

Model hysteresis dimer molecule II: deductions from probability profile due to system coordinates

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The hysteresis dimer reaction of the first sequel is applied to test the Gibbs density-in-phase hypothesis for a canonical distribution at equilibrium. The probability distribution of variously defined internal and external variables is probed using the algorithms described, in particular the novel probing of the energy states of a labeled particle where it is found that there is compliance with the Gibbs' hypothesis for the stated equilibrium condition and where the probability data strongly suggests that an extended equipartition principle may be formulated for some specific molecular coordinates, whose equipartition temperature does not equal the mean system temperature and a conjecture concerning which coordinates may be suitable is provided. Evidence of violations to the mesoscopic nonequilibrium thermodynamics (MNET) assumptions used without clear qualifications for a canonical distribution for internal variables are described, and possible reasons outlined, where it is found that the free dimer and atom particle kinetic energy distributions agree fully with Maxwell–Boltzmann statistics but the distribution for the relative kinetic energy of bonded atoms does not. The principle of local equilibrium (PLE) commonly used in nonequilibrium theories to model irreversible systems is investigated through NEMD simulation at extreme conditions of bond formation and breakup at the reservoir ends in the presence of a temperature gradient, where for this study a simple and novel difference equation algorithm to test the divergence theorem for mass conservation is utilized, where mass is found to be conserved from the algorithm in the presence of flux currents, in contradiction to at least one aspect of PLE in the linear domain. It is concluded therefore that this principle can be a good approximation at best, corroborating previous purely theoretical results derived from the generalized Clausius Inequality, which proved that the PLE cannot be an exact principle for nonequilibrium systems.

KEY WORDS: kinetic energy probability profile, Gibbs ensemble hypotheses, extended equipartition principle, NEMD, principle of local equilibrium, Clausius inequality

AMS mathematical classification (2000): 65-{04,Z05}, 68-{04,W01}, 70-{08,F01,F16}

1. Introduction

The previous sequel provided details of the method and characteristics of the dimer reaction system



where k_1 and k_{-1} are the respective rate constants. The methods used to ensure accuracy and convergence of results for the time steps used were also discussed in that sequel. In this work, the system is probed for probability distribution functions, and an NEMD simulation of the dimer system is also carried out to study the applicability of one aspect of PLE. The details of the principle of local equilibrium computations, together with the precautions used to ensure reproducibility of results are discussed in [1]. Indeed, for the NEMD portion, the verification here of conservation of mass can only imply convergence of the system to a steady state. Comparisons between the theoretical Maxwell distribution to that derived from equilibrium simulations is carried out in section 2 because fundamental deductions can be made concerning the theory and applications of the canonical distribution. Additional results are presented in section 3 from NEMD using a novel difference equation which can be used to check for conservation of matter. Here, it is found that current fluxes exist in regions when this would not be expected according to one aspect of PLE. The NEMD runs were used to ascertain whether PLE is indeed a principle or merely a good approximation for describing general thermodynamical systems (whether reversible or not). It is concluded that simulations provide examples that go beyond linear and local equilibrium theories.

2. Probability histograms

These are provided in figures 1–7 for the translational kinetic energies of the different species probed as well as the total internal energy of the dimer, plotted with the Maxwell distribution relative to the apparent temperature determined from (4). The comparisons provide clues to the following:

- Shape of the probability function P could perhaps be used to determine whether the assumptions used in theories are reasonable or not. The shape even for this equilibrium system is not always Gaussian, and so there is no reason to assume *a priori* that nonequilibrium systems must conform to a Gaussian distribution where certain internal variables are concerned.
- Provide a rationale for extending the theory of equipartition in an equilibrium system where the temperature relative to a particular kinetic

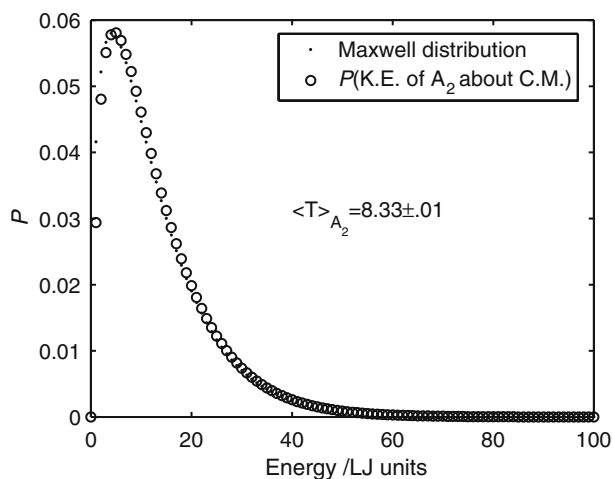


Figure 1. P function for translational kinetic energy of A_2 about C.M. at system temperature $T_{\text{set}}^* = 8.0$ and $\rho = 0.7$, with apparent temperature of molecule indicated.

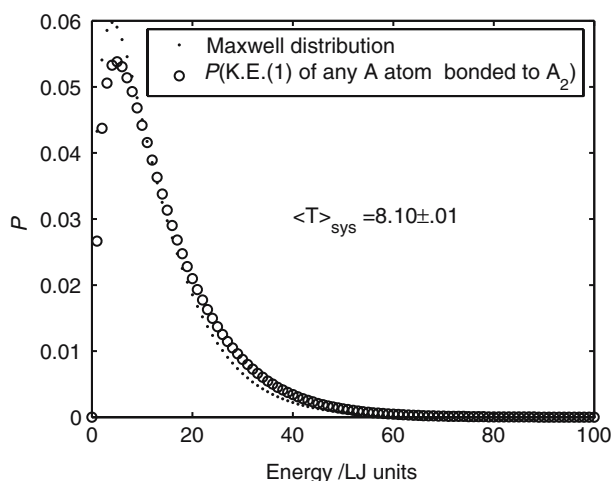


Figure 2. P function for kinetic energy of any atom A bonded to A_2 at system temperature $T_{\text{set}}^* = 8.0$ and $\rho = 0.7$. The apparent nonBoltzmann kinetic energy temperature of these bonded atoms is $\langle T \rangle_{\text{kin}} = 8.10 \pm 0.01$.

energy coordinate is not the same as for the total system temperature determined from standard equipartition. Such a possibility seems to be supported by the evidence below.

The method of determining these probability histograms involve sampling at each time step the respective quantities, binning the values of the particular distribution, followed by normalization. Such a method ensures that an accuracy

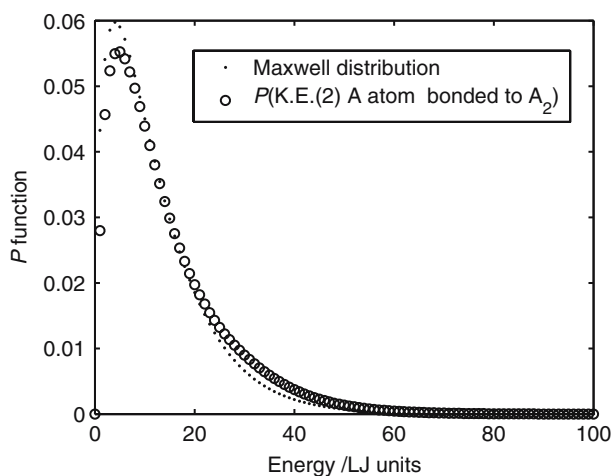


Figure 3. P function for average kinetic energy of atom A by K.E.(2) method at system temperature $T_{\text{set}}^* = 8.0$ and $\rho = 0.7$ with total system temperature indicated where apparent nonBoltzmann kinetic energy temperature of these bonded atoms is $\langle T \rangle_{\text{kin}} = 8.10 \pm 0.01$.

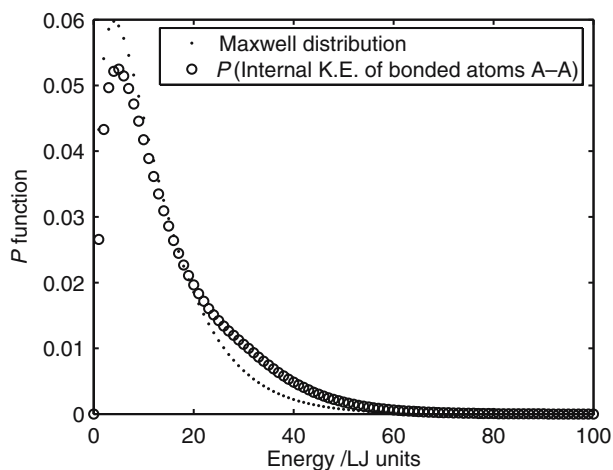


Figure 4. P function for total IKE of the two bonded A atoms about the internuclear axis at system temperature $T_{\text{set}}^* = 8.0$ and $\rho = 0.7$.

is obtained that is able, for instance, to discriminate between the different apparent species temperatures. For a given Hamiltonian \mathcal{H} weakly coupled to a heat bath written

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \mathcal{V}(r_1, r_2, \dots, r_n), \quad (2)$$

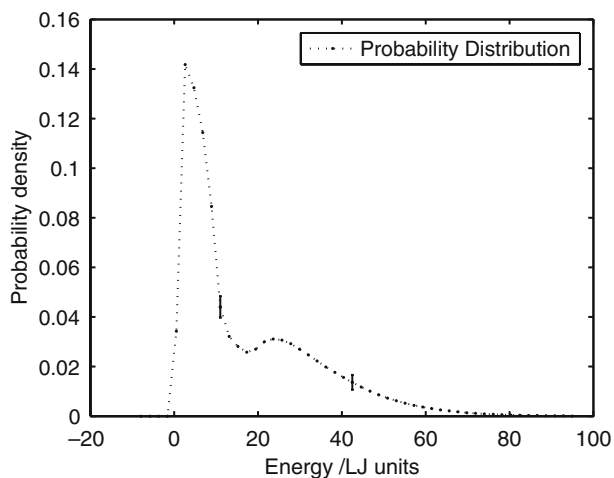


Figure 5. The TIEC distribution as given in the text. The error bars are for 100 standard error units at $T_{\text{set}}^* = 8.0$ and $\rho = 0.7$.

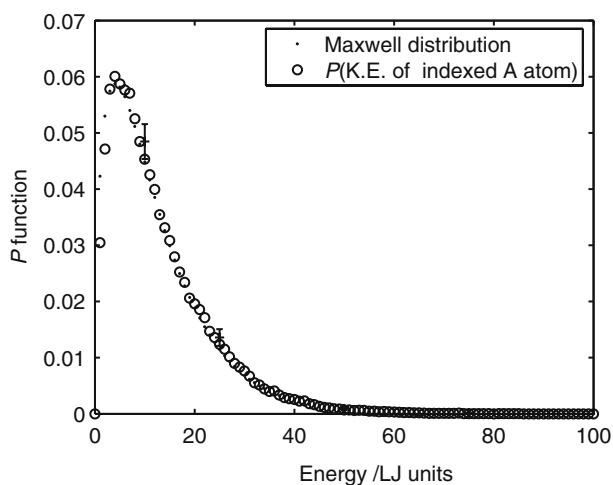


Figure 6. P function for kinetic energy of fixed indexed atom A , which either is bonded to some A_2 dimer or not at system temperature $T_{\text{set}}^* = 8.0$ and $\rho = 0.7$ with apparent temperature of atom $\langle T \rangle_{\text{atom}} = 8.1 \pm 0.2$. The uncertainty here is three standard error units.

where \mathcal{V} is the potential that is position variable \mathbf{r} dependent, the probability density function per unit area of phase space (\mathbf{p}, \mathbf{q}) is

$$\mathcal{P}(\mathbf{p}, \mathbf{q}) = \frac{\exp -\beta\mathcal{H}}{\mathcal{Z}}, \quad (3)$$

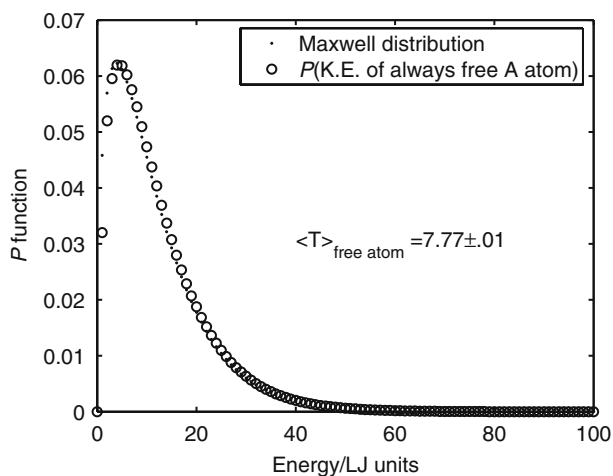


Figure 7. P function for kinetic energy of free (unbonded) random atom at system temperature $T_{\text{set}}^* = 8.0$ and $\rho = 0.7$ with apparent temperature of random atom indicated.

where the partition function \mathcal{Z} has the form

$$\mathcal{Z} = \frac{\int e^{-\beta\mathcal{H}} d\mathbf{p} d\mathbf{r}}{N!}.$$

The separability of the Hamiltonian above for the momentum \mathbf{p} and position variables \mathbf{r} , which is of the same form as our chemical system Hamiltonian (augmented by switches) leads for large N to the exact result [in 3-dimensional (3-D) systems] (usual laboratory units)

$$N \left(\frac{3kT}{2} \right) = \overline{\sum_i p_i^2 / (2m_i)}, \quad (4)$$

which is the method used to determine the system temperature here. The momentum coordinates p_i refer to all atomic species, whether bonded or not. The Gibbs postulate can be directly tested for the chemical reaction system to verify whether or not the switching mechanism modifies or contradicts the postulate, which refers to the time average of a system property being equal to the ensemble average when these limits exist. Experimentally (Figure 6), it is found that switches in nonsingle-valued Hamiltonians *does not* affect the Gibbs postulate. Furthermore, over the time of the simulation, for the indexed particle I , the following (3-D) result must hold so that the particle and system temperature is defined:

$$3kT_I/2 = \left\langle p_I^2 / (2m_I) \right\rangle, \quad (5)$$

where the brackets represents the time average. It is found that the temperature T_t above of this single indexed particle coincides with the mean system temperature whether the particle is bonded or not over the trajectory equally weighted in time for all the states that it traverses. Integrating the \mathcal{P} function in (3) over all equal energy values, the Maxwellian probability density function results, and is given per unit energy increment by

$$P = 2\pi \left(\frac{1}{\pi} kT \right)^{3/2} \epsilon^{1/2} \exp - \left(\frac{\epsilon}{kT} \right). \quad (6)$$

Equation (6) is the standard form used for the absolute velocity distribution function. The above form is still derived from the quantum probability operator/function

$$\hat{P}(\Omega) \propto \exp -\beta \hat{H}(\mathbf{p}, \mathbf{q}), \quad (7)$$

where the phase space is averaged over equi-energy surfaces. Equation (7) also makes the definition of the partition function Q possible as

$$Q = \sum_i \omega_i \exp -\beta E_i(\mathbf{p}, \mathbf{q})$$

for a system where even for Q , (\mathbf{p}, \mathbf{q}) represents the canonical coordinates only. The Gibbsian and other thermodynamical state functions are derived strictly from operations on Q , e.g. $U = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{V,N}$ for the energy and $P = kT \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N}$ for the pressure. Other internal coordinates cannot (unless proved otherwise) give rise to state functions where standard statistical mechanics is concerned.

An apparent temperature parameter $\langle T \rangle_X$ is computed here for some species X and is defined such that

$$\frac{3 \langle T \rangle_X}{2} = \left\langle \frac{p_X^2}{2m_X} \right\rangle, \quad (8)$$

where m_X is the mass of species X and p_X is its momentum variable. This parameter is clearly not well defined as a temperature if it does not obey the equipartition result above for the obvious reasons connected to conjugate transforms. In statistical thermodynamics, the total system Hamiltonian

$$\mathcal{H} = \sum_{i=1}^m p_i^2/2m + \sum_{i<j} V(r_i - r_j) \quad (9)$$

leads to the density-in-phase having form

$$\rho(\mathbf{p}, \mathbf{q}) \propto \exp[-\mathcal{H}(\mathbf{p}, \mathbf{q})/kT] \quad (10)$$

and so for systems with separable coordinates, each kinetic energy coordinate $E_{k,i} = p_i^2/2m$ and potential form $V(|r_i - r_j|)$ will have the above Boltzmann distribution. The (\mathbf{p}, \mathbf{q}) coordinates are termed “canonical” and equipartition and the distribution laws are derived relative to these coordinates only [2].

However, the “internal coordinates” during a chemical reaction or other process refer to an artificial aggregation – meaning they are transient species – such as the center of mass (C.M.) velocity and position for particles k, l forming a molecule which is not permanent, e.g. $\mathbf{P}_j = \mathbf{p}_k + \mathbf{p}_l$ ($k \neq l$), $\mathbf{R}_j = \frac{1}{m_k + m_l} (\mathbf{r}_k + \mathbf{r}_l)$ and so these are not canonical coordinates in the defined sense [2] and there is no immediate reason *a priori* that these coordinates for the internal energy or potential must have Boltzmannized distributions. It could well be that if the mean lifetime τ of the species obeyed $\tau \rightarrow \infty$, then they might qualify as a pseudo-canonical variable, but a theory for such limits does not seem available. Permanent aggregated states can be expressed in terms of canonical transformations $\mathbf{Q} = \mathbf{Q}(\mathbf{p}, \mathbf{q})$, $\mathbf{P} = (\mathbf{p}, \mathbf{q})$ [2, Chap. VII] and the new Hamiltonian that results must by ensemble theory be subjected to the density distribution described above. But for systems which are described by “internal” coordinates of a nonpermanent nature (in the sense that the forces between the particles cease when the molecule decomposes) and which does not refer to the system Hamiltonian, no general theory exists, and no presuppositions can be made regarding their density distributions. It may be remarked that in statistical mechanics for canonical distributions, average quantities \bar{M} (corresponding to classical thermodynamical state functions) are defined as $\bar{M} = \sum_{i=1}^N M_i P_i$, where P_i is the probability of state i with value M_i . The partition function $Q = \sum_{i=1}^N g_i \exp -\frac{\epsilon_i(\mathbf{p}, \mathbf{q})}{kT}$ for the system has been defined so that operations on it $\hat{O}_M[Q]$ yields the average value for property M [3, p. 422], e.g.

$$\hat{O}_E[Q] = NkT^2 \frac{d \ln Q}{dT} = \bar{E} \quad (11)$$

yields the total energy due to translational kinetic energy for systems that conform to the canonical probability law. It follows that the density-in-phase are correlated to the (\mathbf{p}, \mathbf{q}) phase space volume elements, and that the canonical (\mathbf{p}, \mathbf{q}) coordinates or their equivalents are central to the above procedure. Clearly, when the process defined by the coordinates are not canonical, then it is not in general correct to insist *by necessity* that any coordinate combination is “self-similar” to a canonical coordinate set, with a canonical probability distribution. Nevertheless, theories purporting to be fundamental have been created that *assumes* the Gaussian density for internal variables to be true [4,5] without clear qualification concerning the situation when this condition obtains. For instance the Gibbs energy and all other thermodynamical state functions are derived from the partition function through averaging with the canonical distribution, which pertains to the entire system taken as a whole; to infer that each microscopic portion of the system at a

particular phase-space coordinate is necessarily self-similar to the whole is incorrect, as a few counter-examples to this proposition follows below (figures 2–4). Furthermore, the PLE has been proposed as essential [4] for these new theories, and another counter-example to this is also provided, this time from a NEMD simulation. In other words, basic simulation is able to determine the veracity of theories, and in particular, the hysteresis system described here does not support the novel theoretical developments in “mesoscopic” level thermodynamics. The total internal energy coordinate (TIEC) and the internal kinetic energy coordinate (IKE) are not Gaussian distributions for equilibrium systems according to the simulation results below. Of great theoretical interest is that for cases of non-permanent coordinates, some types of distributions are essentially Boltzmannized, others are not, even for an equilibrium system. It would be of great significance and interest to provide criteria which can predict when a Boltzmann distribution can be expected. The apparent temperature parameter $\langle T \rangle_X$ may well qualify as a temperature in an extended equipartition scheme if there is agreement with the Maxwellian distribution *even if this temperature does not correspond to the unique system temperature* $\langle T \rangle_{\text{sys}}$. Here the degree of agreement with the Maxwell distribution is either very good (in some cases), or rather bad. It would be of great theoretical interest if some form of relationship between the apparent temperatures could be made on the basis of internal energetics. The uncertainty (unless stated otherwise) is of the order as given in the error bars of figure 5, which is at 100 standard error units and which would not feature in any figure where errors are typically quoted at three standard error units. This figure corresponds to the TIEC distribution. The errors in the temperature are given in figures 1–7. Figure 1 shows that the C.M. kinetic energy follows quite accurately a Maxwellian P function with a temperature parameter *higher* ($T^* = 8.33$) than the system temperature ($T_{\text{set}}^* = 8.0$). The fact that the shape is Maxwellian at the indicated temperature parameter does seem to imply that theories may be developed *within* an equilibrium system with different coexisting temperatures provided that these parameters require that a Maxwellian form regarding shape prevails, and after that stage one perhaps might also be able to propose generalizations to temperature not requiring a Maxwellian distribution; but a proper theory would have to begin from first principles which can subsume without contradiction the previous axiomatics, including the Zeroth Law. Another inference is that these nonstandard “temperatures” have definite values (or limits), where the degree of scattering is relatively low; hence one might expect some type of stochastic averaging which yields exact values (limits). How these averages are performed, and the theoretical justification for these averages remain significant challenges. The other important scientific question is the explanation of the shift of “temperature” $\langle T \rangle_X$ for such Boltzmann distributions for nonpermanent aggregates.

An atom bonded to a molecule does not have a clear Maxwellian shape, as is evident from figures 2 and 3 since there is interference from the internuclear potentials. The graph in figure 2 computes the absolute kinetic energy (AKE)

(also denoted K.E.(1)) of the particle with respect to the MD cell, whereas figure 3 refers to half the relative kinetic energy and half the translational kinetic energy about the C.M. of the bonded pair, where the relative kinetic energy $\epsilon_{k.e.rel.}$, is written as

$$\epsilon_{k.e.rel.} = \frac{1}{2}\mu(\dot{\mathbf{r}}_1 - \dot{\mathbf{r}}_2)^2 = \frac{1}{2}\mu\dot{\mathbf{r}}^2 \quad (12)$$

for any two bonded atoms 1 and 2, where the reduced mass μ is given as $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ and where the intermolecular axis vector is $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. The total IKE is also defined as the relative kinetic energy of a bonded pair, given as $\epsilon_{k.e.rel.}$ as above. The AKE averages

$$\frac{1}{2} \cdot \frac{1}{2}(\mathbf{v}_1 - \mathbf{v}_2)^2 = \frac{1}{4} \left\{ \mathbf{v}_1^2 + \mathbf{v}_2^2 - \mathbf{v}_1 \cdot \mathbf{v}_2 \right\},$$

whereas the kinetic energy about the C.M. (KCM) averages the expression

$$\frac{1}{2} \cdot 2 \frac{(\mathbf{v}_1 + \mathbf{v}_2)^2}{2^2} = \frac{1}{4} \left\{ \mathbf{v}_1^2 + \mathbf{v}_2^2 + \mathbf{v}_1 \cdot \mathbf{v}_2 \right\}.$$

Adding these expressions and then dividing by 2 would lead to convergence of the result to that for AKE, which is what is presented in figure 3 as K.E.(2), which is almost the same graph as for figure 2. The reason for this computation was to check for consistency of result for the two different sampling techniques.

The IKE distribution, that of an internal coordinate, is clearly non-Gaussian, as depicted in figure 4. This result is not consistent with the assumptions of mesoscopic nonequilibrium thermodynamics [4,5].

TIEC defined above refers essentially to the vibrational and rotational kinetic energy of the molecule E_{tiec} since the translational kinetic energy about the C.M. has been factored away where

$$E_{tiec} = V(|\mathbf{r}_i - \mathbf{r}_j|) + \frac{\mu\dot{\mathbf{r}}^2}{2}, \quad (13)$$

where $V(|\mathbf{r}_i - \mathbf{r}_j|) = u_0 + \frac{1}{2}k(r - r_0)^2$. Hence the intermolecular potential would play an important part in determining the motion along the internuclear axis, with the environmental potential due to other particles playing a moderating role by introducing stochasticity to an otherwise plainly mechanical system. The probability of occurrence of a state is proportional to the time spent at any configuration according to Gibbs, and with a harmonic potential, most of the time spent will be at the turning points in simple harmonic motion (SHM). In the molecular potential used there is a "dissociation hump" just prior to the dissociation limit, leading to a departure from the Maxwell (M) distribution; other reasons for departure from the M distribution include the dissociation itself, precluding higher energy states from being accessed. It is clear that the distribution in figure 5 is non-Maxwellian and corresponds faintly with the shape of

the molecular potential energy function, with its humped potential near the distance of dissociation. SHM in conjunction with permanent canonical coordinates has been used as a classic description of equipartition. If the particles were bonded permanently, this quantity would have a canonical distribution, which it clearly does not because bonds are formed and broken at a rate that precludes adjustment to a Gaussian probability factor. This distribution, which also refers to an internal coordinate for total internal molecular energy, is not consistent with some recent nonequilibrium theories [4,5], which assumes without proof that these Gaussian factors must obtain.

Noting that the accuracy of the single particle is reduced by a factor of ≈ 4000 (the number of particles in this simulation), we find that the Gibbs postulate seems to be verified in terms of the shape of the P function (which appears Maxwellian) as well as the computed value of the temperature with the error estimated as ± 0.2 by studying an atom of fixed label (no. 29) as it forms and breaks bonds with neighboring molecules, as shown in figure 6. Clearly the time average of dynamical properties for this particle would equal the ensemble average. We notice that the reduced accuracy of the sampling is reflected in the greater scatter of the P function points. The time averaged particle temperature corresponds within error to the system temperature.

Finally, since the molecular P function has been mentioned, it would be interesting to compare it to the case of a random, but always free A particle which is given in figure 7, where the determined temperature is slightly *lower*, (to within the error limits) than the system temperature, and where the shape of the P curve is Maxwellian. This particular species type cannot fulfill the Gibbs postulate because its trajectory is confined to those areas where there is no molecular formation, and so its time averaged properties like the temperature need not necessarily equal that for the system as a whole as determined from the equipartition principle. We can conclude that the energy subsystems that can be chosen for devising a theory of unequal temperature distributions in an equilibrium system all of which have a Maxwellian probability profile include at least the following candidates:

- Translational k.e. about C.M. for A_2 ;
- Fixed indexed k.e. of particle A (in both free and bonded state);
- Random, always unbonded k.e. of particle A .

The following is suggested as a result the above observations.

Conjecture 1. If the random forces are external to the subsystem, and they all have the same force law when acting on the particles of the system which may be different from the force law for internal forces acting on the particles of the same

subsystem, then the kinetic energy of the C.M. of the subsystem would have a probability distribution that is Maxwellian.

The above conjecture is weak as it stands and should be supported by a theoretical approach using stochastic calculus.

3. NEMD results

A NEMD simulation was conducted with the thermodynamical variable distribution for temperature and number density depicted in figure 8. The results presented here are additional to the results presented elsewhere (Case 2 simulation) [1] for the same thermodynamical conditions, where this time, we concentrate on the flow properties of the system, rather than the static property of the equilibrium constant variation across the cell given previously. Figures 9 and 10 are the flux and divergence of the flux for “Case 2” simulation where a temperature gradient across the MD cell is imposed together with the making and breaking of bonds at the ends of the cell leading to a molecular flux according to the thermodynamical conditions and rate details of the breaking and formation of bonds as given in [1]. The cell is broken up into 64 layers along the X-direction and the thermostats are placed at the ends of the layers. Figure 9 has overlapping error bars with magnitudes that do not change significantly over the range where the fluxes are evident. The stationary source and sink quantities are denoted σ (σ_f and σ_b are the rate of formation and breakdown of the dimer in unit time and unit volume, respectively, throughout the cell). The conservation of mass equation for atoms and dimers read as follows, where the subscripts refer to the species label for the flow vector J and the concentration c :

$$\begin{aligned} dc_{A_2}/dt &= -\nabla \cdot J_{A_2} + \sigma_f - \sigma_b, \\ dc_A/dt &= -\nabla \cdot J_A - 2\sigma_f + 2\sigma_b. \end{aligned} \quad (14)$$

The steady state conditions are

$$\begin{aligned} \nabla \cdot J_A &= -2(\sigma_f - \sigma_b) = -2\sigma_r, \\ \nabla \cdot J_{A_2} &= \sigma_r, \end{aligned} \quad (15)$$

where $(\sigma_f - \sigma_b) = \sigma_r$ and σ_r is a scalar flux. At thermodynamical equilibrium, $\sigma_r = 0$. If the PLE were valid in the sense that for chemical reactions which are in a state of local equilibrium, the affinity of the reaction A is zero leading to zero σ_r , then the J_A, J_{A_2} fluxes must vanish; clearly here, this is not the case. Some elaboration seems necessary. The affinity is defined as $A = \sum_{i=1}^n \nu_i \mu_i$, where μ_i is the chemical potential. The Gibbs equilibrium criterion is equivalent to the affinity vanishing at constant pressure and temperature. The rate σ_r cannot be linearly proportional to the temperature gradient, if the common understanding of the Curie symmetry principle is used [6, p. 21]. One can couple a

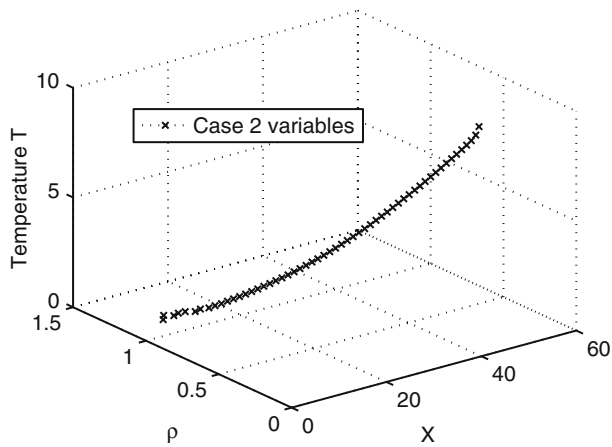


Figure 8. Temperature and density profile for Case 2 simulation along the MD cell which was divided into 64 layers in the X-axis direction.

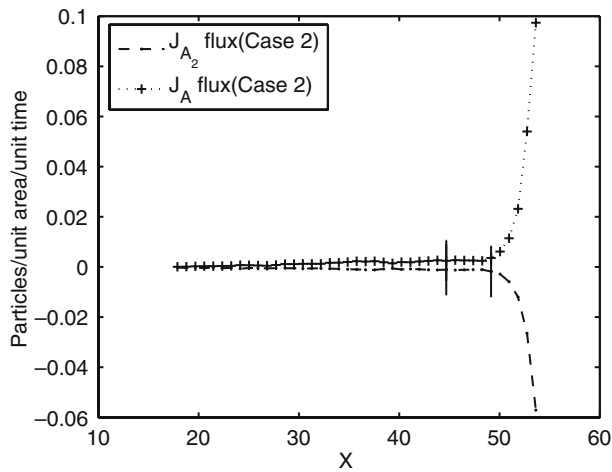


Figure 9. Extreme thermodynamical conditions leading to the presence of steady state atomic and dimer fluxes. The data points are used to construct the difference equation in the text to verify the conservation law.

flow J_i of substance i and rate v according to the linear thermodynamic equations

$$\begin{aligned}
 J_i &= L_{ii} \frac{d}{dx} \frac{1}{T} + L_{ic} \frac{A}{T}, \\
 v &= L_{ci} \frac{d}{dx} \frac{1}{T} + L_{cc} \frac{A}{T}.
 \end{aligned}
 \tag{16}$$

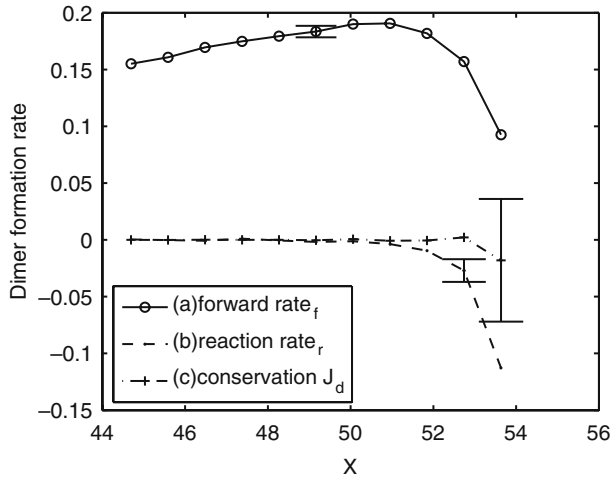


Figure 10. Test of divergence theorem for mass conservation via a difference equation.

In such an understanding, $L_{ic} = 0$ or else a scalar cause A/T produces a vector effect J_i . So $L_{ci} = 0$ also by the reciprocity condition. Hence in the naive sense above, one would not expect flows to be present along the cell where is no artificial (externally imposed) formation or breaking of bonds for the reasons that follow. One might argue that $L_{ii} \neq 0$ induces the flow; but it was found that no perceptible flow was observed when there was no breaking or forming of bonds at the reservoir ends; but in any case (17) suggests that the rate is due only to the Affinity not being zero, and the conservation equations show that the divergence of the flow being related to the chemical rate $v = \sigma_r$. If the rate were zero over the whole length of the cell, then if the flow rate $J_A(J_{A_2})$ were zero at one end of the cell, then by integration it would also be zero along the whole cell length; experimentally the flow is zero at one of the ends (at colder temperature), so a zero reaction rate v everywhere implies zero flow rate elsewhere under these conditions. To check for flux conservation, the divergence term is discretized by integration over one layer, using the trapezoidal rule, where for any layer i ,

$$\int_{i-1}^i \nabla \cdot J_{A_2} dV = \frac{(\sigma_r(i) - \sigma_r(i - 1))\Delta V}{2} = J_{A_2,dif}(i) = J_{A_2}(i) - J_{A_2}(i - 1), (17)$$

where the layer has volume ΔV . Similarly, for the atomic fluxes,

$$J_{A,dif}(i) = J_A(i) - J_A(i - 1) = -(\sigma_r(i) + \sigma_r(i - 1))\Delta V. (18)$$

Equation (15) says that

$$2\nabla \cdot J_{A_2} + \nabla \cdot J_A = 0, (19)$$

which may be expressed as

$$J_d(i) = 2J_{A_2,dif}(i) + J_{A,dif}(i) = 0. \quad (20)$$

The plot of J_d given in (20) in figure 10 complies with the conservation law rather well, within statistical error. We have therefore shown that PLE in the above sense is not a rigorous principle from numerical simulation with this counter-example. Another from NEMD concerning equilibrium constants has been reported [1]. It has been shown that local stochastic equilibrium dynamical variables do not necessarily have Gaussian (Canonical) distributions. Both these conditions are demanded as being essential by some specialists [4,5,7] in their theories. The theoretical developments concerning PLE begins with the generalized Clausius Inequality,

$$\oint \frac{dQ_{[q]}}{T} \leq 0, \quad q \in \{\text{adia, tot}\},$$

where [1] two separate forms of heat obtain where (i) adia refers to a diathermal heat transfer across the primary system boundary whereas (ii) tot refers to a nonlocal heat term which includes various heat transfer terms due to standard state substance and thermal reservoirs, heat pumps and the primary system. The inequality above holds for both types of heat transfers separately. It is deduced [1, Corollary 1] that it is impossible for any irreversible pathway, which exchanges heat P'_{BA} connecting two equilibrium states A, B to contain the same sequence of points as P_{BA} , that for the equilibrium pathway for all P_{BA} . The set of all equilibrium states (which are points in the thermodynamical space) is Σ where $P_{AB} \subset \Sigma$, where the set of points in P_{BA} (or P_{AB}) is denoted $\{\omega\}$. It is shown that $P'_{BA} = \{\omega\} \cup \{\Delta\}$ where $\Delta \notin \Sigma$. The theoretical development [1] does not provide a specific form for Δ but physical considerations suggests that this variable includes spatial gradients and time derivatives of Σ . As such, the theoretical development states that the use of simple differentials of equilibrium state functions used routinely to describe nonequilibrium systems is incomplete. It is suggested here that this incompleteness shows up in the NEMD simulation results provided here which is not well described by the first order linear thermodynamics theory in conjunction with the Gibbs equilibrium criterion.

4. Conclusion

It is shown through numerical counter-examples that the PLE and the canonical averaging assumption used in recent thermodynamical theories as fundamental and required assumptions are approximate in nature, at best. In canonical averaging, the internal variables do not have the same algebraic structure as the variables that are explicitly featured in the system Hamiltonian. A previous

work [1] shows that the PLE neglects other variables not found in the equilibrium state space. It would be of interest to repeat and compare some of the above calculations for a more conventional system without hysteresis to definitively rule the effects of artifacts due to the use of these novel potentials. The NEMD simulation provides an example of a system that may be better described by theories that go beyond linear and local equilibrium theories.

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