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14. ABSTRACT
Small-system thermodynamics provides a novel paradigm for understanding the complex response inside bulk materials. This “nanothermodynamics” yields a systematic way to treat entropic forces, which come from fluctuations in the density, alignment, and number of interacting particles. Although usually neglected in most computer simulations, these entropic forces can alter reaction rates by several orders of magnitude across length scales of nanometers. We show that such entropic forces are necessary to maintain conservation of energy and

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Report Title

Final Report: Nanothermodynamics applied to thermal processes in heterogeneous materials

ABSTRACT

Small-system thermodynamics provides a novel paradigm for understanding the complex response inside bulk materials. This “nanothermodynamics” yields a systematic way to treat entropic forces, which come from fluctuations in the density, alignment, and number of interacting particles. Although usually neglected in most computer simulations, these entropic forces can alter reaction rates by several orders of magnitude across length scales of nanometers. We show that such entropic forces are necessary to maintain conservation of energy and maximum entropy during equilibrium fluctuations. Furthermore, adding entropic forces improves agreement between computer simulations and the measured properties of many materials. Another result is that finite-size thermal effects cause simple models to exhibit complex dynamics. To expand the usefulness of our fundamental research, we collaborate with experts in the area of energetic materials. We have found that similar finite-size thermal effects occur in molecular-dynamics simulations of nitromethane. Future applications of nanothermodynamics will be facilitated by continuing to collaborate with such experts. Our goal is to optimize the accuracy, efficiency, and predictive power of large-scale simulations for the complex dynamics inside energetic materials.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
2012/08/03 1	5	Ralph V. Chamberlin. Monte Carlo simulations including energy from an entropic force, Physica A: Statistical Mechanics and its Applications, (11 2012): 5384. doi: 10.1016/j.physa.2012.06.016
2009/10/05 1	2	Ralph V. Chamberlin, Josh V. Vermaas, George H. Wolf. Beyond the Boltzmann factor for corrections to scaling in ferromagnetic materials and critical fluids , European Journal of Physics, (08 2009): . doi:

TOTAL: **2**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

“Nanothermodynamics and Nonlinear Corrections to Statistical Mechanics” Dynamics Days 2010, Evanston Illinois, January 5, 2010;

"The Big World of Nanothermodynamics” Engineers Club of the West Valley, Sun City West, February 5, 2010

“Nanothermodynamics and Nonlinear Corrections to Statistical Mechanics in Monte Carlo Simulations of Disordered Materials” Viscous Liquids and the Glass Transition (VIII), Sominestationen, Holbaek, Denmark, May 30, 2010

Number of Presentations: 3.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
2011/08/08 1	4	Ralph V. Chamberlin. Monte-Carlo simulations including energy from an entropic force, Physica (08 2011)
2010/08/29 1	3	Ralph V. Chamberlin. Computer Simulations of Semiclassical Particles, (08 2010)

TOTAL: **2**

Number of Manuscripts:

Books

Received	Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Lei Tu	0.50	
Shane Moffet	0.25	
Michael Bell	0.50	
FTE Equivalent:	**1.25**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Ralph V. Chamberlin	0.10	
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Josh Vermaas	0.10	Physics
Alexander Brown	0.10	Physics
FTE Equivalent:	**0.20**	
Total Number:	**2**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	2.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	2.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	2.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:......	1.00

Names of Personnel receiving masters degrees

NAME	
Lei Tu	
Total Number:	1

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

FINAL REPORT

Nanothermodynamics Applied to Thermal Processes in Heterogeneous Materials

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Overview

Nanothermodynamics Applied to Thermal Processes in Heterogeneous Materials

Small-system thermodynamics is used as a guide to investigate some fundamental issues in the behavior of complex systems. This "nanothermodynamics" provides a novel paradigm for interpreting the nonlinear and inhomogeneous response inside bulk materials, leading to improved modeling of the response. Results from computer simulations of standard models agree favorably with a wide range of measurements of local thermal and dynamic properties. Progress in understanding basic thermodynamic principles will enhance the predictive power and accuracy of most computer simulations.

Unlike the usual theoretical limit of linear and homogeneous behavior for large systems, the laws of thermodynamics are more restrictive when applied to small systems. For example, local entropic forces often yield non-extensive changes in energy during normal thermal fluctuations, which must be added to the interaction if total energy is to be conserved. Similarly, local configurational entropies often yield nonlinear terms in the reaction rate, which must be included in the dynamics if total entropy is to be maximized. Nanothermodynamics helps to identify various nonlinear corrections that occur in the dynamics of small systems.

Finite-size effects yield nonlinear corrections due to changes in the local entropy during normal thermal fluctuations. Fluctuations in the configurational entropy come from changes in the local alignment of dipoles, or the local density of particles, which can alter reaction rates by several orders of magnitude across length scales of nanometers. Using computer simulations of standard models, such as the Ising ferromagnet, the nonlinear corrections are shown to restore conservation of energy and maintain maximum entropy. Furthermore, the nonlinear correction improves agreement between computer simulations and the measured properties of many materials. A general result is that finite-size effects cause simple models to exhibit complex thermal and dynamic behavior.

Useful implementation of our basic research requires adapting the fundamental principles we investigate to help guide advanced applications. We now collaborate with experts in the area of energetic materials at the University of Missouri. One result is an analysis of finite-size thermal effects in molecular-dynamics simulations of nitromethane. Future applications of nanothermodynamics will be facilitated by continuing to exchange knowledge with such experts. Our goal is to optimize the accuracy and efficiency of large-scale simulations of the complex dynamics in energetic materials.

Nanothermodynamics Applied to Thermal Processes in Heterogeneous Materials

Table of Contents Pg.

Summary of most important results

I. Introduction

Computer simulations are often the best way to investigate microscopic details in the complex behavior of energetic materials.[1] For example, classical molecular dynamics (MD) simulations allow large-scale and long-time studies of atomic-level motion, revealing details about the structural and chemical consequences of shock waves,[2] and the dynamics of melting.[3] We explore finite-size effects in thermodynamics. Specifically, we investigate nonlinear corrections to Boltzmann statistics that come from local entropic forces. Our goal is to fully understand the statistical thermodynamics of finite-sized systems, which will enhance the efficiency and accuracy of computer simulations.

MD simulations of large-scale models give good agreement with several features in the response of energetic materials, including the density, pressure, velocity, and temperature of detonation waves.[4] However, most computer simulations exhibit non-extensive energy fluctuations in both MD[5] and Monte-Carlo[6] algorithms. In our research we emphasize that these simulations violate the basic laws of thermodynamics, and we investigate ways to improve the algorithms. First I will present evidence that a more-sophisticated model that is commonly used to simulate energetic materials also exhibits some fundamental problems in its thermodynamic behavior, then I will summarize our efforts to use nanothermodynamics as a guide to address these issues.

II. Fundamental issues in the thermal behavior of molecular-dynamics simulations

We analyzed size-dependent energy fluctuations from molecular-dynamics simulations of liquid nitromethane. The system was simulated at a temperature of 360 K using the Sandia National Laboratory program LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). The simulations were kindly provided by Dr. Lan He and Prof. Tommy Sewell from the University of Missouri. We used three files from each simulation. The files give the position, velocity, and force on each atom at a series of 1200 time steps. The data were converted into the kinetic energy (K), potential energy change (ΔU), and total energy ($E=K+\Delta U$) for each atom at each time step. These simulations used 1896 nitromethane molecules (13272 atoms) in a total volume of: $(2*27.9126\ \text{Å})^3$. The size-dependent behavior was analyzed by subdividing the total volume into 2^3, 3^3, 4^3, 6^3, 8^3, or 12^3 cubic-shaped regions; yielding sides for each region ranging in length from L=27.9126/6 Å to 27.9126 Å. With a total number of N(L) atoms in each region, the values obtained were the kinetic energy K(L), potential energy change ΔU(L), and total energy E(L). Specifically, the kinetic energy was found using $K(L)= \frac{1}{2} \Sigma_i m_i (v_{ix}^2+ v_{iy}^2+v_{iz}^2)$, where m_i is the atomic mass of each atom, and the sum is over all atoms in the region. A factor of 2390.06 (kcal/g)/$(\text{Å/fs})^2$ was used to convert the simulation units (g/mole)*$(\text{Å/fs})^2$ into kcal/mole. The potential energy change was calculated by integrating the power over each time step, $U(L)=\int(\mathbf{F}\bullet\mathbf{v})dt$, using a simple trapezoid integration. A factor of 75 fs/(time-step) was used to convert the simulation units [kcal/(mole-Å)]*(Å/fs) into kcal/mole. The energies were averaged over the time steps, and divided by $<N(L)>$ to obtain the per mole values: $<k(L)>$, $<u(L)>$, and $<\varepsilon(L)>$. In a similar manner the average fluctuations per particle were also obtained: $<(\Delta k(L))^2>$, $<(\Delta u(L))^2>$, and $<(\Delta\varepsilon(L))^2>$. Figures 1 and 2 show some results.

Energy fluctuations yield fundamental thermodynamic quantities of heat capacity and entropy. Specifically, $c_V = <((\Delta E/T)^2>/(k_B N)$ gives the specific heat in units of Boltzmann's constant k_B, while $\Delta s_L = \int(c_V/T)dT$ gives the change in entropy per particle between two temperatures. The equipartition theorem states that all classical particles have a heat capacity of $\frac{1}{2}k_B$ per degree of freedom; but the fluctuations shown in Fig. 2 decrease with decreasing system size. Furthermore, small-system thermodynamics (nanothermodynamics) requires that the entropy is additive and extensive, unlike the nonextensive entropy deduced from Fig. 2. Thus, classical MD simulations of energetic materials may exhibit unphysical behavior on small length scales.

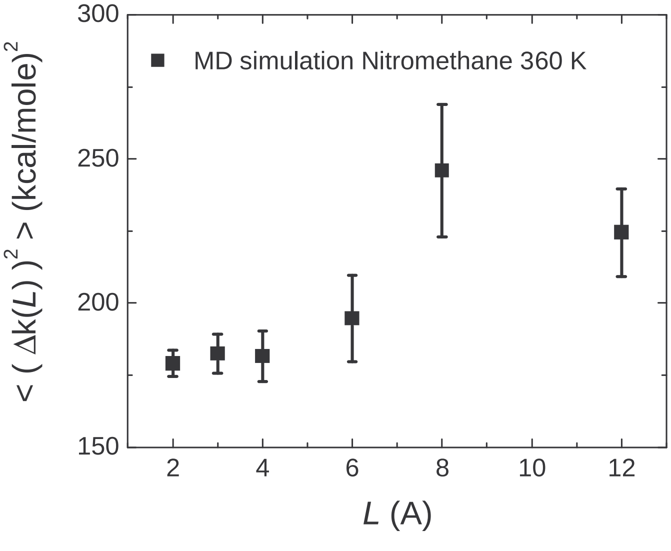

Figure 1 Fluctuations in kinetic energy per mole as a function of the side-length (in Ångstroms) of cube-shaped regions. The results are from MD simulations of liquid nitromethane at a temperature of 360K. Symbols and error bars are from the average and standard deviation over the interval from 600-1200 time steps. The relatively large error bars prohibit a clear choice for the functional form of the size dependence.

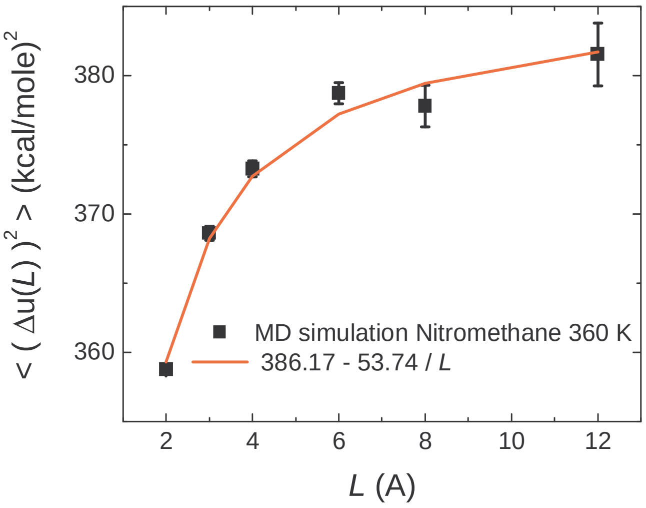

Figure 2 Fluctuations in potential energy per mole as a function of the length (in Ångstroms) of cube-shaped internal regions. Symbols and error bars are from the average and standard deviation over the interval from 1000-1200 time steps. The solid curve is a fit to the data showing that the fluctuations decrease inversely proportional to the length of the region.

We have found similar size-dependent energy fluctuations in MD simulations of simple fluids using the Lennard-Jones (L-J) model, as shown in Fig. 3. Specifically, for fluctuations in the potential energy at low temperatures where the system is liquid-like (red circles), the resulting specific heat approaches the theoretically expected value of $c_V/k_B \rightarrow 3/2$ for large regions, but c_V/k_B decreases inversely proportional to the region length (red-dashed curve). Fluctuations in kinetic energy (black squares) also yield c_V/k_B → 3/2 for large regions, but this c_V/k_B decreases inversely proportional to volume for small regions (black-solid curve). Thus the L-J model provides a simplified system to study basic issues that occur in most MD simulations. The goal of our current research is to understand why these MD simulations show fundamentally non-physical behavior, and how can they be corrected to exhibit more realistic behavior, consistent with the laws of thermodynamics.

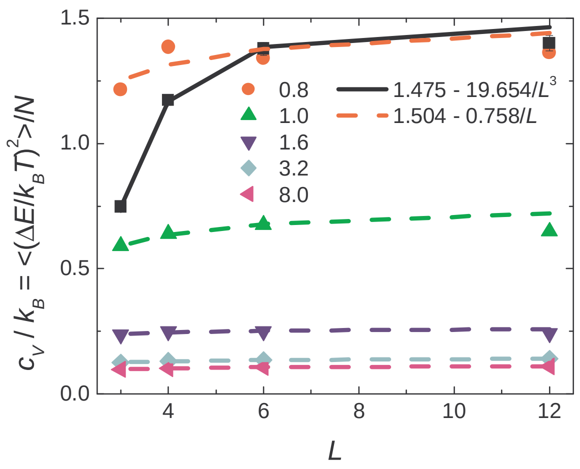

Figure 3 Specific heat as a function of length (in units of the L-J lattice) of cube-shaped regions from MD simulations of the L-J fluid. Colored symbols are from fluctuations in potential energy per particle at five reduced temperatures (given in legend). Black squares are from fluctuations in kinetic energy, after averaging over all five temperatures (error bars are comparable to symbol size). The lines give a best fit to the data using an inverse volume dependence for the kinetic energy (solid black), and an inverse length dependence for the potential energy (dashed colored). Note that both the solid-black and dashed-red lines yield c_V/k_B ~3/2 for large regions (values are given in the legend), as expected by the equipartition theorem. However, the simulations all show a decrease in c_V/k_B for small regions, similar to that shown in Fig. 2 for nitromethane. This size-dependent c_V/k_B violates the equipartition theorem, and the thermodynamic requirement that entropy is extensive.

III. Fundamental issues in the thermal behavior of Monte-Carlo simulations

A major achievement during the just-completed period of ARO support was to characterize and correct violations of fundamental thermodynamic behavior in Monte-Carlo (MC) simulations of the Ising model.[7] The solid black lines in Fig. 4 show results using the uncorrected (Metropolis) algorithm on the standard Ising model. The energy per particle in Fig. 4 a) is independent of system size, whereas the energy fluctuations per particle in Fig. 4 b) decrease with decreasing region size, similar to that shown in Figs. 2 and 3 for MD simulations. Again, because the energy fluctuations yield the heat capacity and change in entropy between temperatures, the behavior in Fig. 4 b) violates the thermodynamic principle that entropy should be extensive.

The Metropolis algorithm that is used for most MC simulations is based on the Boltzmann factor $e^{-\Delta U/k_BT}$. Although this is the most widely used formula in all of statistical mechanics, it is based on some restrictive assumptions: the system must couple instantly to a large heat bath, and heat must be the only source of entropy.[8] In the past 20 years, several experimental techniques have shown that the primary response of most materials comes from an ensemble of effectively independent nanometer-sized regions. Thus, local thermal properties play an important role in the primary response. Indeed, the Boltzmann factor is strictly valid only for independent particles that couple individually to an infinite heat bath, which is never true for classical systems of interacting particles.

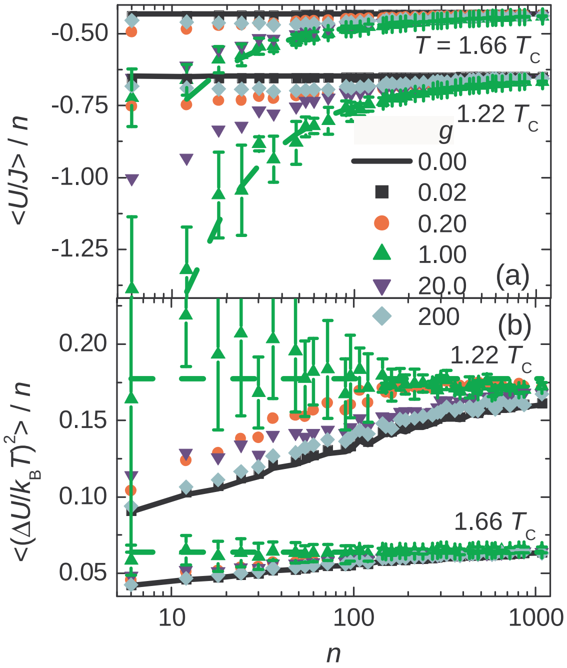

Figure 4 (a) Average interaction energy per particle and (b) specific heat as a function of region size at two temperatures, from ref. 7. Simulations are performed on an Ising system of *N*=27,000 particles with periodic boundary conditions. The system is subdivided into 140 regions, ranging in size from *n*=6 to 1080 particles. The solid (black) lines come from the standard Metropolis algorithm with no correction, i.e. *g*=0 where *g* is the nonlinear constraint parameter. Note that these uncorrected simulations show a reduction in energy fluctuations for small regions, similar to the behavior shown in Figs. 2 and 3 for molecular dynamics simulations. Symbols come from simulations with nonlinear correction values given in the legend. The dashed lines show that for *g*=1, in (a) the energy per particle is reduced inversely proportional to region size $<U/n>\sim 1/n$, and in (b) the specific heat is independent of region size. Error bars are shown for the *g*=1 data.

IV. Beyond the Boltzmann factor

We improve the thermal and dynamic properties of the Ising model by modifying the Boltzmann factor, essentially providing a nonlinear correction to temperature. The correction comes from the entropy of small regions in the sample, which have finite-size effects that are not in standard Boltzmann statistics. Indeed, the Boltzmann factor gives the thermal activation rate only if the local entropy is at its peak value; but local regions often fluctuate into a low-entropy state with dynamics that is significantly slower. Furthermore, we have found that these nonlinear corrections are necessary for conservation of energy in small systems, and for the uniform specific heat that resolves Gibbs' paradox for interacting particles.[8] Moreover, we have shown that the correction factor greatly improves the agreement between simulations of the Ising model and the measured response of ferromagnetic materials and critical fluids,[9] as shown in Fig. 5. The corrections are also necessary for detailed balance between a superposition of equivalent states, allowing computer simulations of classical models to exhibit quantum-like statistics. In fact the nonlinear correction yields an entropic force, similar to the entropic force that favors low-energy states at low temperature. Thus, we use this nonlinear correction to improve standard models of simplified systems, with the goal of transferring our knowledge to help facilitate more accurate and efficient simulations of sophisticated models of energetic materials.

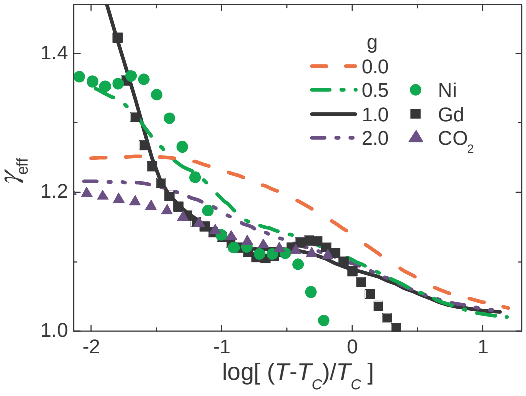

Figure 5 Effective scaling exponent $\gamma_{\text{eff}} = -d\log(\chi) / d\log(\tau)$ as a function of reduced temperature $\tau = (T - T_C)/T_C$, where χ is the susceptibility and T_C is the critical temperature, from Ref. 9. Symbols are from measured susceptibilities of two magnetic materials (Gd-■ from and Ni-●), and one critical fluid (CO_2-▲). Lines are from simulations of the Ising model using: the standard Boltzmann factor g=0 (red, dashed); and fluctuation constraint with constraint parameter g=0.5 (green, dash-dot), g=1 (black, solid), and g=2 (blue, dash-dot-dot). Note the failure of the standard Ising model (g=0) to match measured susceptibilities.

V. **Applications of nanothermodynamics**

We study fundamental issues in the statistical thermodynamics of small systems. Our approach utilizes nonlinear corrections to classical Boltzmann statistics that restore extensive entropy, conservation of energy, and detailed balance between a superposition of equivalent, quantum-like states, as described in the previous sections. Because these corrections yield a type of entropic force, similar to the force that causes heat flow from a thermal gradient, they can be thought of as a nonlinear correction to temperature.

Temperature (T) is the familiar variable that governs thermal fluctuations and reaction rates in materials, but this T comes from just the linear term in the change of entropy with changing energy; nonlinear terms may contribute significantly to the net behavior. The influence of temperature is usually found from the Boltzmann factor $P \propto e^{-\Delta U / k_B T}$, which gives the relative probability (e.g. reaction rate) for a system to change its energy by ΔU. This Boltzmann factor is the most widely used formula in statistical thermodynamics, providing the basis for Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics. However, the Boltzmann factor is a linear approximation, valid only for large systems, in thermal equilibrium at low temperatures, with negligible fluctuations. Thus, for many systems at normal temperatures it is necessary to use the more fundamental expression $P \propto e^{\Delta S / k_B}$ for the probability of a local process, where ΔS is the offset in entropy from thermal equilibrium due to a local fluctuation.

Nonlinear corrections to temperature are necessary to simulate several features in the thermal and dynamic properties of complex materials. As was shown in Fig. 5, the critical behavior of several samples is improved using the nonlinear correction; Fig. 6 shows another example. The solid (black) line in the main part of Fig. 6 comes from the excess specific heat of $LaMnO_3$ measured near the Jahn-Teller structural distortion at T_c=735 K.$^{\textbf{Error! Bookmark not defined.}}$ The dashed (red) line comes from simulations of the antiferromagnetic (AF) Ising model using standard Boltzmann statistics (Metropolis algorithm). The solid squares come from the same model, but with a nonlinear correction from the local entropy of 3x3x3 regions. The inset of Fig. 6 shows the potential energy per particle of this AF Ising model as a function of temperature. Again the dashed (red) line comes from standard simulations using the Boltzmann factor alone. The symbols come from the same model, but with nonlinear corrections from cubic regions of various sizes. Large regions (16x16x16 & 12x12x12) have negligible influence on the energy because they are unlikely to fluctuate into a low-entropy state. Small regions (3x3x3) have large fluctuations that significantly lower the energy at all temperatures, while increasing the transition temperature by nearly 50%. Also note the sharpening of the transition, consistent with the measurements shown in the main part of Fig. 6. Direct evidence for the existence of small correlated regions in $LaMnO_3$ comes from neutron scattering data.[10] The red circles in Fig. 7 show the correlation length deduced from the pair distribution function measured in $LaMnO_3$. The black squares come from our simulations of the AF Ising model, showing similar short-range order above T_c. The simulations use the measured value of 0.40 nm for the average lattice parameter, and 3x3x3 regions consistent with the lowest energy shown in the inset of Fig. 6, with no other adjustable parameters.

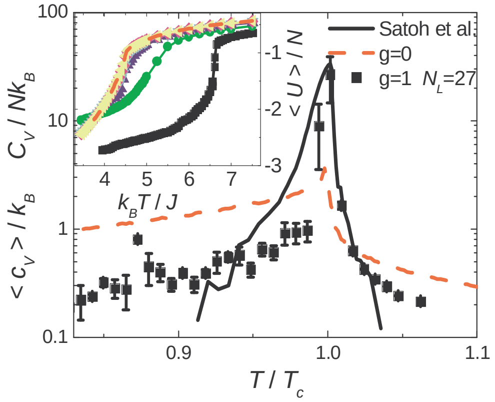

Figure 6. Main plot shows specific heat as a function of normalized temperature. Solid line is from measurements of $LaMnO_3$. Dashed line is from simulations of the AF Ising model using the standard Boltzmann factor. Solid squares with error bars are from our simulations of the same model, but include a nonlinear correction to temperature from the local entropy of 3x3x3 regions, with no other adjustable parameters. Inset shows the average energy per particle as a function of temperature. Again the dashed line is from simulations using the standard Boltzmann factor. The symbols include a nonlinear correction factor from the local entropy of regions of size 16x16x16-◀, 12x12x12-♦, 8x8x8-▼, 6x6x6-▲, 4x4x4-●, and 3x3x3-■. Because of negligible correction for large regions, several symbols lie underneath the dashed line.

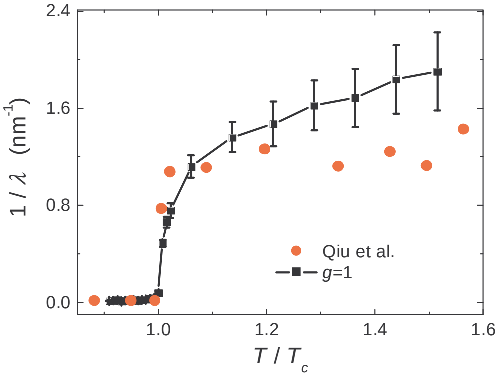

Figure 7 Inverse correlation length as a function of normalized temperature. Circles are from neutron-scattering measurements of $LaMnO_3$.[10] Squares (with error bars) are from our simulations of the AF Ising model with a nonlinear correction to Boltzmann statistics from 3x3x3 regions. The 3x3x3 regions were chosen to minimize the energy (as shown in the inset of Fig. 8) with no other adjustable parameters. Conversion of the simulation results to physical units is made using 0.40 nm for the average lattice parameter of $LaMnO_3$, as measured by neutron scattering

VI. Additional accomplishments

Finite-size thermal effects are found to significantly influence the fluctuations and reaction rates of many materials. Another example is the slow relaxation of disordered systems. We have succeeded in simulating several features in the dynamics of viscous liquids, including the non-Arrhenius activation and stretched-exponential relaxation. We find that the slow dynamics comes from a distribution of sharp jumps, as shown in Fig. 8. The jumps come from “entropic entrapment,” where the nonlinear correction to temperature enhances the stability of low-entropy states, until the region fluctuates into a high-entropy state that facilitates rapid relaxation, somewhat like an avalanche. Direct evidence for this picture of complex relaxation comes from NMR measurements of jump-angle distributions (Fig. 8 inset).[11] Understanding the dynamics of complex systems helps guide a search for ways to enhance the stability of disordered materials by decreasing their local entropy. Maintaining low entropy will help avoid outlier points exhibiting fast relaxation, which may act as “hot spots” that initiate unwanted chemical reactions.

In our research we use simplified models that allow us to focus on fundamental issues in statistical thermodynamics. We seek to understand the most basic laws that yield universal features in the response of complex systems. We address the question: what minimal rules capture the essence of complex dynamics? Most of the work during the previous funding period involved the thermal and dynamic properties of the Ising model, which is the simplest model for a thermodynamic phase transition. Figure 9 shows an Arrhenius plot of the average time for a biased Ising model to activate over an energy barrier, from a state of high potential energy to the ground state. Note that the simplicity

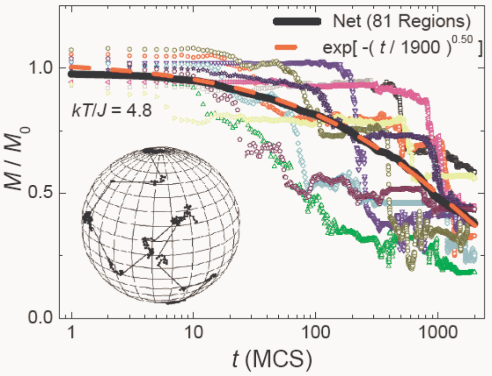

Figure 8 Non-exponential relaxation as a function of time after removing an applied field in a simulation of a supercooled liquid. The solid (black) curve shows the net alignment from 81 regions, each of size 16x16x16. The dashed (red) curve shows a fit to the net behavior using the stretched-exponential function. The symbols show the response of 10 individual regions, showing sharp jumps and steps in the local response. The relatively static periods come from entropic entrapment, when the region is in a state of low entropy. The large jumps arise when the region becomes activated by high entropy. The inset shows results from NMR measurements of the molecular rotation angles in a supercooled liquid,[11] showing similar small-angle diffusion combined with occasional large-angle jumps.

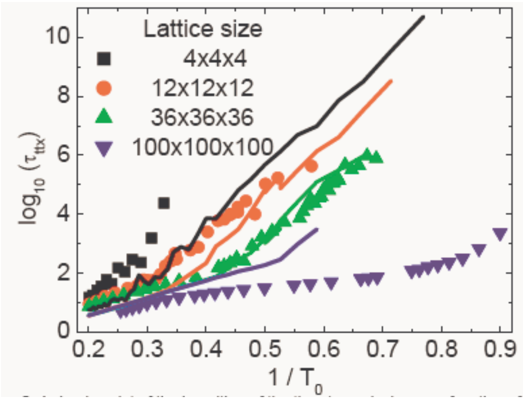

Figure 9. Arrhenius plot, showing the logarithm of the activation time as a function of the inverse of the initial temperature. The solid lines are from our simulations of the Ising model (canonical ensemble), and symbols are from simulations of the Creutz model (microcanonical ensemble). The different colors are for different system sizes, as given in the legend. The activation time is determined by averaging multiple simulations of the time taken for the initial (metastable) state to activate over an energy barrier into the ground state, causing a sudden release of energy. Each data point comes from the average of several simulations.

of the Ising model allows simulations over more than 10 orders of magnitude in time, comparable to the range of experimental time scales for Arrhenius activation in HMX.[12] We continue to use Monte-Carlo simulations of the Ising model to efficiently explore the minimal complexity needed for realistic dynamics.

Also shown in Fig. 9 are the activation rates found from the Creutz model. The Creutz model starts with the interaction energy of the Ising model, but adds a source of kinetic energy so that the simulations can be done in the microcanonical ensemble. This ensemble, which uses conservation of energy instead of fixed temperature, is crucial for studying transient behavior using a self-consistent local temperature for systems that are out of equilibrium. Figure 10 shows an example of how the Creutz model gives the temperature as a function of time as the system activates out of the high-energy initial state. The inset shows details about the activation process. Note the brief reduction in temperature (kinetic energy) just prior to the initiation of activation, as the system surmounts the energy barrier before releasing its excess potential energy. The Creutz model is the simplest way to simulate microcanonical processes, thus providing an elementary link between Monte-Carlo and molecular-dynamics simulations.

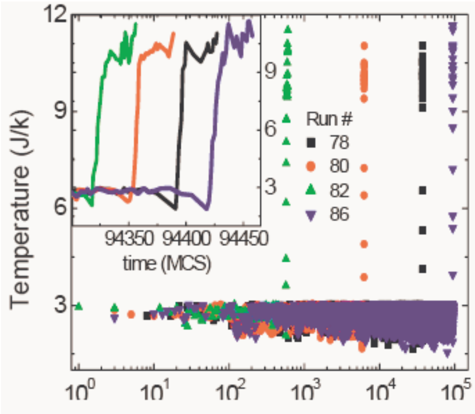

Figure 10. Semi-log plot of temperature as a function of time. The data points are from our simulations of the Creutz model using the microcanonical ensemble. Each color represents a different repeat of the same simulation, starting from a statistically different point, showing the range of stability in the initial state. The inset shows details of the energy release. Note the sharpness of the exothermic activation, and the brief reduction in temperature (kinetic energy) that precedes the energy release as the system surmounts the energy barrier. In the inset, the simulations have been offset in time for clarity.

Practical application of our fundamental ideas is most efficiently accomplished by collaboration. Recently I have collaborated with Professors Don Thompson and Tommy Sewell at the University of Missouri, who are experts in detailed simulations of energetic materials using realistic models. Through many e-mails, two lengthy teleconference calls, and four visits to Columbia, we have discussed the evidence for nonlinear corrections to temperature, and the possible importance for energetic materials. We developed a plan on how to proceed. 1) Run a test simulation of liquid nitromethane to establish the relevance of nonlinear corrections for MD simulations of energetic materials, as shown in Figs. 1 and 2. 2) Investigate nonlinear corrections to MD simulations for simplified models, starting with the Lennard-Jones fluid as shown in Fig. 3, then transfer the ideas to more-sophisticated models. 3) Explore models that bridge the scale of complexity between the Ising model and models for energetic materials, such as the Potts model for multiple degrees of freedom on a lattice. 4) Evaluate various moments in the distribution of jump rates, focusing on outlier statistics, as shown in Fig. 8. 5) Maintain our collaboration via frequent discussions and timely visits. In summary, we will continue to use computer simulations to investigate nonlinear corrections to temperature that are necessary to fully describe the thermal properties of complex systems, including fluctuations and hot spots that may significantly influence the local reaction rates in energetic materials.

List of publications and reports

(a) Refereed Journal Articles

1. R.V. Chamberlin and G.H. Wolf, “Fluctuation theory constraint for extensive entropy in Monte-Carlo simulations,” *Eur. Phys. J. B* **67**, 495-499 (2009).
2. R.V. Chamberlin, J.V. Vermaas, and G. H. Wolf, “Beyond the Boltzmann factor for corrections to scaling in ferromagnetic materials and critical fluids,” *Eur. Phys. J. B* **71**, 1-6 (2009).
3. R.V. Chamberlin, “Monte Carlo simulations including energy from an entropic force,” available on line: http://dx.doi.org/10.1016/j.physa.2012.06.016

(b) Presentations at Meetings

1. “Nanothermodynamics and Nonlinear Corrections to Statistical Mechanics” Dynamics Days 2010, Evanston Illinois, January 5, 2010
2. “The Big World of Nanothermodynamics” Engineers Club of the West Valley, Sun City West, February 5, 2010 (invited)
3. “Nanothermodynamics and Nonlinear Corrections to Statistical Mechanics in Monte Carlo Simulations of Disordered Materials” Viscous Liquids and the Glass Transition (VIII), Sominestationen, Holbaek, Denmark, May 30, 2010 (invited)

(c) Invited Presentations at Universities and Research Institutes

“Nanothermodynamics Applied to the Local Thermal Properties of Disordered Systems”

1. Elettra Synchrotron Light Laboratory, Trieste, Italy, May 14, 2009
2. University of Gottingen, Germany, May 18, 2009
3. University of Dortmund, Germany, May 19, 2009
4. University of Augsburg, Germany, May 22, 2009

“Thermal and Dynamic Heterogeneity in Materials”

5. PSM Nanoscience Seminar, Arizona State University, September 30, 2009

“Hole-burning measurements, Landau theory, and nonlinear corrections for computer Simulations”

6. University of Roskilde, Denmark, June 10, 2010

“Nanothermodynamics and Nonlinear Corrections to Statistical Mechanics”

7. Nanoscale Science Seminar, Arizona State University, October 5, 2009
8. University of Texas, Austin, April 20, 2010
9. University of Dortmund, Germany, June 22, 2010
10. Technical University of Munich, Germany, June 24, 2010
11. University of Antwerp, Belgium, June 25, 2010
12. University of Duisburg, Germany, June 28, 2010
13. University of Muenster, Germany, July 1, 2010
14. Arizona State University, Tempe, September 16, 2010
15. University of Missouri, Columbia, March 14, 2011

“Stretched Exponential Relaxation: Experiments, Theory, and Simulations”
16. University of Missouri, Columbia, November 10, 2011
“Can the Canonical Ensemble Give Thermal Equilibrium?”
17. University of Missouri, Columbia, March 22, 2012

List of participating scientific personnel

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Lei Tu, MS degree, December 2010
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