

Nonextensivity and Nonintensity in Nanosystems: A Molecular Dynamics Simulation

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Using extensive molecular dynamics simulations, we have investigated the extensivity of the internal energy and entropy as well as the intensity of temperature and pressure in small thermodynamic systems. Atomic systems consisting of n^3 ($n = 2, 3, \dots, 10$) argon-like particles interacting through the Lennard-Jones potential energy function have been studied. It is found that in small systems, contrary to macroscopic systems, internal energy and entropy are nonextensive whereas temperature and pressure are nonintensive. These deviations from macroscopic thermodynamics, that continue to remain detectable even in systems containing as many as 1000 particles, are in agreement with theoretical predictions.

Keywords: Extensivity, Intensity, Thermodynamics, Nanosystems.

1. INTRODUCTION

This report is concerned with one of the important aspects of computational nanotechnology, namely thermodynamics and statistical mechanics of small systems to predict the properties and performances of nanoscale structures. A scientific and technological revolution has begun in our ability to systematically organize and manipulate matter on a bottom-up fashion starting from atomic level as well as design tools, machinery, and energy conversion devices in nanoscale towards the development of nanotechnology. There is also a parallel miniaturization activity to scale down large tools, machinery, and energy conversion systems to micro and nanoscales towards the same goals.¹⁻⁴ The science of miniaturization is being developed and the limitations in scaling down large systems to nanoscale are under investigation. Advancement and knowledge of the thermodynamics of small systems is essential to achieve these goals.

The principles of thermodynamics and statistical mechanics for macroscopic systems are well understood and mathematical relations between thermodynamic properties and molecular characteristics are derived. The basic principles of thermodynamics and statistical mechanics for

small systems have been recently formulated.⁵ This will help link the foundation of molecular based study of matter and the basis for nano science and technology. Development of predictive computational and modeling options for the behavior of nano systems will depend on advancements in their thermodynamics.

The subject of thermodynamics of small systems was first introduced by Hill in 1963 and 1964^{6,7} to deal with chemical thermodynamics of mixtures, colloidal particles, polymers, and macromolecules. Nanothermodynamics, a term recently introduced by Hill,⁸⁻¹⁰ is a revisitation of his original work on thermodynamics of small systems.

Significant accomplishments in the performance and changes of manufacturing paradigms are only possible with the advancement of principles of science of small systems including thermodynamics. The answer to the question of how soon will this next industrial revolution takes place depends largely on the intensity of such scientific activities.

The basic principles of thermodynamics for small systems, which are of interest to the field of nanotechnology, miniaturization, and the science of conversion of thermal energy to mechanical energy have been discussed in the literature.¹¹ The thermodynamics of a system in nanoscale is quite similar to that of a macroscopic system. Nevertheless, the validity of the relationships among various

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thermodynamic quantities that apply to macroscopic systems is an open question for small systems.

The simplest system in nanoscale is a single particle, such as an atom or a molecule, in a closed space with rigid boundaries. In the absence of any chemical reactions, the only process possible is the exchange of energy and momentum between the particle and the walls of the container. The state of this one-particle system at any time is specified by a point in the 6-dimensional configuration space consisting of its position and momentum coordinates. Likewise, for a system of N particles the state of the system at any time is specified by a point in the $6N$ -dimensional configuration space. The position of the point in the configuration space, which defines the set of $3N$ position coordinates and $3N$ momentum coordinates, completely determines all the thermodynamic properties of the system. For macroscopic systems, consisting of very large number of particles in equilibrium, these thermodynamic relations are already well established.¹²⁻¹⁴ For small systems, containing a limited number of particles, on the other hand, the thermodynamic relationships are yet to be established.

One of the important concepts in the thermodynamics of macroscopic systems is the number of independent variables, also known as the variance or the degree of freedom of the system. The number of independent variables is the smallest number of properties that must be specified in order to completely describe the entire thermodynamic state of the system. Among other differences, in small systems the number of independent variables is not the same as that for the corresponding macroscopic system.

Systems of interest to nanoscience and nanotechnology are isolated nanostructures and their assemblies, small droplets and bubbles, clusters, and fluids and solids confined in small regions of space like inside nanotubes and fullerene. Nano systems are larger than individual molecules but smaller than micro systems. One of the main characteristic features of nanosystems is their high surface-to-volume ratio. Furthermore, their electronic and magnetic properties are often distinguished by quantum mechanical behavior and their mechanical and thermal properties can be formulated within the framework of classical statistical mechanics of small systems⁶⁻¹⁰ and through the newly developed nonextensive statistical mechanics.¹¹

Small systems of interest in nanotechnology are generally made up of condensed matter of various kinds, soft or hard, organic or inorganic, and/or biological components. A deep understanding of the interactions between individual atoms and molecules composing the nanosystems and their statistical mechanical modeling is essential for nanotechnology.

The success of the predictive tools developed through statistical mechanics depends on two factors; the accuracy of the molecular and intermolecular interactions and properties, and the accuracy of the statistical mechanical

theory used for such calculations. Statistical mechanical prediction of the behavior of matter in macroscopic systems ($N \rightarrow \infty$, $V \rightarrow \infty$, N/V finite) is well developed and a variety of molecular-based theories and models are available for the prediction of the behavior of such systems. There is also a wealth of data available for thermodynamic and transport properties of matter for macroscopic systems, which can be used for testing and comparing the molecular based theories of matter in these systems. For small systems, on the other hand, there is little or no such data available and the molecular theories of matter in nanoscale are in their infancy. With the recent advent of tools to observe, study, and measure the behavior of matter in nanoscale it is expected that in the near future experimental nanoscale data will become available. In addition, computer simulation techniques have been proposed and used as a tool for the molecular based study of matter in nanoscale.

Statistical mechanics of small systems is not a new subject. Many investigators have studied small systems consisting of one or more macromolecule, droplets, bubbles, clusters, etc., utilizing the techniques of statistical mechanics.^{4,6-10} Computer simulation techniques such as Monte Carlo and molecular dynamics have been used extensively for such studies.^{15,16} However, a general analytical formalism of statistical mechanics for dealing with small systems and developing working equations for their thermodynamic properties, without regard to their nature, is still lacking.

Recent nanotechnology advances, both bottom-up and top-down approaches, have made it possible to envision complex and advanced systems, processes, reactors, storage tanks, machines, and other moving systems which include matter in all possible phases and phase transitions. There is a need to understand and develop analytic predictive models, for example, for the behavior of matter confined in a fullerene, or flowing in a nanotube at various pressures, temperatures, and compositions. For such diverse circumstances and for application of such components in the design of nanomachinery, the development of analytic predictive approaches of properties of matter in nanoscale is necessary to build accurate computational techniques to model such nanomachinery.

It is a well-known fact that the behavior of matter confined in nano-containers (inside a fullerene, in a nanotube, etc.) is a function of the environmental geometry, size, and wall effects that are surrounding it. This is not the case with macroscopic-scale matter where we are able to develop universal correlations and equations of state to be applied in all possible applications regardless of the geometry of the confining systems. For example the equation of state of water is universally needed for many applications including the use of water as working fluid in thermal to mechanical energy conversion devices, the use of water as the reagent or solvent in various chemical processes,

as well as oceanographic, meteorological, and geothermal applications and studies. However, the same equation of state for water may not be applicable to different small water systems. Furthermore, even if we compile such database for a particular nanosystem, the results may not be applicable to other nanosystems. This explains the need for a methodology for the development of universal analytic techniques of thermodynamic property relations in nanoscale. One prime approach for achieving this goal is the study of the extensivity and intensity of thermodynamic functions in small systems, which is the subject of this investigation.

2. EXTENSIVE AND INTENSIVE PARAMETERS

A function $f(x_1, x_2, \dots, x_n)$ is called homogeneous of degree λ in its arguments x_1, x_2, \dots, x_n if and only if¹⁷

$$f(hx_1, hx_2, \dots, hx_n) = h^\lambda f(x_1, x_2, \dots, x_n). \quad (1)$$

In other words, if every participating argument is scaled by h then the function itself is scaled by h^λ . Furthermore, it can be shown that if $f(x_1, x_2, \dots, x_n)$ is continuously differentiable, then

$$\sum_{i=1}^n x_i \frac{\partial f}{\partial x_i} = \lambda f(x_1, x_2, \dots, x_n) \quad (2)$$

which is known as the Euler's theorem on homogeneous functions. We, therefore, refer to λ in this article as the Euler exponent.

In macroscopic systems, a thermodynamic quantity is called *extensive* if it is homogeneous of degree one ($\lambda = 1$) and is called *intensive* if it is homogeneous of degree zero ($\lambda = 0$). Thus, internal energy and entropy are examples of extensive parameters whereas temperature and pressure are examples of intensive parameters. Therefore, if we change the size of the system by scaling V and N by the same factor (keeping everything else the same), the internal energy and entropy will change proportionally whereas temperature and pressure remain unchanged.

In nano systems the definition of extensivity and intensity based on the value of the Euler exponent λ loses its significance. Furthermore, definitions of the intensive properties such as temperature and pressure also lose their firmness due to large fluctuations. Accordingly, in small systems we need to propose a relation similar to Eq. (1) for extensive and intensive properties but with $\lambda \neq 1$ and $\lambda \neq 0$, respectively. In fact, the numerical value of λ may be non-integer or even negative and it may vary from system to system depending on their size and nature. Thus, if we change the size of the system by scaling V and N by the same factor (keeping everything else the same), extensive parameters will change inproportionately and intensive parameters will not be retained. This unusual behavior

of the Euler exponent in small systems stems from the fact that in such systems we are faced with a new class of thermodynamic properties which do not lend themselves to the usual mathematical and physical interpretations of the extensive and intensive properties of the macroscopic systems. Consequently, for determining λ some experimental data or reliable computations on the relevant properties of the small system under consideration need to be carried out.

3. MOLECULAR DYNAMICS SIMULATIONS

We have simulated systems of various number of identical particles in three dimension in microcanonical ensembles. The particles are argon-like of mass m , interacting according to the pairwise Lennard-Jones (6-12) (hereafter referred to as LJ) interatomic potential energy function,¹⁸

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3)$$

where ϵ is the depth of the potential and σ is the hard-core radius. The system is confined to a fixed volume V during the simulation. We did not use periodic boundary condition as surface effects are important in our calculations. Thus, particles are reflected elastically upon collision with the walls of the container. Since the interparticle collisions are also elastic, the internal energy of the system remains constant during each simulation.

In order to avoid computations with very small numbers, we adopted a reduced dimensionless system of units as follows:^{19,20} we choose the mass of the particles m to be the unit of mass, the hard-core radius of the potential energy function σ to be the unit of length, and the depth of the potential energy function ϵ to be the unit of energy. Thus, the units of mass, length, and energy are 6.63×10^{-26} kg, 3.40×10^{-10} m, and 1.67×10^{-21} J, respectively. Accordingly, in this system the units of time, speed, and pressure are $\sigma(m/\epsilon)^{1/2} = 2.14 \times 10^{-12}$ s, $(\epsilon/m)^{1/2} = 159$ m/s, and $\epsilon/\sigma^3 = 4.25 \times 10^7$ Pa = 419 atm, respectively.

The Boltzmann constant k has the units of energy divided by temperature. We define our unit of temperature, τ , such that Boltzmann constant becomes unity. Thus,

$$k = (1) \frac{\epsilon}{\tau}, \quad (4)$$

which gives

$$\tau = \frac{\epsilon}{k} = \frac{1.67 \times 10^{-21} \text{ J}}{1.381 \times 10^{-23} \text{ J/K}} = 121 \text{ K} \quad (5)$$

Since the unit of entropy is energy divided by temperature, in our system of units it will be $\epsilon/\tau = \epsilon/(\epsilon/k) = k$. Thus, the unit of entropy is the Boltzmann constant.

Finally, the Planck constant is given by,

$$h = 6.626 \times 10^{-34} \text{ J.s} \left(\frac{1\epsilon}{1.67 \times 10^{-21} \text{ J}} \right) \left[\frac{1\sigma(m/\epsilon)^{1/2}}{2.14 \times 10^{-12} \text{ s}} \right] = 0.185\sigma(m\epsilon)^{1/2} \quad (6)$$

Therefore, in our system of units the Planck constant has a value of 0.185.

The initial configuration of each system is generated by placing n^3 particles (where $n = 2, 3, 4, \dots, 10$) on a square lattice with a nearest neighbor distance of $2^{1/6}\sigma$. This choice of nearest neighbor distance corresponding to the equilibrium separation between two particles interacting according to LJ potential. Thus the initial interaction energy between each pair is simply $-\epsilon$. The particles are then randomly assigned a velocity of $\pm v$ in each spacial direction, while keeping the center of mass of the system at rest. Throughout our investigation we used a value of 0.1 reduced units for v . The simulations are carried out on a Pentium III platform in Fortran 77 environment. The equations of motion are solved using the velocity form of the Verlet algorithm^{19,20} with a time step of 0.001 reduced unit. Systems containing 8, 27, 64, 125, 216, 343, 512, 729, and 1000 particles were simulated.

The total internal energy of the system (kinetic plus potential) is accumulated and its average calculated after each time step. The temperature of the system is calculated by taking the time average of the mean kinetic energy per particle of the system²¹

$$kT = \frac{1}{3N} \sum_{i=1}^N m_i \overline{\mathbf{v}_i \cdot \mathbf{v}_i} \quad (7)$$

The pressure of the system is calculated using the direct definition of pressure, i.e., change of the momentum of the particles per unit time per unit area as a result of their collisions with the walls of the container. This direct method is more suitable as compared with the virial theorem when periodic boundary conditions are not used.

Although calculations of the internal energy, temperature, and pressure are straightforward, that of the entropy requires some discussion.

3.1. Computation of Entropy

According to the Boltzmann's definition, for an isolated system in equilibrium in microcanonical ensemble (N, V, E) , the entropy is given by²²

$$S = k \ln \Omega(N, V, E) \quad (8)$$

where k is the Boltzmann constant and $\Omega(N, V, E)$ is the number of discrete microstates in the configurational Γ -space consistent with (N, V, E) . This definition of entropy is based on the equal *a priori* postulate, which assumes that all microstates in the ensemble are equally

likely. Consequently, if $p(N, V, E)$ is the probability that the system is in a given microstate, we have $p(N, V, E) = 1/\Omega(N, V, E)$ and Eq. (8) can be written as

$$S = -k \ln p(N, V, E) \quad (9)$$

The entropy of any thermodynamic system in equilibrium is given by²³

$$S = -k \sum_i p_i \ln p_i \quad (10)$$

where p_i is the probability of the microstate i , and the summation is over all possible microstates compatible with the system. Equation (10) is quite general and does not resort to any particular system, thermodynamic constraint, or the equal *a priori* postulate. Hence in general the values of the various probabilities $\{p_i\}_{i=1,2,3,\dots}$ are not known, except for the normalization condition, $\sum_i p_i = 1$.

According to Eq. (10), the entropy of a system in equilibrium is, in general, equal to the *weighted* average of the natural logarithm of its microstate probabilities, multiplied by the Boltzmann constant,

$$S = -k \langle \ln p \rangle \quad (11)$$

If the generalized coordinates and momenta are independent of one another, we can decompose the probability of each microstate P_i into the product of the six probabilities in the direction of generalized coordinates and momenta (for example $x, y, z, mv_x, mv_y, mv_z$),

$$P_i = \prod_{n=1}^6 p_i^{(n)} \quad (12)$$

and Eq. (11) reduces to

$$S = -k \ln \left\langle \prod_{n=1}^6 p^{(n)} \right\rangle = -k \sum_{n=1}^6 \ln \left\langle p^{(n)} \right\rangle = -k \sum_{n=1}^6 \ln p^{(n)} \quad (13)$$

where $\ln p^{(n)}$ is the *weighted* average of the probabilities in the direction of the n -th generalized coordinate or momentum.

When two systems are combined, the number of microstates increases to $\Omega_A \Omega_B$ and, according to the Boltzmann's definition, Eq. (8), the entropy of the combined system is simply the sum of the entropies of its constituents. Therefore, the entropy should be an extensive parameter. We can show that this is also true for the extended definition of entropy, Eq. (10). If two systems are brought together, for each state $i (i = 1, 2, 3, \dots)$ of the first system there is a state $j (j = 1, 2, 3, \dots)$ of the second system. The probability of the first system (A) being in state i and the second system (B) being in state j is $p_i p_j$. Therefore, the entropy of the combined system, $S(A+B)$, is given by

$$S(A+B) = -k \sum_i \sum_j p_i p_j \ln(p_i p_j) = -k \sum_i \sum_j p_i p_j \ln p_i - k \sum_i \sum_j p_i p_j \ln p_j$$

$$\begin{aligned}
&= -k \sum_i \left(\sum_j p_j \right) p_i \ln p_i - k \sum_j \left(\sum_i p_i \right) p_j \ln p_j \\
&= -k \sum_i p_i \ln p_i - k \sum_j p_j \ln p_j \\
&= S(A) + S(B)
\end{aligned} \tag{14}$$

3.2. Evaluation of Entropy from the Trajectory of Motion

While many thermodynamic quantities of a system are easily calculated by molecular dynamics simulations, calculation of the total entropy from the trajectory in configuration space is still a subject of investigation. Recently, Peter et al.²⁶ suggested that the entropy of a thermodynamic system can be estimated from molecular dynamics simulations using the thermodynamic derivatives

$$S = - \left(\frac{\partial A}{\partial T} \right)_{N, V} = - \left(\frac{\partial G}{\partial T} \right)_{N, P} \tag{15}$$

where A and G are the Helmholtz free energy and the Gibbs free energy, respectively. Although this method appears to produce reliable results, we will not use it in our computation to estimate entropies. Instead we will directly compute, among other things, the entropy of the system in order to investigate the validity of the thermodynamic derivatives for small systems.

The entropy defined by Eq. (10) is also known as the information-theoretic entropy.²⁸ It has been suggested that although Eq. (10) is a basic formula in information theory, it should not be used in statistical mechanics to evaluate the entropy of a system from the trajectory of its particles.²⁵ The rationale here is as follows: in information theory i denotes a symbol and P_i is the probability of the appearance of that symbol in a message. Each symbol corresponds to a configuration in statistical mechanics and the appearance of the symbol in a message corresponds to the trajectory. In information theory the number of symbols is very small and the probabilities can be determined accurately. In statistical mechanics, on the other hand, the number of configurations is very large. Therefore, a computer simulation of the trajectory samples only a small fraction of the possible configurations. Instead, it has been suggested that entropy of a system in statistical mechanics should be calculated from the trajectory in the configuration space using the coincidence method.²⁵

Here we would like to comment on both techniques described above. First, the coincidence method is elegant and effective in discrete systems such as the Ising model. In a system with continuous configuration space and continuous trajectory, such as the velocity of particles in a gas, the method becomes ineffective simply because the probability of coincidence for a continuous random variable is always zero. Of course, one can always divide the configuration space into bins. However, depending on the bin

size chosen, the coincidence probabilities become somewhat arbitrary.

The second issue is that the portion of the configuration space that is sampled in a computer simulation of a statistical mechanical system, in addition to length of the simulation time, depends on the size of the system. Admittedly, for large systems one cannot sample a meaningful portion of the configuration space. But for small systems, such as those investigated in this work, the simulation does indeed sample the configuration space. This is evidenced by the fact that during the simulations the velocity distribution function of the particles of the system evolve into nearly perfect Maxwellian, as we shall see later.

Equations (8) and (10) can be used to calculate the entropy of a system as long as the number of microstates is finite. For continuous microstates, such as those involving positions and velocities of a classical gas, the number of microstates is infinite, thus Eqs. (8) and (10) return an infinite value for entropy. To avoid this difficulty, one can divide the continuous microstate space into bins. However, the question is how small should the bins be, because depending on the size of the bins one would obtain a different value for the entropy from Eqs. (8) and (10). Here quantum mechanics provides an answer for us. According to the Heisenberg's uncertainty relations,

$$\Delta q_i \Delta p_i \geq \frac{\hbar}{2} \tag{16}$$

where Δq_i and Δp_i are the uncertainties in any pair of conjugate coordinates and momenta and \hbar is the Planck's constant divided by 2π .²⁷ This sets the limit on the bin size if the entropy is to be meaningful.²⁸ Therefore, a reasonable choice of the bin size for each coordinate or momentum would be $\sqrt{\hbar}/2 = 0.1213$ reduced unit. In our simulations, we have used a bin size of 0.1 reduced units.

We can now explain how entropy is calculated in our simulations using the trajectory of the motion. For individual systems, we use Eq. (13). Thus, after every time step, the positions and velocities of the particles are accumulated in bins which are used later on to calculate the corresponding probabilities. When two such systems are combined, we use

$$S(A+B) = -k \sum_{n=1}^6 \ln p_{A(AB)}^{(n)} - k \sum_{n=1}^6 \ln p_{B(AB)}^{(n)} \tag{17}$$

where the subscripts $A(AB)$ and $B(AB)$ on the right hand side indicate evaluation of the designated quantities for the subsystem A and B after they are combined. More specifically, after every time step each particle is checked for its position. If the particle is located on the A -side of the combined system, it is assigned to subsystem A , otherwise it is assigned to subsystem B even though there is no physical boundary separating the two subsystem, as shown schematically in Figure 1.

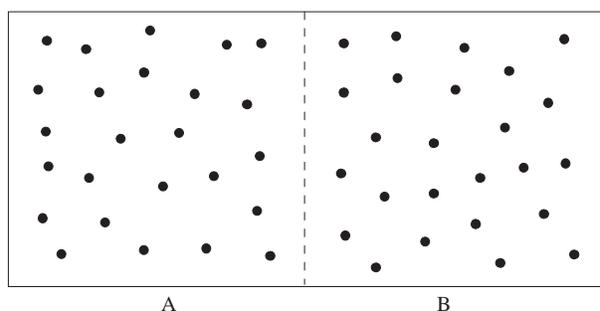


Fig. 1. A system hypothetically divided into two parts. Even though there is no physical partition separating the two subsystems *A* and *B*, if a particle is found in the left half of the system it is assigned to subsystem *A*, otherwise it is assigned to subsystem *B*.

4. RESULTS

Computer simulation results are obtained on cubic volumes containing 8, 27, 64, 125, 216, 343, 512, 729, and 1000 particles, using 200000 time steps in each case. In all cases studied, the internal energy of the system remained constant to a high degree of accuracy, ranging from 0.3% for the 8-particle system to less than 0.02% for the 1000-particle system. In all cases the system equilibrated fairly quickly. Figures 2 and 3 show the temperature and pressure of the 512-particle system as a function of time step. Ignoring the first 50000 time steps to allow for equilibration and using the next 150000 time steps, we find mean values of 0.553 ± 0.001 and 0.205 ± 0.001 reduced units,²⁹ respectively, for the temperature and pressure of the system. Figure 4 shows the *x*-component of the velocity distribution function for the same system. A graph of the Maxwell-Boltzmann distribution function,

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \quad (18)$$

corresponding to the temperature of the system (0.553 reduced units) is also shown for comparison. Clearly, the two are in excellent agreement.

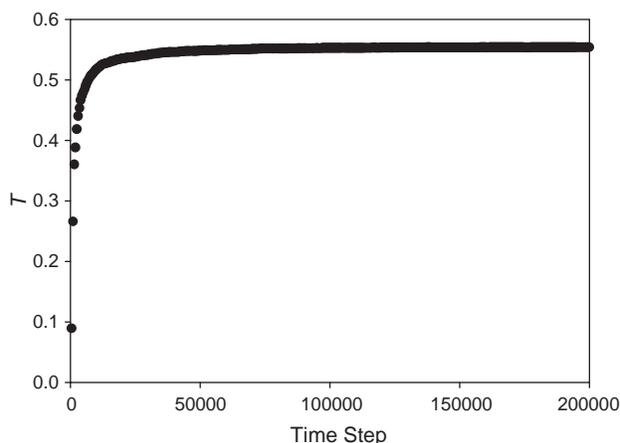


Fig. 2. Evolution of temperature during the simulation of a system of 512 particles.

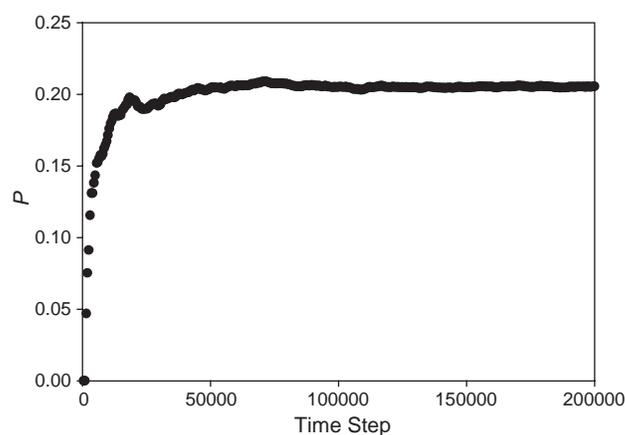


Fig. 3. Evolution of pressure during the simulation of a system of 512 particles.

In order to investigate the extensivity of the small systems with respect to internal energy, we plotted the internal energy of the systems as a function of the number of particle in Figure 5. If the internal energy is extensive, the plot must be a straight line with a slope equal to the internal energy per particle of the system. However, as can be seen from Figure 5, the plot of *E* as a function of *N* shows a slight upward curvature, indicative of a small nonextensivity in the internal energy. Indeed, a regression analysis of the data with respect to the function $-E = a + bN^\gamma$ gives $a = -19.3165$, $b = 2.8055$, $\gamma = 1.0668$, all in reduced units, with a correlation coefficient of better than 0.99999. Since $\gamma > 1$, the internal energy of the system is slightly subextensive (the internal energy of the combined system is more negative than it should be).

We continued further investigation of the extensivity of energy and entropy, as well as the intensity of temperature and pressure as follows: pairs of identical systems, each with 8, 27, 64, 125, 216, 343, 512, 729, and

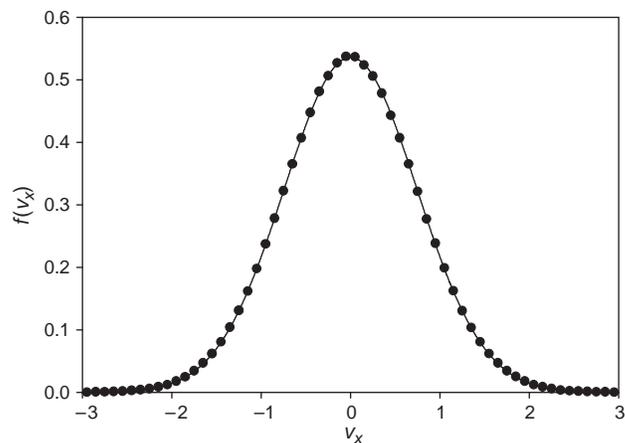


Fig. 4. The *x*-component of the velocity distribution function for a system of 512 particles. The dots are the molecular dynamics results and the continuous curve is the Maxwell-Boltzmann distribution corresponding to the temperature of the system.

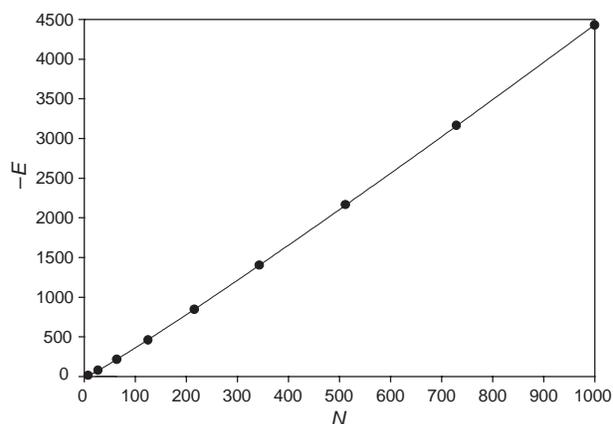


Fig. 5. Absolute value of internal energy as a function of particle number for systems consisting of cubic volumes with n^3 ($n = 2, 3, 4, \dots, 10$) particles. The dots are the computer simulation results and the solid line is the regression result $-E = -19.3165 + 2.8055N^{1.0668}$.

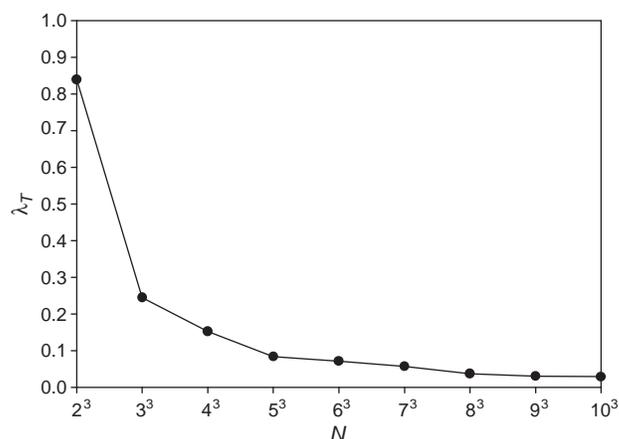


Fig. 8. Euler exponent for temperature as a function of system size. The straight line segments connecting the dots are aids to the eye only.

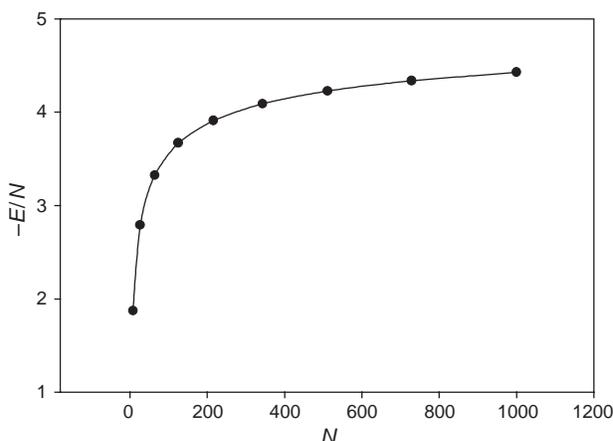


Fig. 6. Absolute value of internal energy per particle as a function of particle number for systems consisting of cubic volumes with n^3 ($n = 2, 3, 4, \dots, 10$) particles. The dots are the computer simulation results and the solid line is only an aid to the eye.

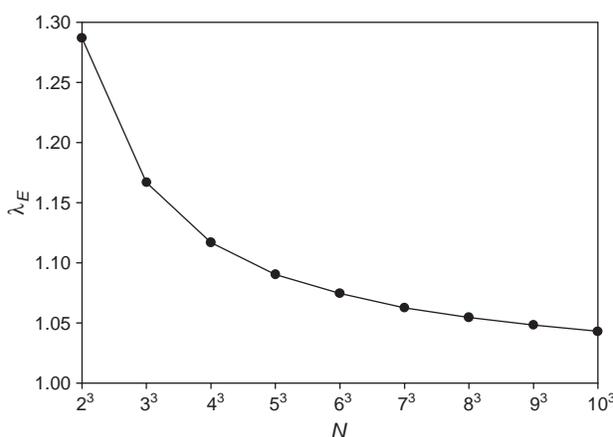


Fig. 7. Euler exponent for internal energy as a function of system size. The straight line segments connecting the dots are aids to the eye only.

1000 particles, respectively, were prepared. Each pair were not only identical in terms of (N, V, E) , but also identical in terms of the initial positions and velocities of the particles. We then investigated the thermodynamics of one of the members of each pair, as well as both members combined. The latter system was obtained by placing the two systems side by side and allowing them to combine. If E_1 and E_2 are the internal energies of one of the systems and both systems combined, extensivity of the internal energy requires that $E_2 = 2E_1$. Similarly, the extensivity of the entropy requires that $S_2 = 2S_1$. Furthermore, the intensivity of pressure and temperature requires that $P_2 = P_1$ and $T_2 = T_1$, respectively. Figures 7–10 show the results of our simulations for internal energy, temperature, entropy, and pressure, respectively, as a function of the size of the system. These results clearly indicate that in small systems internal energy and entropy are not extensive. Similarly, in small systems pressure and temperature are not intensive. As the size of the system increases, however, internal energy and entropy become extensive and pressure and

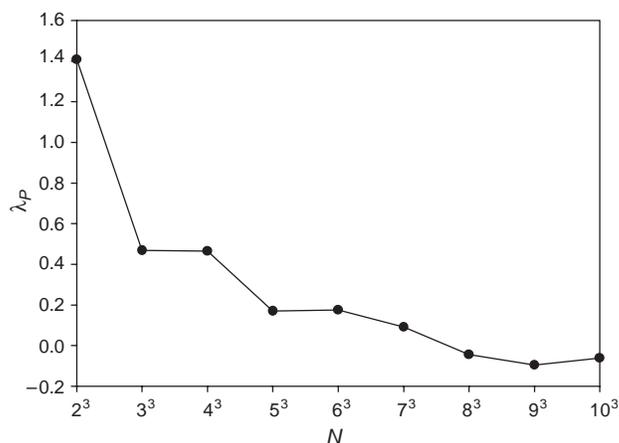


Fig. 9. Euler exponent for pressure as a function of system size. The straight line segments connecting the dots are aids to the eye only.

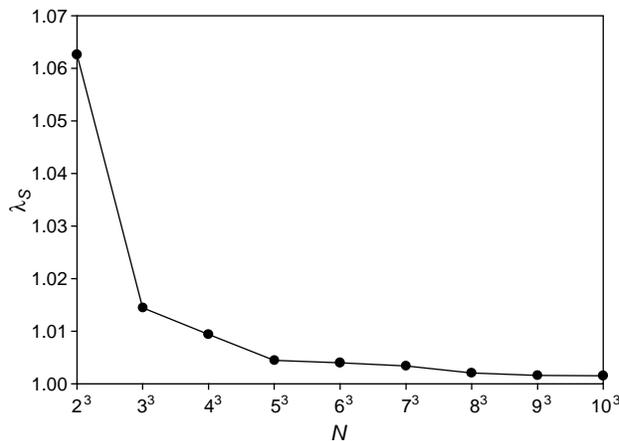


Fig. 10. Euler exponent for entropy as a function of system size. The straight line segments connecting the dots are aids to the eye only.

temperature become intensive. The reasons for these observations will be addressed in the next section.

5. DISCUSSION AND CONCLUSION

We now discuss the rationale behind the results obtained in our molecular dynamics investigation and interpret them.

5.1. Internal Energy

Figure 5 shows a plot of absolute value of the internal energy as a function of particle number for systems of cubic volume containing n^3 ($n = 2, 3, 4, \dots, 10$) particles. In all these systems the particles are located on a cubic lattice points and each particle has an initial velocity of magnitude $\sqrt{3}$ but randomly oriented while keeping the center of mass of the system at rest.

As the size of the system scales with the number of particles, the magnitude of the internal energy increases. Consider a cubic system of N particles. The number of particles that are located on the surface of the cube is approximately given by $N_s = CN^{2/3}$, where C is a constant. If we now add dN particles to the system while keeping the cubic shape of the system, it is straightforward to show that

$$\frac{dN_s}{N_s} = \frac{2}{3} \left(\frac{dN}{N} \right) \quad (19)$$

which simply states that the number of surface particles increases at a slower rate than the total number of particles, and hence the number of bulk particles. If they both increased at the same rate, then one would expect the plot in Figure 5 to be linear. But since this is not the case and the number of surface particles grows slower than the number of bulk particles and since each LJ pair interaction lowers the internal energy of the system and becomes more negative, the plot in Figure 5 is slightly concave upward. In other words, as the total number of particles increases, the internal energy of the system becomes slightly more

negative compared to a linear relationship. However, as the system becomes very large, this nonlinearity effect gradually fades out.

The above behavior of the dependence of internal energy on particle number becomes more evident if we plot the internal energy *per particle* as a function of particle number. This is shown in Figure 6. Since the ratio of the number of surface particles to that of total particles is proportional to $N^{1/3}$, for small N the energy per particle increases as surface contributions are large. As N increase, eventually every added particle goes into the bulk and the internal energy per particle asymptotically approaches a constant as in Figure 6.

Figure 7 shows the Euler exponent for internal energy when two exactly identical cubic systems are combined by placing them together side by side, as a function of particle number. The nonextensivity is relatively large for small systems but decreases and approaches zero as the size of the systems grows. Since the internal energy of the combined system is more negative than the sum of the internal energies of the two systems, it is subextensive. This behavior again is related to surface effects, as we shall explain below semi-quantitatively.

Consider a three-dimensional system of N particles in the form of a cube. The particles are initially on a simple-cubic lattice with LJ nearest-neighbor interactions among them. Out of N particles, there are $6N^{2/3}$ particles on the faces of the cube, $12N^{1/3}$ particles on the edges of the cube, and 8 particles on the corners. However, since some of the particles in each category are shared between more than one region, these numbers are reduced by some fraction in each case. Thus, there are $6\alpha N^{2/3}$, $12\beta N^{1/3}$, and 8γ particles, respectively, on the faces, edges, and corners of the cubic system, where α , β , and γ are each a positive number less than one but greater than zero. Therefore, the number of bulk particles would be $N - 6\alpha N^{2/3} - 12\beta N^{1/3} - 8\gamma$.

If the LJ interaction energy between two particles is $-\epsilon$, then the total internal energy of the system is given by

$$E = K - \frac{\epsilon}{2} \left[6(N - 6\alpha N^{2/3} - 12\beta N^{1/3} - 8\gamma) + 5(6\alpha N^{2/3}) + 4(12\beta N^{1/3}) + 3(8\gamma) \right] \quad (20)$$

where K is the total kinetic energy of the particles, and the factor 1/2 in front of the second term is introduced to avoid counting each interaction twice. Equation (20) simplifies to

$$E = K - 3N\epsilon \left(1 - \alpha N^{-1/3} - 4\beta N^{-2/3} - 4\gamma N^{-1} \right) \quad (21)$$

Suppose that we have two exactly identical but isolated (infinitely apart) such systems. The energy of each system is given by Eq. (21). If we bring the two systems together, the total internal energy of the combined system is given by $E_2 = 2E_1 + \delta E$, where E_2 is the internal energy

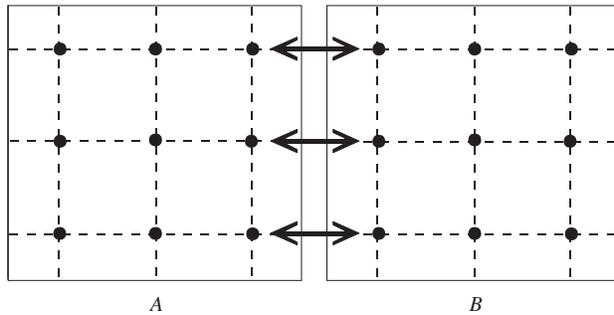


Fig. 11. When two systems combine, cross interactions of the particles, especially those near the joining region, reduce the internal potential energy of the combined system.

of the combined system and E_1 is that of each component. The additional energy, δE , comes from the interaction of the particles on near faces of the two systems that are placed together, as shown schematically in Figure 11. More specifically, some *external* potential energy is converted into internal energy. This energy is $\delta E = -N^{2/3}\epsilon$. Therefore,

$$E_2 = 2K - 6N\epsilon \left[1 + \left(\frac{1}{6} - \alpha \right) N^{-1/3} - 4\beta N^{-2/3} - 4\gamma N^{-1} \right] \quad (22)$$

As we can see, $E_2 \neq 2E_1$, and the system is nonextensive with respect to the total energy. The term $(-6N\epsilon) \cdot (\frac{1}{6}N^{-1/3}) = -\epsilon N^{2/3}$ on the right hand side of Eq. (22), which is a negative quantity, is the contribution to nonextensivity.

If we now increase the size of the system by increasing the number of particles of the system without bound, we can see from Eq. (21) that

$$E_1(\infty) = \lim_{N \rightarrow \infty} E_1 = K - 3N\epsilon \quad (23)$$

And from Eq. (22) we see that

$$E_2(\infty) = \lim_{N \rightarrow \infty} E_2 = 2K - 6N\epsilon = 2E_1(\infty) \quad (24)$$

Therefore, this simple analysis shows that a small system is nonextensive but as the size of the system increases, it eventually becomes extensive in the macroscopic limit, as it should.

5.2. Temperature and Pressure

Figure 8 shows that in small systems temperature is a nonintensive parameter. But as the number of particles increases, the nonintensity gradually fades out. For two identical systems each of 8 particles joining together, the temperature of the combined system is about 79% higher than the temperature of the constituent components. The difference decreases to about 2% when the number of particles in each system increases to 1000.

The increase in the temperature of the system can be explained as follows: when the two systems are brought

together, some of the external potential energy between the two systems³⁰ is transformed into the internal energy, making it more negative as we have seen in the previous section. This decrease of the internal energy becomes kinetic energy of the particles, thus increasing the temperature of the gas.

Similarly, Figure 9 shows that pressure is a nonintensive parameter in small systems. And, again as the size of the system grows, it becomes intensive. For the systems studied, when two identical systems with 8 particles each combined, the pressure of the new system was higher than that of the individual systems by about 165%. This difference dropped to near zero when each constituent system contained 1000 particles.

The increase in the pressure is attributed to the increase in the temperature of the system. At a higher temperature, the average speed and hence the average linear momentum of the particles is higher. Since pressure is the time rate of change of linear momentum of the particles per unit area as they collide with the walls of the container, it must increase when temperature increases.

5.3. Entropy

Figure 10 shows that entropy, like internal energy, becomes nonextensive in small systems. However, there are two differences here. First, the nonextensivity in the entropy is not as profound as in the internal energy. For two systems of 8 particles each combining, the nonextensive contribution to the entropy is only about 4.4% as compared to 22% for internal energy. Similarly, when the size of each system increases to 1000 particles, the nonextensivity of the entropy drops to about 0.10% as compared to 3.0% for internal energy. Second, while the internal energy decreased (became more negative) due to nonextensivity, the entropy increases and hence is superextensive.

The superextensivity of entropy in small systems can be explained as follows: because the temperature of the combined system is higher than that of the individual systems, each component of the velocity distribution functions widens and shortens slightly. Figure 12 shows the velocity distribution function in the x direction for one of the systems with 8 particles before the combination as well as after the combination. Before and after the combination, the temperatures of the systems are, respectively, 0.191 ± 0.002 and 0.342 ± 0.002 reduced units. The plots in Figure 12 are generated by using these temperatures in the one-dimensional Maxwell-Boltzmann distribution function, Eq. (18).³¹

In 1988 Tsallis introduced a new definition for entropy,^{32,33}

$$S_q = k \frac{1 - \sum_{i=1}^W p_i^q}{q - 1} \quad (25)$$

where $0 \leq q \leq 1$ ($q = 1$ in the sense of $q \rightarrow 1$). According to this definition, the entropy of the combination of

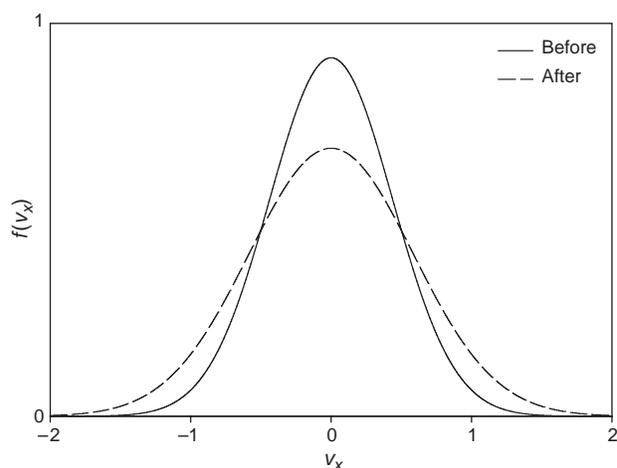


Fig. 12. The x -components of the velocity distribution functions for one of the 8-particle systems before and after the combination.

two systems A and B that are independent in the sense of the theory of probability, i.e., $p_{ij}(A+B) = p_i(A)p_j(B)$, is given by

$$S_q(A+B) = S_q(A) + S_q(B) + \frac{1-q}{k} S_q(A)S_q(B) \quad (26)$$

Therefore, the entropy as defined by Eq. (25) is nonextensive for $q < 1$, regardless of the size of the system. For $q = 1$ Tsallis's definition of entropy reduces to the Boltzmann-Gibbs definition and becomes extensive.

The nonextensivity of the entropy observed in this work for small systems is not a consequence of the Tsallis' definition. The entropies investigated here are all in the framework of the Boltzmann-Gibbs definition. Indeed, all the nonextensivities and nonintensities observed here are triggered by conversion of some of the external potential energy into the internal potential energy of the system, an effect that is significant only in small systems.

Based on the results of this investigation and in conclusion we observe that even in systems with as many as 1000 particles there are still some traces of deviation from extensivity and intensity of the thermodynamic quantities. Consequently, in simulating small systems one has to keep these effects in mind and special care has to be taken when new thermodynamic quantities (such as the heat capacities) are to be calculated from simulation results of some other quantities using the thermodynamic relations of macroscopic systems. Unless several thousand particles are simulated these effects remain significant, depending on the required accuracy of the calculations.

References

1. K. E. Drexler, *Nano systems: Molecular Machinery, Manufacturing and Computation*, Wiley, New York (1992).
2. M. C. Roco, S. Williams, and P. Alivisatos (Eds.), *Nanotechnology Research Directions: IWGN Workshop Report—Vision for Nanotechnology R&D in the Next Decade*, WTEC, Loyola College in Maryland, Baltimore (1999).
3. M. J. Madou, *Fundamentals of Microfabrication: The Science of Miniaturization*, CRC Press, Boca Raton, Florida (2002), 2nd ed.
4. G. A. Mansoori, in *Nanotechnology*, United Nations Tech Monitor, 53, (2002).
5. K. Esfarjani and G. A. Mansoori, in *Handbook of Theoretical and Computational Nanoscience and Nanotechnology* (Forthcoming) (2005).
6. T. L. Hill, *Thermodynamics of Small Small Systems*, Benjamin, New York (1963), Vol. I.
7. T. L. Hill, *Thermodynamics of Small Small Systems*, Benjamin, New York (1964), Vol. II.
8. T. L. Hill, *Nano Lett.* 1, 273 (2001).
9. T. L. Hill, *Nano Lett.* 1, 111 (2001).
10. T. L. Hill, *Nano Lett.* 1, 159 (2001).
11. G. A. Mansoori, *Principles of Nanotechnology: Molecular-Based Study of Condensed Matter in Small Systems* (Forthcoming) (2005).
12. J. M. Haile and G. A. Mansoori, (Eds.), *Molecular-Based Study of Fluids, Adv. Chem. Series*, 204, ACS, Washington D.C. (1983).
13. E. Matteoli and G. A. Mansoori, (Eds.), *Fluctuation Theory of Mixtures*, Taylor & Francis, London (1990).
14. D. A. McQuarrie, *Statistical Mechanics*, University Science Books, Herndon, VA (2000).
15. D. H. E. Gross, *Microcanonical Thermodynamics*, World Sci. Lect. Notes in Physics, 65, World Sci. Press, Hackensack, NJ (2001).
16. I. Brovchenko, A. Geiger, and A. Oleinikova, *J. Chem. Phys.* 120, 1958 (2004).
17. G. A. Korn and T. M. Korn, *Mathematical Handbook for Scientists and Engineers*, McGraw-Hill, New York (1968), 2nd ed., p. 99.
18. R. G. Mortimer, *Physical Chemistry*, Harcourt/Academic Press, San Diego (2000), 2nd ed., p. 346.
19. H. Gould and J. Tobochnik, *An Introduction to Computer Simulation Methods*, Addison Wesley, New York (1996), 2nd ed., pp. 123, 223–224.
20. P. Mohazzabi and L. Cumaranatunge, *Can. J. Phys.* 81, 1121 (2003).
21. H. Gould and J. Tobochnik, *An Introduction to Computer Simulation Methods*, Addison Wesley, New York (1996), 2nd ed., p. 230.
22. F. Mandl, *Statistical Physics*, Wiley, New York (1991), 2nd ed., p. 41.
23. F. Mandl, *Statistical Physics*, Wiley, New York (1991), 2nd ed., p. 61.
24. M. Plischke and B. Bergersen, *Equilibrium Statistical Physics*, Prentice-Hall, Englewood Cliffs, NJ (1989), p. 40.
25. Shang-Keng Ma, *Statistical Mechanics*, translated by M. K. Fung, World Scientific, Singapore (1985), pp. 426–429.
26. C. Peter, C. Oostenbrink, A. van Dorp, and W. F. van Gunsteren, *J. Chem. Phys.* 120, 2652 (2004).
27. E. Merzbacher, *Quantum Mechanics*, Wiley, New York (1998), 3rd ed., p. 219.
28. M. Plischke and B. Bergersen, *Equilibrium Statistical Physics*, Prentice Hall, Englewood Cliffs, NJ (1989), p. 41.
29. The uncertainties here are the standard deviations of the data themselves, not of the means. The standard deviations of the means are much smaller.
30. This is the interaction potential energy between particles of system A and particles of system B .
31. The actual velocity distribution data are in excellent agreement with these plots.
32. C. Tsallis, *J. Stat. Phys.* 52, 479 (1988).
33. G. R. Vakili-Nezhaad and G. A. Mansoori, *J. Comput. Theor. Nanosci.* 1, 233 (2004).