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Total and fractional densities of states from caloric relations

S. F. Chekmarev and S. V. Krivov
Institute of Thermophysics, Novosibirsk 630090, Russia

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An approach that allows a detailed investigation of a system possessing a large number of inherent structures is proposed: the total density of states (DS) is suggested to be calculated from the total caloric relation, and the fractional DSs for the structures of interest from the corresponding fractional relations. The latter are found by confinement of the system to the respective catchment basins on the potential surface. The approach is illustrated for the 13-atom Lennard-Jones cluster. [S1063-651X(98)05801-2]

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A many-body system that is characterized by a large number of inherent structures (mechanically stable atomic configurations) remains a challenge to statistical mechanics [1]. A typical example are clusters [2,3]. In a methodological respect, the Lennard-Jones (LJ-*n*) clusters are best suited for consideration since, on one hand, they present the simplest and most workable system, and on the other, they display the characteristic set of the problems in full measure. In particular, even for the LJ-13 cluster the number of geometrically distinct structures (isomers) is about 10^3 [4], and it is expected to grow with cluster size exponentially [5].

A general approach to the description of such systems consists in partitioning the potential surface into catchment basins; each basin surrounds a local minimum [6]. In particular, calculation of the density of states (DS) is then reduced to two complementary but feasible steps: (i) to consider a manifold of the minima (isomers), and (ii) to calculate the DS for each basin.

The interaction potential being known, all the information necessary to realize this approach can, in principle, be obtained with the help of molecular dynamics (or Monte Carlo) simulations combined with quenching at regular intervals [6] (see [3,7] for the current state of the art). However, two problems persist here. The first is that both methods sample the potential surface not uniformly, but according to the fractional DSs of states for the isomers. As a result, for systems such as, e.g., LJ-55 (where the number of isomers is estimated to reach 10^{21} [5]) most of high-lying minima may not occur at all [8]. The second problem arises when one calculates the DSs. If the harmonic approximation were valid, one would need only the characteristics of the minima [9]. Unfortunately, it is not quite consistent with the cases of actual interest (isomerization, melting, etc. [2,3]). As a result, one faces the need to take anharmonic effects into account. In principle, this is achievable [8,10], but the reverse of the success is that many details about every basin must be known.

A peculiarity of the situation is that such detailed information is often excessive, which is certainly true for the equilibrium and also for small deviations from it. All that one actually needs in many cases is the total DS and some fractional DSs. The former describes the behavior of the system as a whole, and the latter characterize the isomers of interest. The fractional DSs also allow one to estimate the interplay between particular isomers, and moreover, when they are coupled with the total DS, the interplay between certain isomers and all others.

Calculations of the total DS are quite practicable currently [11–13]. For this purpose the multiple histogram method [14] and the method based on adiabatic invariants [15] are in use. Though these methods can possibly be modified to allow the calculation of the fractional DSs as well, another method can also be applied, which is easy to implement and offers a uniform procedure to calculate both the total and fractional DSs. It is currently employed in thermodynamics to calculate the entropy via caloric data. In particular, the relations between system's total energy and temperature (so-called caloric curves) can be used for this purpose. The caloric curves belong to the characteristics that have been extensively studied for many systems, among them for clusters [16]. Moreover, some caloric data are available from experiments, which can be incorporated into the caloric curves (see, e.g., [17]). This may be a considerable advantage of this method, particularly in application to the systems for which the interaction potential is not well defined (all other methods need this potential be known explicitly).

Specifically, in this work the total DS is suggested to be calculated from the total caloric curve, and the fractional DSs from the respective fractional caloric curves. The latter are found by confining the system to particular catchment basins on the potential surface [18].

This approach also allows one to verify the correspondence between molecular dynamics simulation results and the predictions of statistical mechanics. Such a verification may be necessary for complex systems, where both the simulations and theoretical predictions are challenging. For this purpose, the probability for the system to be found in the basin corresponding to a particular isomer can be estimated as the relative density of states for this isomer, and then it can be compared with the relative residence time of the system in this basin, which is found by direct counting in the course of simulation [19].

In this paper we demonstrate the proposed approach for the LJ-13 cluster. Free clusters with no overall translation and rotation were under consideration. The system of Newtonian equations governing the atomic motion in the cluster was solved by using the numerical algorithm of Ref. [20], the time step being equal to 0.0025 (here and below we assume the LJ units: $\sigma=1$, $\varepsilon=1$, and also $m=1$, m is the atomic mass).

Since clusters are susceptible to a decay at high energies, statistics were collected in a twofold manner: both over a molecular dynamics run for a given cluster and over an ensemble of the clusters. To form the ensemble, a stochastic molecular dynamics trajectory [21] was issued, from which the points were selected for a desirable cluster total energy E. Then cluster overall translation and rotation were eliminated, and cluster total energy was fitted to E by rescaling the atomic velocities. This was followed by a relaxation run of Newtonian molecular dynamics. The number of copies in the ensemble was 50.

When the ensemble for a given E has been formed, a molecular dynamics run, typically 6×10^5 time steps for every copy, was executed to collect statistics. If a cluster had experienced a decay, the run was terminated, but the points obtained prior to the act of decay contributed to the statistics. Every 250 time steps each of the clusters was quenched in order to specify the cluster isomer to which the current representative point should be related.

To group the isomers (and the basins to be associated with them) into equivalence classes [6], the following rule was accepted: the isomers were taken to be equivalent if they possessed the same minimum energy and the spectrum of normal frequencies. Neither the permutations of atoms in cluster nor the inversion of atomic coordinates affect these quantities. The same is valid for rigid rotations. We thus conclude that $2n!$ basins, each containing all possible orientations of the cluster, correspond to every distinct isomer ($2n!$ is the order of the complete nuclear permutation and inversion group [22]). Since the set of orientations is continuous, these basins are a sort of valley rather than the true basins [23].

The total caloric curve was calculated in the usual fashion [16]. To calculate fractional caloric curves, confinement of molecular dynamics trajectory to a catchment basin [18] was applied: The system was placed into one of the basins corresponding to the given isomer, and a molecular dynamics run for a given E was executed. At regular intervals the location of the system was checked. If the system was found in another, neighboring basin, the checking interval was reduced until the position of the boundary was fixed with an accuracy of one time step [24]. Then the trajectory was subjected to a reverse process at the last point belonging to the true basin: atomic velocities changed their signs and experienced a small uniform random scattering [25]. This was followed by the correction of the cluster total energy, and linear and angular momenta. Since the system was able to leave the basin only at high total energies when nonlinear effects are pronounced, the divergency of phase point trajectories [26], amplified by the velocity scattering at the reverse point, led to rapid deviation of the reversed trajectory from the ‘‘forward’’ one. Due to this, a proper level of stochastization in the system was maintained.

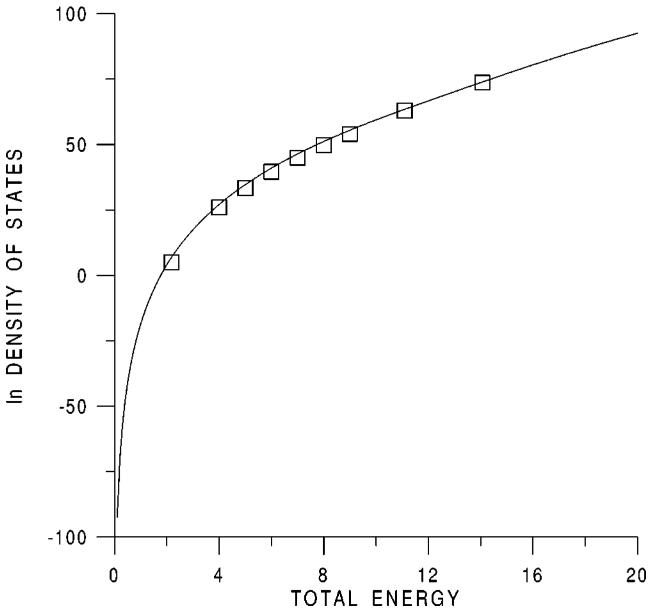

FIG. 1. The total density of states: the solid line corresponds to this work, and the squares to Ref. [12], where a combination of the methods of Refs. [14] and [15] was used.

The conditions under consideration correspond to a microcanonical ensemble ($E=\Sigma_i\mathbf{p}_i^2/2m+V=\text{const}$) with cluster total linear $\mathbf{P}=\Sigma_i\mathbf{p}_i$ and angular $\mathbf{L}=\Sigma_i\mathbf{r}_i\times\mathbf{p}_i$ momenta, and also its center-of-mass position $\mathbf{R}=\Sigma_i m\mathbf{r}_i/M$ being zero ($\mathbf{r}_i$ and $\mathbf{p}_i$ are the coordinates and momenta of ith atom, $M=nm$ the total mass, n the number of atoms, and V the potential energy of the cluster). In the general case of nonlinear atomic configurations, which is assumed hereafter, the phase volume associated with the ensemble is

$$G(E)=\int d\mathbf{r}^{(3n)}d\mathbf{p}^{(3n)}\delta(\mathbf{R})\delta(\mathbf{P})\delta(\mathbf{L})\Theta(E-H), \qquad (1)$$

where $d\mathbf{r}^{(3n)}$ and $d\mathbf{p}^{(3n)}$ are $3n$-dimensional elements of the volume in configuration and momentum space, respectively, δ the delta function, Θ the step function, and $H=\Sigma_i\mathbf{p}_i^2/2m+V$ the cluster Hamiltonian.

The integrals over momenta in Eq. (1) can be carried out [27] to yield

$$G(E)=C\int d\mathbf{r}^{(3n)}\delta(\mathbf{R})\frac{(E-V)^{N/2}}{(I_1I_2I_3)^{1/2}\Gamma(N/2+1)}\Theta(E-V), \qquad (2)$$

where $C=(2\pi)^{N/2}m^{3n/2}/M^{3/2}$, $N=3n-6$ is the number of vibrational degrees of freedom in the cluster, $I_k(k=1,2,3)$ its principal momenta of inertia, and Γ the gamma function.

For further calculation of $G(E)$, let us separate the potential surface into the basins. Since the number of distinguishable atomic configurations is equal to $2n!/h$ (h is the order of the point group of current configuration), $G(E)$ may be written as

$$G(E)=\sum_r (2n!/h_r)G_r(E), \qquad (3)$$

where h_r is the order of the point group for rth isomer at its minimum energy, and $G_r(E)$ is the phase volume for rth isomer, which is defined by the same expression as $G(E)$ (2) except that the integral is taken over the basin associated with a particular rth isomer: the atoms are labeled in a given order, there is no inversion of atomic coordinates, but all orientations of the cluster are possible. Though most of the configurations in the basin do not retain the type of symme-

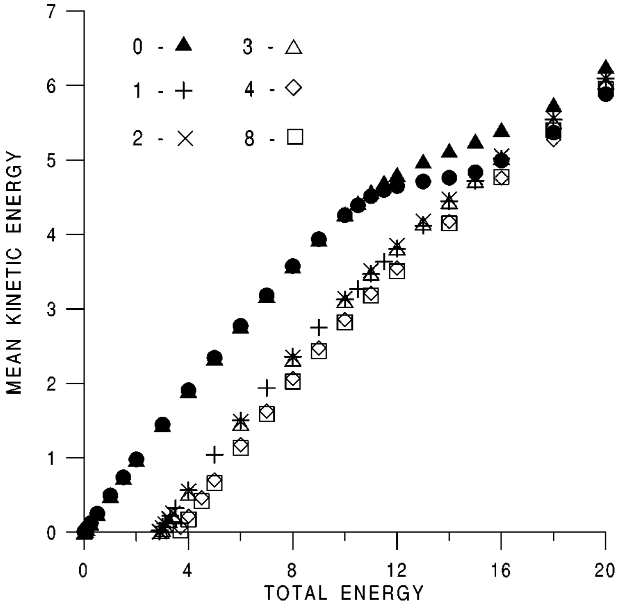

FIG. 2. Caloric curves: solid circles correspond to the total caloric curve, and the other symbols, numbered as given in Table I, to the curves for particular isomers. The total energy is counted from the ground state isomer minimum energy.

try of the minimum, the factor $1/h_r$ is assigned to the whole basin. This implies that the number of atomic configurations of order h in the basin is equal to h_r/h; it is in the line with the results of group-theoretical consideration of symmetry properties of potential surfaces [23] as well as with the arguments used in the theory of reaction path degeneracy (see, e.g., [28]).

With the factor $n!$ in Eq. (3) omitted (the correct Boltzmann counting [29]), the total DS is

$$\rho(E)=dG/dE=\sum_r (2/h_r)\rho_r(E), \tag{4}$$

where $\rho_r(E)=dG_r/dE$ is the DS for a particular rth isomer. Correspondingly, the probability that the system will be found in a basin related to rth isomer is estimated as

$$f_r(E)=(2/h_r)\rho_r(E)/\rho(E). \tag{5}$$

As one can find from Eq. (2)

$$d\ln G/dE=N/(2\langle E_{\rm kin}\rangle), \tag{6}$$

where $\langle E_{\rm kin}\rangle$ is the mean kinetic energy. This equation is an analog of the thermodynamic equation $TdS=dE$, where $S=k_B\ln G$ is the entropy (k_B is the Boltzmann constant), and $T=2\langle E_{\rm kin}\rangle/Nk_B$ is the temperature. Similar equations are valid for every isomer.

TABLE I. Characteristics of isomers.

Isomers	U_0	$\overline{\nu}$	h
0	-44.326801	1.750316	120
1	-41.471979	1.636509	2
2	-41.444597	1.635673	2
3	-41.394398	1.635996	2
4	-40.758513	1.638231	4
8	-40.670170	1.632131	1

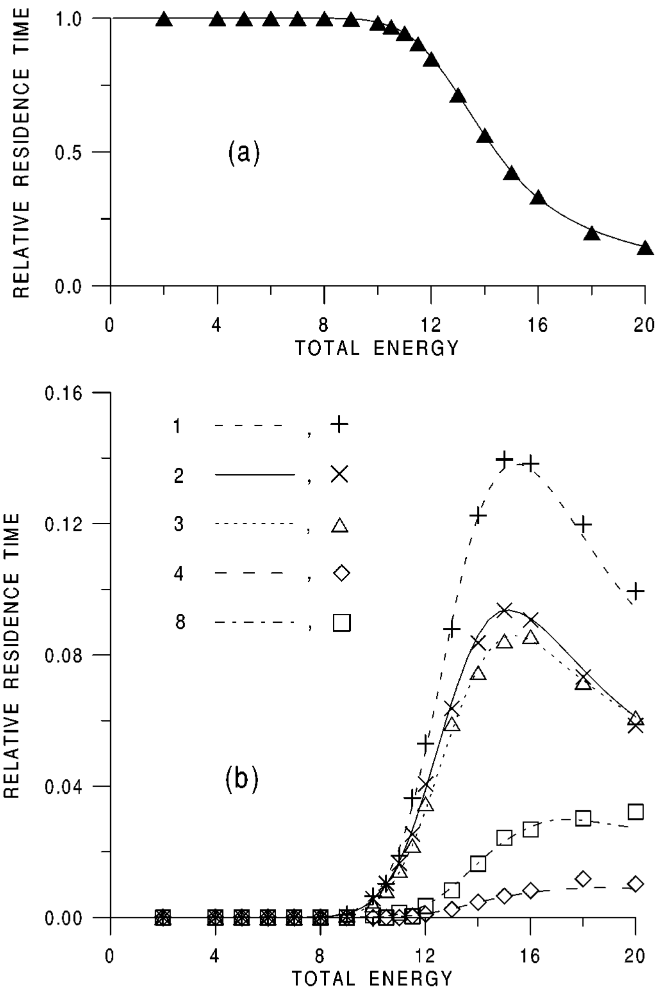

FIG. 3. Relative residence time for the isomers: (a) the ground state isomer, and (b) the excited state isomers. The symbols correspond to direct counting, and the lines show the theoretical predictions based on Eq. (5), and the data of Table I and Fig. 2.

With the characteristics of the isomers and the caloric curves being known, Eq. (6) can be numerically integrated to give $G(E)$ or $G_r(E)$, depending on which of the caloric curves, total or fractional, is used. The arbitrary factor appearing in the integral is found by matching the solution, in the lowest energy limit, to the harmonic one, which is $G_{rh}(E)=8\pi^2(E-U_0^{(r)})^N/[\Gamma(N+1)\overline{\nu_r^N}]$, where $U_0^{(r)}$ is the minimum energy for the rth isomer, $\overline{\nu}_r=(\Pi_{i=1}^N\nu_i^{(r)})^{1/N}$ is the geometrical mean of normal frequencies $\nu_k^{(r)}$; the factor $8\pi^2$ is due to various orientations of the cluster. When calculating $G(E)$, the harmonic solution for the ground state isomer is used. To circumvent the difficulties that one meets in attempting a direct matching (see, e.g., [12]), the right-hand part of Eq. (6) was divided into two parts: the harmonic one, which is N/E in accordance with the equipartition principle, and the rest, $N[1/(2\langle E_{\rm kin}\rangle)-1/E]$, which is an anharmonic correction. The first part is integrated analytically, which provides an automatic matching to the harmonic solution. Figure 1 shows the total DS so obtained from the total caloric curve presented in Fig. 2.

As particular isomers to be considered, the ground state isomer and five of the low-lying excited-state ones were chosen (Table I; the isomers are numbered according to their order in the energy spectrum, with 0 standing for the ground state isomer). The fractional caloric curves for these isomers are shown in Fig. 2. The total number of the isomers which occurred in the course of simulations is 1012.

Figure 3 compares the relative residence time for the isomers estimated according to Eq. (5) with that found by direct counting. As seen, the data are in excellent agreement.

A significance of Fig. 3 is twofold: not only does it testify to the feasibility of the proposed approach but also presents a direct test for some issues of general importance. In particular, it indicates that the system visited a range of phase space, in our case the range corresponding to the basins associated with a given isomer, exactly as statistical mechanics suggests by the hypothesis of equal *a priori* probabilities [29], i.e., according to the contribution of this range to the total DS.

Another important issue is incorporating the properties of symmetry into the phase volume (3). Figure 3 unambiguously evidences that if $G_r(E)$ is calculated by integration over *all* atomic configurations in the basin, the point group of symmetry characteristic of the basin minimum should be related to the whole basin.

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