On the temperature, equipartition, degrees of freedom, and finite size effects: Application to aluminum clusters

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The relationship between statistical ensembles (especially microcanonical ensemble) and dynamics, the equipartition theorem, and the notion of dynamical temperature are reexamined with an emphasis on finite size effects. A (dynamical) equipartition ansatz (postulate) is formulated and the notion of dynamical degrees of freedom is introduced. The utility of the dynamical degrees of freedom as an analysis tool is discussed and illustrated in applications to model aluminum clusters.

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I. INTRODUCTION

Atomic and molecular clusters, a field of vigorous research activity and impressive achievements within the last three decades (see, e.g., Refs. 1–3, and references therein), underscore more than any other objects the role of the (finite) size as an important, often defining, characteristic of physical, chemical, and biological systems. They provide a strong impetus, as well as fertile grounds, for reexamination of the role of the size at the fundamental/conceptual level.

One of the most active areas of cluster research deals with the issue of phases and phaselike, e.g., solid-to-liquid-like, changes in these systems (see, e.g., Refs. 1, 2, 4–8, and references therein). Whereas traditionally phase transitions belong to the realm of thermodynamics and statistical physics, phase changes in clusters, or more generally finite systems, especially those of small to moderate sizes, can be described and understood in dynamical terms (the size limit for what operationally is defined as ‘‘moderate’’ rapidly increases with progress in computer hardware and software). Consequently, clusters are a natural ‘‘laboratory’’ for testing the general correspondence between the dynamical and statistical approaches, for critically reexamining the fundamental notions and concepts of the traditional thermodynamics and statistical physics as applied to small systems (most, if not all, of these notions and concepts are originally introduced for large systems), and for introducing, if needed, modifications that account for the size effects; of course, the modifications should be such that they lead to the traditional picture in the appropriate limiting and special cases. An additional issue that can be addressed within the framework of this ‘‘laboratory’’ is that of differences between the various statistical ensembles in the regime far from the thermodynamic limit.

Among the fundamental notions and concepts of especial relevance to the problem of phase changes are those of temperature, equipartition theorem, and degrees of freedom. The goal of this paper is to reexamine these notions and concepts, as well as some other related quantities, as applied in the finite size regime and from the point of view of conservative dynamics. This is done in Sec. II, where we present a brief critical review, introduce the dynamical equipartition ansatz, and formulate the notion of the dynamical degrees of freedom. The issues and quantities introduced in Sec. II are illustrated in Sec. III through applications to model aluminum clusters. In particular, we demonstrate the utility of the dynamical degrees of freedom as a tool of detailed analysis of the energy dependence of dynamics and discuss their other possible applications. A summary is given in Sec. IV.

II. TEMPERATURE, EQUIPARTITION, DEGREES OF FREEDOM, FINITE SIZE EFFECTS, AND HEAT CAPACITY

First, we revisit the concepts of temperature and the equipartition theorem with the goal of reemphasizing the assumptions they are based on and their implications. Then we introduce a dynamical microcanonical equipartition ansatz (postulate) that leads to the definition of active, or dynamical, degrees of freedom. The discussion of the latter includes finite size effects and connection with the heat capacity.

A. Temperature and equipartition theorem

One of the fundamental characteristics of systems is the temperature $T$. Thermodynamically, temperature, an intensive state variable, is defined as

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_V ,$$

(1)

where $S$, $E$, and $V$ are, respectively, the entropy, total energy, and volume of the system. Within a statistical mechanical description the temperature is defined as the control parameter of a canonical ensemble, i.e., an ensemble of systems in thermal equilibrium with a heat bath. The canonical ensemble temperature $T_c$ satisfies what is often referred to as the equipartition theorem,

$$\frac{kT_c}{2} = \frac{\langle E_{\text{kin}} \rangle_c}{3N} ,$$

(2)

where $E_{\text{kin}}$ is the kinetic energy of a system, $N$ is the number of atoms in it, $k$ is the Boltzmann constant, and $\langle \rangle_c$ stands for the canonical ensemble average. The interpretation of $T_c$ as a measure of the canonically averaged total kinetic energy equipartitioned between all the degrees of freedom is based on the notion of the kinematical degrees of freedom (to be referred in what follows simply as degrees of freedom), which
are aliases for the dimensions of the configuration space of the system and which are assumed to be all equally probable (i.e., equally involved). This assumption is inherent in all statistical mechanical treatments. Without it Eq. (2) still holds, but its “equipartition content” remains valid only in a weaker form, on average per degree of freedom. The assumption of equiprobability of the degrees of freedom is a sufficient (but not a necessary, see below) condition for the canonical ensemble temperature to preserve the fundamental attribute of intensity of the thermodynamic temperature. The essence of this attribute is that in a state of thermal equilibrium a specified temperature characterizes not only the system as a whole, but also any and all parts of it, including the individual atoms and their individual degrees of freedom.

The microcanonical temperature \( T_w \) can be introduced using Eq. (1) and the microcanonical entropy,

\[
S_w = k \ln \omega, \tag{3}
\]

where

\[
\omega(N,V,E) = C \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N \times \delta(E-H(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)), \tag{4}
\]

\( H \) is the Hamiltonian of the system, and \( C \) is a constant. The result is\(^2\)

\[
T_w = k \left[ \frac{3N-6}{2} - 1 \right] \left( \langle E_{\text{kin}}^{-1} \rangle_\mu \right)^{-1}, \tag{5}
\]

where \( \langle \cdot \rangle_\mu \) stands for the microcanonical ensemble average defined over the phase space density \( C \delta[E-H(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)] \). \( T_w \) is still related to a (in this case microcanonical) ensemble average, but of \( E_{\text{kin}}^{-1} \) and through a functional form other than that in Eq. (2). The form of Eq. (2), with \( \langle \cdot \rangle_\varepsilon \) replaced by \( \langle \cdot \rangle_\mu \), holds though for the “\( \Omega \)-microcanonical” temperature \( T_\Omega \) (Ref. 11) obtained by substituting into Eq. (1) the “cumulative” entropy \( S = S_\Omega \),

\[
S_\Omega = k \ln \Omega, \tag{6}
\]

where

\[
\Omega(N,V,E) = C \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N \times \delta[E-H(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)]. \tag{7}
\]

If \( E_{\text{kin}} \) in the above expressions is viewed as the internal (vibrational) kinetic energy, the factor \( 3N \) is replaced by \((3N-6)\) and the resulting temperatures are interpreted as vibrational temperatures. In what follows we consider only quantities referring to the vibrational motion.

In Newtonian, or Hamiltonian, constant-energy molecular dynamics simulations a dynamical temperature \( \langle T_d \rangle_\Omega \) is often introduced through the equation

\[
k\langle T_d \rangle_\Omega = \frac{\langle E_{\text{kin}} \rangle_\Omega}{(3N-6)^{1/2}}, \tag{8}
\]

where \( \langle \cdot \rangle_\Omega \) stands for time average over the trajectory. (In simulations, the translational energy is trivially removed by converting to the center-of-mass of coordinates, whereas an exact specification of the vibrational kinetic energy in a rotating and vibrating \( N \)-body system is accomplished via the technique described in Ref. 12, cf. also Ref. 13.) The dynamical temperature \( \langle T_d \rangle_\Omega \) correlates with the ensemble temperature \( T_d \), rather than \( T_w \) [hence the label \( \Omega \) in \( \langle T_d \rangle_\Omega \)]. Conceptually, this is unsatisfactory since (ergodic) conservative dynamics sample manifolds of microstates defined by \( \omega \), rather than \( \Omega \). [More precisely, the \( \omega \) corresponding to an ergodic conservative dynamics is obtained by multiplying the integrand in Eq. (4) by \( \delta \)-functions representing conservation of the total linear and angular momenta.] Notwithstanding the fact that \( T_w \) and \( T_\Omega \) approach the same value in the thermodynamic limit\(^3\) and that the difference between the two is only moderate even in the small size range (cf. next section), the correct expression for the dynamical microcanonical vibrational temperature is

\[
\langle T_d \rangle_w = \frac{1}{k} \left[ \frac{3N-6}{2} - 1 \right] \left( \langle E_{\text{kin}}^{-1} \rangle_\Omega \right)^{-1} \tag{9}
\]

or, alternatively,

\[
k\langle T_d \rangle_w = \frac{\langle E_{\text{kin}} \rangle_\Omega}{(3N-8)^{3/2} Z}, \tag{10}
\]

where

\[
Z = \langle E_{\text{kin}} \rangle_\Omega / \langle E_{\text{kin}}^{-1} \rangle_\Omega. \tag{11}
\]

The above discussion can be summarized in the form of the following three observations: (1) The rigorous formulation of the traditional canonical (and \( \Omega \)-microcanonical) equipartition theorem includes (usually implicitly) the assumption of equal probability of all, or relevant (e.g., vibrational), degrees of freedom understood as aliases of the relevant dimensions of the configuration space. This assumption may hold true for some systems (e.g., ideal gas) or at certain energies or temperatures, but it is lacking general justification (see below); (2) The traditional equipartition theorem is consistent with the intensive nature of temperature as a state variable; (3) Even under the assumption of equal probability of all (or relevant) degrees of freedom, the microcanonical temperatures \( T_w \), Eq. (5), and \( \langle T_d \rangle_w \), Eqs. (9)–(11), do not satisfy the equipartition theorem in its traditional form of Eq. (2) or Eq. (8). An exception is the thermodynamic limit, where the \( \omega \) and \( \Omega \)-labeled temperatures become the same.

**B. Dynamical equipartition ansatz and dynamical degrees of freedom**

Our emphasis is on the size range where the implications of the different ensembles are different and on the (conservative) dynamics perspective. One of the underlying differences between the dynamical and statistical methodologies is that dynamics do not incorporate the \textit{a priori} assumption on the equal probability of the different degrees of freedom. To the contrary, in a dynamical treatment the forces, or the constraints, define the actual partitioning (distribution) and flow (redistribution) of the energy between the individual degrees of freedom and specify which of them and to which extent actually participate in the time evolution of the system.
Our goal is to formulate an equipartition ansatz, or postulate, which is consistent with the intensive nature of temperature, on the one hand, and which is free from the assumption of equiprobability of degrees of freedom, on the other. This is achieved by requiring a function of the time averaged kinetic energy of any subsystem of the system to have the same value for all subsystems, when referred to a unit (value "one") of the dynamical degrees of freedom (see below) of the subsystem, and interpreting the temperature as a measure of that value. The subsystems may range from the entire system to any number of its atoms or associated with them degrees of freedom, including a single atom or even only one of its degrees of freedom.

The necessary and sufficient condition for the fulfillment of the above requirement is its fulfillment for the subset of those subsystems that represent the individual degrees of freedom. We stress that no assumption on the equiprobability of the latter is made.

Two possible choices for the mentioned function of the time averaged kinetic energy are suggested by Eqs. (10) and (11). The first is \( \langle E_{\text{kin}}^l \rangle \cdot Z^{-1} \), where \( \langle E_{\text{kin}}^l \rangle \) is the time averaged kinetic energy of an arbitrary, \( l \)th subsystem. Equation (12) is the microcanonical dynamical equipartition postulate. It states that it is the \( Z^{-1} \)-scaled corresponding time averaged kinetic energy that is equally distributed per unit of the dynamical degrees of freedom (ddf). Both, \( \langle E_{\text{kin}}^l \rangle \) and \( Z^{-1} \), as well as their product, depend on the total (internal) energy.

The ddf are not necessarily aliases for the dimensions of the relevant configuration spaces; the values of the \( f_l \)s may differ from the dimensionalities of these spaces. The \( f_l \)s may have different values for subsystems with the same number of atoms, or even when the subsystems are the individual degrees of freedom. An \( f_l \) has a nonzero value only when the corresponding \( \langle E_{\text{kin}}^l \rangle \) is different from zero. It may appear from Eq. (12) that the ddf \( f_l \) depend on \( Z \), whereas in fact they do not. Substitution of the r.h.s. of Eq. (10) into Eq. (12) gives

\[
\frac{k(T_d)_{\omega}}{2} = \frac{\langle E_{\text{kin}}^l \rangle \cdot Z^{-1}}{f_l}.
\]

(12)

With \( (T_d)_{\omega} \) specified by Eq. (9), or Eqs. (10)–(11), Eq. (12) defines \( f_l \), the number of the active, or dynamical, degrees of freedom of the \( l \)th subsystem. Equation (12) is the microcanonical dynamical equipartition postulate. It states that it is the \( Z^{-1} \)-scaled corresponding time averaged kinetic energy that is equally distributed per unit of the dynamical degrees of freedom (ddf). Both, \( \langle E_{\text{kin}}^l \rangle \) and \( Z^{-1} \), as well as their product, depend on the total (internal) energy.

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\[
f_l = \frac{\langle E_{\text{kin}}^l \rangle}{\langle E_{\text{kin}}^l \rangle} (3N-8).
\]

(13)

For any subdivision of the system into \( l \) subsystems,

\[
\sum_l f_l = (3N-8).
\]

(14)

The total of the \( 3N-8 \) ddf may, in principle, be distributed between \( m < N \) atoms, which would result in "unnaturally" large values of ddf. This apparent defect (which, depending on the application, may have no physical consequences, cf. next section) is easily corrected by considering the appropriately reduced configuration space.

The second choice of the function of the time averaged kinetic energy is \( \langle E_{\text{kin}}^l \rangle \), itself. The microcanonical dynamical equipartition postulate takes then the form of the equation

\[
\frac{k(T_d)_{\omega}}{2} = \frac{\langle E_{\text{kin}}^l \rangle}{F_l},
\]

(15)

where now \( F_l \) is the number of the ddf of the \( l \)th subsystem. The ddf \( F_l \) do depend on \( Z \). Substitution of the r.h.s. of Eq. (10) into Eq. (15) gives

\[
F_l = \frac{\langle E_{\text{kin}}^l \rangle}{\langle E_{\text{kin}}^l \rangle} (3N-8) \cdot Z.
\]

(16)

The \( F_l \)s satisfy the sum rule

\[
\sum_l F_l = (3N-8) \cdot Z.
\]

(17)

The involvement of the function \( Z \) in the microcanonical dynamical equipartition postulate, either in the form of Eqs. (12) and (14) or Eqs. (15) and (17), is an additional element that differentiates this postulate from the canonical equipartition theorem, Eq. (2), or its dynamical analog, Eq. (8). Function \( Z \) plays the role of a finite size correction in the microcanonical concept of equipartitioning; its value becomes unity in the thermodynamic limit.

C. Heat capacity

Thermodynamically, the heat capacity at constant volume \( C_V \) is defined as

\[
\frac{1}{C_V} = \left( \frac{\partial T}{\partial E} \right)_V.
\]

(18)

Use of \( T=T_{\omega} \) and \( T=T_{\Omega} \) in Eq. (18) leads\(^11\) to the corresponding (vibrational) heat capacities \( (C_V)_{\omega} \) and \( (C_V)_{\Omega} \).

\[
\frac{(C_V)_{\omega}}{Nk} = \left\langle \frac{3N-6}{2} - 1 \right\rangle \left[N \left( \frac{3N-6}{2} - 1 \right) \right.
\]

\[
- N \left( \frac{3N-6}{2} - 2 \right) \frac{\langle E_{\text{kin}}^l \rangle}{\langle E_{\text{kin}}^l \rangle} \right],
\]

(19)

\[
\frac{(C_V)_{\Omega}}{Nk} = \left[ N - N \left( \frac{2}{3N-6} \right) \frac{\langle E_{\text{kin}}^l \rangle}{\langle E_{\text{kin}}^l \rangle} \right]^{-1}.
\]

(20)

Equations (19) and (20) define, respectively, the specific heats \( (c_V)_{\omega} \) and \( (c_V)_{\Omega} \) referred to an atom and expressed in units of \( k \). Using energy-conserving dynamical simulations\(^14\) these specific heats can be computed as

\[
(c_V)_{\omega} = \left\langle \frac{3N-6}{2} - 1 \right\rangle \left[ N \left( \frac{3N-6}{2} - 1 \right) \right.
\]

\[
- N \left( \frac{3N-6}{2} - 2 \right) \frac{W^2}{Z} \right]^{-1},
\]

(21)

and

\[
(c_V)_{\Omega} = \left[ N - N \left( \frac{2}{3N-6} \right) \frac{Z}{Z} \right]^{-1},
\]

(22)

where \( Z \) is defined by Eq. (11) and
\[ W = \langle E_{\text{kin}} \rangle^2 / \langle E_{\text{kin}}^2 \rangle. \]  

(23)

Although \((c V)_{\omega}\) is the rigorous microcanonical specific heat, \((c V)_{\Omega}\) is different from it only moderately even in the relatively small size range (cf. next section), and the two approach the same value in the thermodynamic limit.  

It is clear from Eq. (22) that an extremum point \(E_0\) of \(Z(E)\) and, consequently, also of \((3N-8)Z\), which is the total number of the ddf \(F_1\), Eq. (17),  

\[ \frac{dZ(E_0)}{dE} = 0, \]  

(24)

is also an extremum point of \((c V)_{\Omega}\),  

\[ \frac{d((c V)_{\Omega}(E_0))}{dE} = 0, \]  

(25)

provided the expression in the bracket in the r.h.s. of Eq. (22) is different from zero at \(E = E_0\). It is easy to see that an extremum point \(\bar{E}\) of the function \(\ln(W(E)/Z^2(E))\),  

\[ \frac{d}{dE} \ln \frac{W(E)}{Z^2(E)} = 0, \]  

(26)

is also an extremum point of \((c V)_{\omega}\),  

\[ \frac{d((c V)_{\omega}(E))}{dE} = 0, \]  

(27)

provided the term in the bracket in the r.h.s. of Eq. (21) is different from zero at \(E = \bar{E}\). The energies at which the terms in the brackets in Eqs. (21) and (22) vanish are discontinuity points of the corresponding specific heats. Depending on the size \(N\) (and, of course, the material, i.e., the potential energy function), there may, at least in principle, be none, one, a finite number, and a continuum of such points. Two such points are necessary for the caloric curve (temperature as a function of the total energy) to possess a so-called backbending portion (cf. next section).

The energy dependent functions \(Z\), Eq. (11), and \(W\), Eq. (23), represent finite size corrections in the expressions for the specific heat, Eqs. (21) and (22) \((W/Z)^2\) becomes unity in the thermodynamic limit. They involve the \(\langle \rangle\), time averaging, which in the case of ergodic dynamics represents also the (constant linear and angular momenta) microcanonical \(\langle \rangle_{\mu}\) averaging. One can readily verify (cf. also Ref. 11) that  

\[ Z = \left( \frac{1}{1+\delta E_{\text{kin}}} \right)^N \quad \text{and} \quad W = \left( \frac{1}{1+\delta E_{\text{kin}}} \right)^2, \]  

(28)

where  

\[ \delta E_{\text{kin}} = \frac{E_{\text{kin}} - \langle E_{\text{kin}} \rangle}{\langle E_{\text{kin}} \rangle}, \]  

(29)

and \(\langle \rangle\) stands for \(\langle \rangle_t\) or \(\langle \rangle_{\mu}\).

III. ILLUSTRATIVE EXAMPLES AND ANALYSIS

We present here results illustrating the quantities introduced and the issues discussed in the previous section. These results are obtained for model aluminum clusters, mimicked by a many-body Gupta-type potential, using energy conserving molecular dynamics simulations. The specifications of the potential can be found in Refs. 15–19, whereas the details of the simulations are the same as those described in Refs. 17–19. Four clusters—\(\text{Al}_7\), \(\text{Al}_{13}\), \(\text{Al}_{55}\), and \(\text{Al}_{147}\)—are considered. Their lowest energy structure, as defined by the mentioned potential, is the pentagonal bipyramid for \(\text{Al}_7\), and the icosahedron for the other three. The binding energies per atom of these structures are 2.353 eV for \(\text{Al}_7\), 2.601 eV for \(\text{Al}_{13}\), 2.892 eV for \(\text{Al}_{55}\), and 3.020 eV for \(\text{Al}_{147}\). These structures are chosen as the respective zero-temperature forms of the clusters. For \(\text{Al}_7\) the analysis is performed considering also its second isomer (see below) as the zero-temperature form. For a given isomer the dynamics are initialized by slight random distortions of the equilibrium structure and assigning zero initial velocities (and, consequently, zero initial linear or angular momenta) to the atoms. After 10⁴ propagation steps with the step size of 2 fs the acquired instantaneous velocities are rescaled by a constant factor to supply the cluster the desired total energy. The thus prepared initial conditions are used to generate the fixed-energy trajectories that are propagated for time intervals ranging from 10 to 40 ns.

First, we compare results obtained using the entropies \(S_{\omega}\), Eq. (3), and \(S_{\Omega}\), Eq. (6). The temperatures \((T_{\omega})_{\omega}\), Eq. (9), and \((T_{\mu})_{\Omega}\), Eq. (8), and the corresponding specific heats \((c V)_{\omega}\), Eq. (21), and \((c V)_{\Omega}\), Eq. (22), are shown for the four clusters in Fig. 1 (in all figures the energy for each cluster size is measured from the bottom of the potential energy well corresponding to its lowest energy structure). The difference in the \(\omega\)- and \(\Omega\)-labeled quantities is only moderate even for \(\text{Al}_7\), and it practically vanishes for \(\text{Al}_{55}\) and, even more so, for \(\text{Al}_{147}\). The specific heats for \(\text{Al}_7\), \(\text{Al}_{13}\), and \(\text{Al}_{55}\) are continuous functions of the total (internal) energy. Accordingly, the graphs of the caloric curve do not exhibit a backbending loop for these clusters. Such a loop, however, is present in the caloric curve of \(\text{Al}_{147}\). Its signature in the graph of the specific heat is the two discontinuity points and a continuous negative-valued segment between them. A maximum (or maxima) in the specific heat is an indicator of a solid-to-liquid-like transition (see, e.g., Refs. 18, 19, and references therein). The graphs show that the height of the maximum increases and its width decreases with an increase of the cluster size; the signature of a first order phase transition (e.g., bulk melting) is a point singularity in the specific heat.

The central quantities of our analysis are the (vibrational) dynamical degrees of freedom. Figure 2 shows \(f_j/N_j\) as a function of the cluster energy per atom for different subsystems of the \(\text{Al}_{13}\) and \(\text{Al}_{55}\) clusters (\(N_j\) is the number of atoms in the \(j\)th subsystem). In \(\text{Al}_{13}\) the atoms are divided into two subsystems. The first contains only one atom, the one which is the central atom in the zero-temperature icosahedral isomer. The second subsystem is comprised of the remaining twelve (‘‘surface’’) atoms. In \(\text{Al}_{55}\) the atoms are partitioned into four subsystems. These represent, respectively, the central atom, the twelve atoms of the internal layer (first shell), the thirty ‘‘edge’’ atoms of the external layer (second shell), and the twelve ‘‘vertex’’ atoms of the external layer (third shell) in the zero-temperature icosahedral \(\text{Al}_{55}\).  

The distances of the three shells from the
central atom scale as 1:1.73:1.99. The major features to notice are (1) At low energies the values of $f_l/N_l$ are different for different subsystems; (2) As the energy increases, these values change; (3) At certain energies the values for some subsystems converge; (4) As the energy is increased further, the ddf $f_l$ approach the same value per atom for all subsystems.

In the case of Al$_{13}$ at low energies, the (initially) central atom has a higher degree of dynamical freedom than a (initially) surface atom. At the energy of about 0.146 eV/atom the values for the “central” and “surface” atoms start to approach each other, and at the energy of approximately 0.176 eV/atom they become equal within the statistical uncertainty; an indication of the degree of this uncertainty is given by the fluctuation in the values of ddf for the individual subsystems. It is of interest to correlate these observations with the behavior of the root-mean-square (rms) bond length fluctuations, power spectra, and mean square...
displacements of the atoms as a function of energy. We consider these quantities for the entire cluster, its “surface,” and its “central” atom.

The rms bond length fluctuations are computed using the general definitions

$$\delta_l = \frac{2}{N_l(N_l-1)} \sum_{i(l) \neq j(l)} \frac{(\langle r_{ij}^2 \rangle_t - \langle r_{ij} \rangle_t^2)^{1/2}}{\langle r_{ij} \rangle_t},$$

and

$$\delta_{ll'} = \frac{1}{N_l N_{l'}} \sum_{i(l), j(l')} \frac{(\langle r_{ij}^2 \rangle_t - \langle r_{ij} \rangle_t^2)^{1/2}}{\langle r_{ij} \rangle_t},$$

where $\delta_l$ characterizes the $l$th subsystem (e.g., the “surface” or a “shell;” the subsystem may also be the entire system, in which case $N_l = N$), and $\delta_{ll'}$ is the rms fluctuation in the bonds between the atoms of subsystems $l$ and $l'$ (e.g., the bonds between the “central” atom and the atoms of the “surface” or a “shell,” or between the atoms of two “shells”); $r_{ij}$ is the distance between atoms $i$ and $j$; and $i(l)$ is the $l$th atom of the $l$th subsystem. The results for Al$_{13}$ are shown in Fig. 3. The overall abrupt increase in the $\delta$-graphs is a signature of structural or phase-like transitions. The two distinct segments comprising the abrupt increase in $\delta$ for the entire cluster correspond to surface isomerizations (i.e., transitions that involve only surface atoms), the lower energy segment, and to global isomerizations (i.e., transitions that also allow for the central atom and a surface atom to exchange positions), the higher energy segment (cf. the discussion in Refs. 18, 19). This is corroborated by the $\delta$-graphs for the bonds between the surface atoms, on the one hand, and the bonds between the central atom and the surface atoms, on the other: the abrupt increase in the graph for the latter starts at a higher energy than in the graph for the former. The value of this higher energy is about 0.146 eV/atom, that is the same at which the ddf $f_l/N_l$ for the “central” atom and a representative (in averaged sense) “surface” atom start to approach each other. The two $\delta$-graphs eventually merge at the same energy (about 0.176 eV/atom) as the corresponding graphs of the ddf. The surface isomerizations taking place at energies between about 0.116 and 0.146 eV/atom have no noticeable effect on the value of $f_l/N_l$ either for the “central” atom or the “surface” of the cluster.

The power spectra $I_l(w)$ are computed using the expression

$$I_l(w) = 2 \int_0^\infty C_l(t) \cos wt dt,$$

where $w$ is the cyclic frequency and $C_l(t)$ is the velocity autocorrelation function of the subsystem $l$. 

![Fig. 2. Dynamical degrees of freedom $f_l$ per atom as a function of energy for subsystems of Al$_{13}$ and Al$_{55}$ (see text for details). The difference in the statistics is the reason for the larger fluctuations in the values for the “central” atoms.](image1)

![Fig. 3. Rms bond length fluctuations as a function of energy for Al$_{13}$ and its subsystems (see text for details). C stands for “central” and S for “surface.” The assignment of the atoms to the subsystems corresponds to their positions in the zero temperature form of the cluster. The reason for a slight difference between the graph labeled “Total” and that published earlier (Refs. 18, 19) is that results of longer (20–30 ns) runs are presented here.](image2)
\[ C_i(t) = \frac{\sum_{i=1}^{N_i} \sum_{j=1}^{n_i} v_i(t+t_{oj}) v_i(t_{oj})}{\sum_{i=1}^{N_i} \sum_{j=1}^{n_i} v_i^2(t_{oj})}, \]  

\[ \langle \Delta r^2(t) \rangle = \frac{1}{N_i n_i} \sum_{i=1}^{N_i} \sum_{j=1}^{n_i} [r_i(t+t_{oj}) - r_i(t_{oj})]^2. \]  

FIG. 4. Power spectra (intensities in arbitrary units as a function of frequency \( w \)) for Al\(_{13}\) and its subsystems at five different energies (see text for details).

The mean square displacements are computed using the expression

C\(_i\) is the velocity of atom \( i \), and \( n_i \) is the number of the different time origins \( t_{oj} \). Results for the entire Al\(_{13}\), its "central" atom, and its "surface" are shown in Fig. 4. At energies below 0.176 eV/atom the graphs for the "central" atom and the "surface" are qualitatively different. At that energy, however, they become similar, and as the energy is increased further they become practically indistinguishable. The overall change in the pattern of the graphs with energy (broadening and shift towards lower frequencies) is typical of a solid-to-liquid-like transition (cf., e.g., Ref. 21).

The mean square displacements are computed using the expression

where \( r_i \) specifies the position of atom \( i \). Results for Al\(_{13}\) and its subsystems are shown in Fig. 5. The slopes of the graphs define the diffusion coefficient (cf., e.g., Ref. 21). At low
energies neither subsystem exhibits diffusion. As the energy is increased, the diffusive motion first sets in in the “surface” of the cluster. At the energy of 0.176 eV/atom the diffusion coefficients for the “central” atom and the atoms in the “surface,” although still small, are already very close. As the energy is increased further the diffusion coefficients for both subsystems increase and become equal.

For Al$_{55}$ the low-energy values of $f_i/N_i$ corresponding to the individual subsystems, Fig. 2, are ordered similarly to those of Al$_{13}$. The values for the “central” atom are the highest, and those for the “shells” decrease with an increase of the number of the shell. At an energy just above 0.10 eV/atom the values for the most external (third) “shell” and its neighboring (second) “shell” start to approach each other. They merge at the energy of about 0.12 eV/atom. The common value then increases with the energy of the cluster. The values for the first “shell” and the “central” atom undergo an abrupt decrease at the energies of 0.142 and 0.144 eV/atom, respectively. At approximately 0.15 eV/atom the values for all four subsystems become equal within the statistical uncertainty. As in the case of Al$_{13}$, the peculiarities of the energy dependence of $f_i/N_i$ for subsystems of Al$_{55}$ correlate with the behavior of the rms bond length fluctuations, power spectra, and mean square displacements. The reader can establish the correlations by examining the graphs in Figs. 6, 7, and 8 and comparing them with the graphs for Al$_{55}$ in Fig. 2.

The graphs of the alternative dynamical degrees of freedom $F_i/N_i$ are shown in Fig. 9. Their overall features—the low-energy differences in and the gradual coalescence of the values of $F_i/N_i$ as the energy is increased—mimic those of the $f_i/N_i$ graphs, Fig. 2. There is, however, a notable differ-
ence. After coalescence for all subsystems, the common value of $F_l/N_l$ continues to change with energy exhibiting a maximum, whereas that for $f_l/N_l$ remains constant. This difference is defined by the function $Z(E)$; cf. Eqs. (13) and (16). The graphs of $Z(E)$ are shown for the four clusters in Fig. 10 [cf. the discussion on the properties of $Z(E)$ in the preceding section]. They display the following trends as a function of size: the larger the system the smaller the range of its $Z$ values and the closer they are to unity. For a fixed size, the “asymptotic” value at high energies is larger than that at low energies. The difference between the two, however, vanishes with increase of the size.

The above illustrations and discussion show the utility of the ddf as an analysis tool of dynamics. The level of detail
The number of subsystems in the examples considered is defined by the number of topologically (or geometrically) different types of atoms in the zero-temperature structures of the systems. A more detailed description is to consider the ddf of each individual atom, or even the degree of dynamical freedom of each atom along the individual dimensions of, or directions of interest in, its configuration space. Atoms, or their dynamics in chosen directions, with the same value of the ddf can be grouped into classes of dynamical similarity. The choice of the degree of accuracy in the criterion for "sameness" depends on the nature of the phenomena studied and the desired degree of detail of the analysis. Figure 11 shows the ddf $f_i$ for each of the seven atoms of Al$_7$ as a function of energy. Two cases are considered—they correspond to dynamics generated from the first and the second lowest energy isomers of the cluster; Al$_7$ forms four isomers shown in Fig. 12. At low energies, the atoms of isomer I form two classes of dynamical similarity containing two (atoms number 1 and 2) and the remaining five atoms, respectively. The low-energy behavior of isomer II is well represented by three classes of dynamical similarity with one (number 1), three (number 2, 3, and 4), and three (number 5, 6, and 7) atoms, respectively. As verified by simulated thermal quenchings
The details of the procedure are described in Ref. 17, at energies below 0.053 eV/atom the dynamics initialized from isomer I remain confined to the catchment area of that isomer. In the longest run (20 ns) at 0.053 eV/atom the trajectory visited also the basin of isomer II, but the fraction of the sampled configurations that correspond to this isomer is only about 1%; the branching ratio is evaluated from the numbers of times a total of 10,000 quenchings performed with a time interval of 2 ps produced isomer I and isomer II. At energies of 0.063 to 0.083 eV/atom transitions from isomer I to isomer II and vice versa become ever more frequent. This is reflected in the abrupt change in the values of the ddf associated with the two initial classes of dynamical similarity. In fact, the two lose their original identity over this energy range. Starting from the energy of about 0.1 eV/atom the values of the ddf converge within the statistical uncertainty for all atoms. At 0.1 eV/atom the trajectory visits already all four isomers, though the contribution of isomers III and IV to the dynamics is still negligible.

The three groups of values of the ddf characterizing the dynamics of the seven atoms initially in the arrangement of isomer I are distinct at the energy of 0.033 eV/atom and lower. At these energies the dynamics are confined to the basin of isomer II. At 0.043 and 0.053 eV/atom the dynamics visit the basins of isomer II and isomer I. The sampled configurations corresponding to isomers II and I constitute about 9% and 91%, respectively, at 0.043 eV/atom, and about 1% and 99%, respectively, at 0.053 eV/atom. This seemingly intriguing result can be rationalized as follows. At a higher energy the cluster trajectory crosses the barrier to the basin of isomer I more readily. Once there, it has little chance to recross the barrier; most probably because of a much larger “area” of the basin of isomer I accessible at energies close to the barrier; another reason could be a less favorable “topography” of the potential energy “landscape” for an interbasin passage from the side of isomer I. The values of the ddf at 0.043 eV/atom and, even more so, at 0.053 eV/atom group the atoms into two classes of dynamical similarity with two and five atoms, respectively. This pattern, as well as the magnitudes of the ddf associated with the two classes, are characteristic of the low-energy dynamics of isomer I and are consequences of its dominance in the overall time evolution of the cluster. As the energy is increased further, the behavior of the ddf characterizing the dynamics generated from isomer II becomes indistinguishable from that characterizing the dynamics generated from isomer I. The reason for this is that at higher energies the dynamics do not retain memory of the isomer chosen as the zero-temperature form of the cluster, cf. Ref. 19. The features of the dynamics exhibited in Fig. 11 in terms of the ddf, specifically the interconversion of isomer II into isomer I, correlate with the behavior of the temperatures computed from the isomer-labeled dynamics, Fig. 13.

FIG. 11. Dynamical degrees of freedom as a function of the cluster energy for each of the seven atoms of Al7 (fi is the ddf of the ith atom). A and B correspond to dynamics generated from isomers I and II, respectively (cf. Fig. 12). The dashed and dotted rectangles indicate the classes of dynamical similarity characteristic of dynamics confined to the catchment area of isomer I and isomer II, respectively.

FIG. 12. The four isomers of Al7. Their binding energies are: (I) 16.470 eV, (II) 16.335 eV, (III) 16.124 eV; (IV) 16.123 eV.

FIG. 13. The ω-labeled dynamical temperatures computed along trajectories initialized from isomer I (open circles) and isomer II (full circles) of Al7 as a function of the cluster energy.
The general prescription for grouping the atoms (or their dynamics in chosen directions) into classes of dynamical similarity is based on a dynamical, rather then geometrical, criterion. At low energies the classes of dynamical similarity may or may not coincide with the classes of geometrical similarity. In the case of Al$_3$, they do coincide for isomer I and do not coincide for isomer II. The atoms of isomer I form two classes of geometrical similarity. One contains atoms 1, 2, and the other the five atoms of the pentagonal ring (Fig. 12). The atoms of isomer II fall into five classes of geometrical similarity. Three of these contain only one atom each (atoms 1, 2, and 7, respectively) and two contain two atoms each (atoms 3–4, and 5–6, respectively). However, as discussed above, the atoms of isomer II may be viewed with a good approximation as forming at low energies only three classes of dynamical similarity. For icosahedral Al$_{13}$ and Al$_{35}$ the considered subsystems of atoms (“central,” “surface,” and “shell”) represent both classes, of geometrical and of dynamical similarity.

The ddf, and consequently the classes of dynamical similarity, may be evaluated on different time scales, and therefore they depend, in general, on the sampling time. One can introduce time dependent instantaneous (“’t’”) and short-time averaged (“’st’”) ddf $f^t_j(t)$, $f^s_j(t)$, $F^t_i(t)$, and $F^s_i(t)$ defined as

$$f^t_j(t) = \frac{E^t_{\text{kin}}(t)}{\langle E_{\text{kin}} \rangle^t} (3N-8), \quad f^s_j(t) = \frac{\langle E^s_{\text{kin}} \rangle^s(t)}{\langle E_{\text{kin}} \rangle^t} (3N-8),$$

and

$$F^t_i(t) = \frac{E^t_{\text{kin}}(t)}{\langle E_{\text{kin}} \rangle^t} (3N-8) \cdot Z,$$

$$F^s_i(t) = \frac{\langle E^s_{\text{kin}} \rangle^s(t)}{\langle E_{\text{kin}} \rangle^t} (3N-8) \cdot Z,$$

where $t$ denotes, as appropriate, either the instantaneous time or a short-time interval (labeled, e.g., by the value of its midpoint); $\langle \cdot \rangle^t$ stands for short-time average; and $Z$ is specified by Eq. (11). The ddf defined by Eqs. (35) and (36) can be used to characterize the dynamics of subsystems of a system as a function of time. A detailed discussion of the time dependent ddf and their utility will be given elsewhere. The ddf $f_j^t$, Eq. (13), and $F_i$, Eq. (16), are averages of the time dependent ddf defined by Eqs. (35) and (36), respectively. Of especial interest are the so-called converged values of $f_j^t$ and $F_i$, which correspond to a sufficiently complete, or at least sufficiently representative, sampling. The number of classes of dynamical similarity defined by such $f_j^t$ and $F_i$, the number and identity of the elements in them, and the way these evolve as a function of energy (or temperature) give quite a comprehensive characterization of the energy (or temperature) dependence of the dynamics. They can form a basis for the assignment of stages in and formulation of classification schemes and order parameters for energy (or temperature) dependent transitions in finite systems. The fact that the meltinglike transition in these systems is spread over a finite range (cf., e.g., Refs. 17–19, 21, and references therein) is a reflection and a direct consequence of the existence of energy (temperature) intervals over which the atoms of these systems get partitioned into different classes of dynamical similarity. Not before these classes merge into one do the systems attain their liquidlike state. The qualitative explanation for the sharp (first order) melting transition in crystalline bulk materials (we abstract ourselves from the phenomenon of surface melting) is that all their (bulk) atoms form a single class of dynamical similarity at all relevant temperatures. Classes of dynamical similarity should prove especially useful in analyses of dynamics of more complex systems, e.g., those with low (or no) symmetry, systems comprised of different types of atoms (e.g., heterogeneous clusters; cf. Refs. 17–19, and references therein), and others.

The dynamical equipartition postulate can be formulated for any definition of temperature. The differences (or similarities) in the dynamics of the subsystems, as exhibited through the associated with them dynamical degrees of freedom, do not depend on the definition of temperature. One could, for example, use the temperature $(T_d)_\Omega$ defined by Eq. (8) and write the equipartition postulate in the form

$$\frac{k(T_d)_{\Omega}}{2} = \frac{\langle E^t_{\text{kin}} \rangle^t}{\langle \mathcal{J} \rangle^t}.$$

Although, as discussed above, use of $(T_d)_{\Omega}$ is lacking general conceptual justification, the dynamical degrees of freedom $\mathcal{J}$ possess the same features as $f_j$, except their values are scaled to sum up to $3N-6$. We advocate using the correct quantities $f_j$ or $F_i$, rather than $\mathcal{J}$, as a means of emphasizing the specificity of the microcanonical dynamics. And, what is more, adherence to “conceptual purity” does not entail here extra computational cost.

In the illustrations presented above the ddf are computed in the cartesian space (a convenient choice for description of structural and phaselike transitions). It is, however, straightforward to define and to evaluate them in any space, including that of normal modes. The extension to the quantum case should include obvious modifications: in quantum dynamics each degree of freedom possesses at least the amount of its zero-point energy, and it can acquire or lose energy only in quanta compatible with its energy spectrum.

One can introduce ensemble, as distinct from dynamics, versions of the equipartition postulate. The microcanonical ensemble version is

$$\frac{kT^\omega}{2} = \frac{\langle E^t_{\text{kin}} \rangle^t_{\mu}}{\langle f_j \rangle_{\mu}^t} Z_{\mu}^{-1} \quad \text{or} \quad \frac{kT^\omega}{2} = \frac{\langle E^s_{\text{kin}} \rangle^s_{\mu}}{\langle F_i \rangle_{\mu}},$$

where $Z_{\mu}$ is defined by Eqs. (28) and (29) with $\langle \cdot \rangle_{\mu} = \langle \cdot \rangle_{\mu}$. The canonical ensemble version takes the form

$$\frac{kT^\omega}{2} = \frac{\langle E^t_{\text{kin}} \rangle^t_{\mu}}{\langle \mathcal{J} \rangle_{\mu}^t}.$$

In order to compute the dynamical degrees of freedom $f_j$, $F_i$, and $\mathcal{J}$ defined by the ensemble equipartition postulates, Eqs. (38) and (39), one has to know the actual values of the corresponding ensemble temperatures and averaged kinetic energies. These are not to be obtained through ensemble averaging based on assumed equiprobability of the degrees of freedom (this is indicated by the “primed” $\langle \cdot \rangle$). Rather they should come from ensemble-specific measurements or appropriately force-biased (e.g., Nose-type or force-biased...
Monte Carlo) sampling of the phase space. Work on this issue is in progress. Other related subjects for future exploration include the relevance and utility of the dynamical degrees of freedom as a tool in analyses of order-chaos transitions, and in generation and characterization of fractal manifolds.

IV. SUMMARY

In this paper we re-examined issues related to the correspondence between dynamical and thermodynamical/statistical descriptions of finite, in particular small, systems, and formulated the dynamical equipartition ansatz, which leads to the definition of the dynamical degrees of freedom. The dynamical equipartition ansatz is a generalization of what usually is referred to as the “equipartition theorem.” The fundamental difference between the two is that the ansatz does not involve the a priori assumption of equal probability, or equal engagement, of all the (relevant) dimensions of the configuration space of the system, whereas the “theorem” does. The ansatz is based on the notion of the (not necessarily equiprobable) dynamical degrees of freedom, whereas the theorem involves the (equiprobable) kinematical degrees of freedom. The ansatz is a postulate that states that the time-averaged kinetic energy (or a time-averaged function of that energy) is equally distributed between all the dynamical degrees of freedom, when measured per unit of the latter. The heuristic basis for this postulate is the intensive nature of the thermodynamic temperature as a state variable.

One can also formulate ensemble versions of the equipartition postulate. Either in its dynamical or ensemble forms, it is the necessary and sufficient condition for the corresponding dynamical or ensemble temperature to possess the intensivity property of the thermodynamic temperature. This underscores the fundamental nature of the postulate. Its ensemble versions and the dynamical degrees of freedom defined by them lay ground for axiomatic formulations of statistical mechanics and statistical analyses that are free from the assumption of equiprobability of the degrees of freedom and that correspond to (i.e., “are ergodic” with) the actual dynamical behavior of systems, irrespective of whether these latter are “ordered” or “chaotic.” In the special case, when a system explores all the (relevant) dimensions of its configuration space with equal probability, the equipartition postulate becomes the traditional equipartition theorem and the dynamical degrees of freedom coincide with the traditional (kinematical) degrees of freedom. We presented a number of illustrations of the utility of the dynamical degrees of freedom in analyses of structural and phase-like transformations in atomic clusters. Because of their generality one may expect the ddf to find many applications in explorations of a broad variety of systems and phenomena.

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14. In practice, dynamical simulations with free boundary conditions do not incorporate the constraint of constancy of volume. But if the system is isolated (i.e., it does not interact with other systems or fields) its state is completely specified by its (internal) energy. As a consequence, its thermodynamic characteristics can be defined as total derivatives, rather than partial derivatives at constant volume. The difference between the two is insignificant when the “thermal expansion” due to the anharmonicity of the potential can be neglected.