^{N} (\pm 1)^{K+1} X_K(N) \right] \qquad (A-3)$$

where

$$Q^{cl} = \frac{1}{N!} q^N \qquad (A-4)$$

is the classical partition function and where $X_K(N)$ includes all corrections involving groups with $K$ particles or fewer per state. The general form we derive for $X_K(N)$ is

$$X_K(N) = f_K(N) b_K + f_{K-1,2}(N) b_{K-1} b_2 + \cdots + f_{K_1^{L_1}, K_2^{L_2}, \ldots, K_i^{l_i}, \ldots K_P^{L_P}}(N) \prod_{i=1}^{P} b_{K_i}^{l_i} + \ldots \qquad (A-5)$$

where the general numerical factor is

$$f_{K_1^{L_1}, K_2^{L_2}, \ldots, K_i^{L_i}, \ldots, K_P^{L_P}}(N) = \frac{N!}{(N-S)!} \cdot \frac{1}{\prod_{i=1}^{P} L_i! K_i^{L_i}} \qquad (A-6)$$

and

$$b_{Ki}^{L_i} = \left( \frac{q_{K_i}}{q^{Ki}} \right)^{L_i}$$

Here the general term involves $S$ particles in multiply occupied orbitals

$$N \geq S = \sum_{i=1}^{F} K_i L_i \geq 2 \qquad (A-7)$$

where $L_i$ is the number of cases with $K_i$ particles in the same level and where

$$N \geq K \geq K_1 \geq K_2 \geq ... \geq K_{l_i} \geq ... \geq K_F \geq 2 \qquad (A-8)$$

we can write

$$K - 1 = \sum_{i=1}^{P} (K_i - 1)\, L_i \qquad (A-9)$$

where the $L_i$ are positive integers,

$$L_i = 1, 2, ... \qquad (A-10)$$

The proof is carried out in two steps. First, we test the formula for the $N = 1, 2, 3$ cases. From (A-1) we have,

$$Q(0) = 1 \qquad (A-11)$$

$$Q(1) = q \qquad (A-12)$$

$$Q(2) = \frac{1}{2}q^2 \pm \frac{1}{2}q_2 = \frac{1}{2}q^2(1 \pm b_2) \qquad (A-13)$$

where

$$b_2 \equiv \frac{q_2}{q^2} \qquad (A-14)$$

$$Q(3) = \frac{1}{3}Q(2)q \pm \frac{1}{3}q_2 q + \frac{1}{3}q_3 = \frac{1}{6}q^3(1 \pm 3b_2 + 2b_3) \qquad (A-15)$$

where

$$b_3 = \frac{q_3}{q^3} \qquad (A-16)$$

¿From (A-3) we have,

$$Q(1) = q \qquad (A-17)$$

in agreement with (A-12). From (A-3) we obtain

$$Q(2) = \frac{1}{2}q^2\,(1 \pm X_2(2)) \qquad (A-18)$$

and (A-5) leads to

$$X_2(2) = \frac{2!}{0!} \cdot \frac{1}{2} \cdot b_2 = b_2 \qquad (A-19)$$

Substituting (A-19) into (A-18) leads to (A-13),

$$Q(2) = \frac{1}{2}q^2(1 \pm b_2) \qquad (A-20)$$

¿From (A-3) we obtain

$$Q(3) = \frac{1}{3!}q^3\left(1 \pm X_2(3) + X_3(3)\right) \qquad (A-21)$$

and (A-5) leads to

$$X_2(3) = \frac{3!}{1!} \cdot \frac{1}{2}b_2 = 3b_2 \qquad (A-22)$$

and

$$X_3(3) = \frac{3!}{0!} \cdot \frac{1}{3}b_3 = 2b_3 \qquad (A-23)$$

Substituting (A-22) and (A-23) into (A-21) leads to (A-15),

$$Q(3) = \frac{1}{6}q^3\left(1 \pm 3b_2 + 2b_3\right) \qquad (A-24)$$

Thus (A-3) with (A-5) is equivalent to (A-1) for $N = 1, 2, 3$ cases. Now we consider the general case from (A-3) we want to prove

$$Q(N+1) = \frac{1}{(N+1)!}q^{N+1}\left[1 + \sum_{K=2}^{N+1}(\pm 1)^{K+1}X_K(N+1)\right] \qquad (A-25)$$

where

$$\begin{aligned} X_K(N+1) =& f_K(N+1)b_K + f_{k-1,2}(N+1)b_{K-1}b_2 + ... + \\ & f_{K_1^{L_1},K_2^{L_2},...,K_i^{L_i},...,K_P^{L_P}}(N+1)\prod_{i=1}^{P} b_{K_i}^{L_i} + ... \end{aligned} \qquad (A-26)$$

and

$$f_{K_1^{L_1},K_2^{L_2},...,K_i^{L_i},...K_P^{L_P}}(N+1) = \frac{(N+1)!}{(N+1-S)!} \cdot \frac{1}{\prod_{i=1}^{P} L_i! K_i^{Li}} \qquad (A-27)$$

For any $M$, where $M < N+1$, we already have by induction that

$$Q(M) = \frac{1}{M!}q^M\left[1 + \sum_{j=2}^{M}(\pm 1)^{j+1}X_j(M)\right] \qquad (A-28)$$

where

$$X_j(M) = f_j(M)b_j + f_{j-1,2}(M)b_{j-1}b_2 + \cdots + \\ f_{j_1{}^{P_1}, j_2^{P_2}, \ldots, j_m^{P_m}, \ldots, j_G^{P_G}}(M) \prod_{m=1}^{G} b_{jm}^{Pm} + \ldots \qquad (A-29)$$

and

$$f_{j_1^{P_1}, j_2^{P_2}, \ldots, j_m^{P_m}, \ldots, j_G^{P_G}}(M) = \frac{M!}{(M-T)!} \cdot \frac{1}{\prod_{m=1}^{G} P_M! j_m^{P_m}} \qquad (A-30)$$

with

$$T = \sum_{m=1}^{G} j_m P_m \qquad (A-31)$$

Thus substituting (A-28)-(A-31) into (A-25) leads to

$$
\begin{aligned}
Q(N+1) = {} & \frac{1}{N+1}\left[Q(N)q \pm Q(N-1)q_2 + \cdots\right. \\
& \left. +(\pm 1)^{K+1} Q(N+1-K)q_K + \cdots + (\pm 1)^{N+2} q_{N+1}\right] \\
& = \frac{1}{N+1}\left\{\frac{1}{N!}q^{N+1}\left[1+\sum_{j=2}^{N}(\pm 1)^{j+1}X_j(N)\right]\right. \\
& \pm \frac{1}{(N-1)!}q^{N-1}q_2\left[1+\sum_{j=2}^{N-1}(\pm 1)^{j+1}X_j(N-1)\right] \\
& + \cdots + (\pm 1)^{K+1}\frac{1}{(N+1-K)!}q^{N+1-K}\cdot q_K\left[1+\sum_{j=2}^{N+1-K}(\pm 1)^{j+1}X_j(N+1-K)\right] \\
& \left. + \cdots + (\pm 1)^{N+2}\cdot q_{N+1}\right\} \\
& = \frac{1}{(N+1)!}q^{N+1}\left\{\left[1+\sum_{j=2}^{N}(\pm 1)^{j+1}X_j(N)\right] \pm Nb_2\left[1+\sum_{j=2}^{N-1}(\pm 1)^{j+1}X_j(N-1)\right]\right. \\
& + \cdots + (\pm 1)^{K+1}N(N-1)\cdots(N+2-K)b_K\left[1+\sum_{j=2}^{N+1-K}(\pm 1)^{j+1}X_j(N+1-K)\right] \\
& \left. + \cdots + (\pm 1)^{N+2}N!b_{N+1}\right\} \\
& = \frac{1}{(N+1)!}q^{N+1}\left\{1 \pm \left[X_2(N)+Nb_2\right] + \cdots\right. \\
& + (\pm 1)^{K+1}\left[X_K(N)+\sum_{j=2}^{K}N(N-1)\cdots(N-j+2)b_jX_{K-j+1}(N-j+1)\right] \\
& \left. + \cdots + (\pm 1)^{N+2}N!b_{N+1}\right\} \\
& = \frac{1}{(N+1)!}q^{N+1}\left\{1+\right. \\
& \left.\sum_{K=2}^{N+1}(\pm 1)^{K+1}\left[X_K(N)+\sum_{j=2}^{K}N(N-1)\cdots(N-j+2)b_jX_{K-j+1}(N-j+1)\right]\right\} \qquad (A-32)
\end{aligned}
$$

Thus the induction is proven if

$$X_K(N+1) = X_K(N) + \sum_{j=2}^{K} b_j \cdot N(N-1)\cdots(N+2-j)X_{K-j+1}(N-j+1) \quad (A-33)$$

or alternatively,

$$f_{K_1^{L1},K_2^{L2},\ldots,K_i^{Li},\ldots,K_P^{LP}}(N+1) = f_{K_1^{L1},K_2^{L2},\ldots,K_i^{l_i},\ldots,K_P^{LP}}(N) + \sum_{i=1}^{P} N(N-1)\cdots(N-K_i+2)f_{K_1{}^{L1},K_2^{L2},\ldots,K_i^{Li-1},\ldots K_P^{LP}}(N-K_1+ \quad (A-34)$$

Starting with the right hand side (RHS) of (A-34) we obtain

$$\begin{aligned}RHS &= \frac{N!}{(N-S)!} \cdot \frac{1}{\prod_{i=1}^{P} L_i!K_i^{Li}} + \\ &\sum_{i=1}^{P} N(N-1)\cdots(N-K_i+2)\frac{(N-K_i+1)!}{(N-K_i+1-S+K_i)!} \cdot \frac{K_i Li}{\prod_{i=1}^{P} L_i!K_i^{Li}} \\ &= \frac{N!}{(N-S)!}\frac{1}{\prod_{i=1}^{P} L_i!K_i^{Li}}\left[1+\frac{S}{N-S+1}\right] \\ &= \frac{(N+1)!}{(N+1-S)!}\frac{1}{\prod_{i=1}^{P} L_i!K_i^{Li}}\end{aligned}$$

This is exactly the expected $f$ coefficient for $Q(N+1)$. For the last term, the original formula leads to

$$f_{N+1}(N+1) = N!$$

QED

**Table 1.** Illustration of the sequence of terms in (10).

| | | | | | | |
|---|---|---|---|---|---|---|
| K | | | | | | |
| K-1 | 2 | | | | | |
| K-2 | 3 | | | | | |
| | 2 | 2 | | | | |
| K-3 | 4 | | | | | |
| | 3 | 2 | | | | |
| | 2 | 2 | 2 | | | |
| K-4 | 5 | | | | | |
| | 4 | 2 | | | | |
| | 3 | 3 | | | | |
| | 3 | 2 | 2 | | | |
| | 2 | 2 | 2 | 2 | | |
| K-5 | 6 | | | | | |
| | 5 | 2 | | | | |
| | 4 | 3 | | | | |
| | 4 | 2 | 2 | | | |
| | 3 | 3 | 2 | | | |
| | 3 | 2 | 2 | 2 | | |
| | 2 | 2 | 2 | 2 | 2 | |
| K-6 | 7 | | | | | |
| | 6 | 2 | | | | |
| | 5 | 3 | | | | |
| | 5 | 2 | 2 | | | |
| | 4 | 4 | | | | |
| | 4 | 3 | 2 | | | |
| | 4 | 2 | 2 | 2 | | |
| | 3 | 3 | 3 | | | |
| | 3 | 3 | 2 | 2 | | |
| | 3 | 2 | 2 | 2 | 2 | |
| | 2 | 2 | 2 | 2 | 2 | 2 |