

HEAT CAPACITY OF ISOLATED CLUSTERS

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The character of interaction between the thermal (vibrational) and configurational cluster excitations is considered under adiabatic conditions when a cluster is a member of a microcanonical ensemble. A hierarchy of equilibration times determines the character of atomic equilibrium in the cluster. The behavior of atoms in the cluster can be characterized by two effective (mean) temperatures, corresponding to the solid and liquid aggregate states because a typical time for equilibration of atomic motion is less than the time of transition between the aggregate states. If the cluster is considered for a time much longer than the typical dwell time in either phase, then it is convenient to characterize the system by only one temperature, which is determined from the statistical-thermodynamical long-time average. These three temperatures are not far apart, nor are the cluster heat capacities evaluated on the basis of these definitions of temperature. The heat capacity of a microcanonical ensemble may be negative under some circumstances in a region of coexistence of two phases, provided the mean temperature is defined in terms of the mean kinetic energy, not as a the derivative of the energy with respect to the microcanonical entropy. However, we show that if the configurational excitation energy is small relative to the total excitation energy separating the phases, then, within the model of two aggregate states, the heat capacity is positive whichever definition is used for temperature. In addition, for a sufficiently large cluster, the maximum values of the microcanonical and canonical heat capacities are the same.

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1. INTRODUCTION

The contemporary description of cluster evolution is based on saddle-crossing dynamics involving a large number of local minima for the potential energy of this system at zero temperature depending on the configuration of atoms [1–6]. Each local minimum corresponds to a locally stable configuration. Certain of these lie at the point of lowest energy in a basin, while others, at higher energies in the same basin, correspond to configurational excitations from that lowest point. Neighboring local minima are separated by saddle points of the potential energy surface [7]. At low temperatures, much of the time the cluster is then found near the local energy minima, and the durations of intermediate states during transitions across saddles between neighboring minima are brief. Taking the cluster aggregate

states as a group of atomic configurations near local minima of the cluster potential energy [8], we obtain a precise picture of the cluster phase transitions, characterized by bands of dynamical coexistence of phases [9–12]. In the case of solid–liquid equilibrium, this means that the system is found in the solid aggregate state during certain periods; the remainder of the time, it is found in the liquid state, if the cluster can be located in two aggregate states. (It is also possible for a cluster to exhibit more than two phases in such a dynamic equilibrium, e.g., a «surface-melted» state together with a solid and a liquid [13, 14].)

Using these concepts, one can generalize thermodynamics of bulk systems and relate these to clusters as systems of small, finite numbers of bound atoms or molecules. Within the framework of the saddle-crossing dynamics, one can define the cluster aggregate states as sets of atomic configurations near local minima of the cluster potential energy with nearby energies [8],

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and a cluster aggregate state can therefore include a finite number of elementary configurational excitations. In the classical thermodynamics of bulk systems, the aggregate state includes many configurational excitations, which leads to a uniform spatial distribution of atoms for a liquid. Next, the hierarchy of cluster times leads to the corresponding phenomenon of phase coexistence in clusters [9–12].

Thus, the properties and dynamics of cluster evolution allow one to apply thermodynamics to clusters. One must use a Gibbsian ensemble to describe the thermodynamics of clusters; some of the familiar concepts and characteristics of bulk systems disappear and some that are equivalent in common situations become inequivalent. For example, the distinction between phase and component is lost because phase equilibrium occurs on the same short time scale as the equilibrium among reacting components. Hence, the Gibbs phase rule loses its meaning for small systems [3]. Using this perspective, we here consider the heat capacity of a cluster that does not exchange energy with an environment, i.e., the cluster is in a microcanonical ensemble of atoms [15].

For clusters, a typical time for establishing vibrational thermal equilibrium is brief compared with a typical time to establish configurational equilibrium in the solid and liquid states [16]. Under microcanonical conditions, this time scale separation in clusters allows one to identify the temperatures of the solid and liquid states separately; the cluster is submitted to a two-temperature description. Likewise, under canonical conditions, the solid and liquid states can be assigned different mean energies and potential energies. If the time of cluster observation is long compared with a typical time for dynamic equilibration between the aggregate states, it becomes appropriate to use a single cluster temperature, i.e., to model this cluster by one averaged aggregate state.

In an ensemble at constant energy, the effective temperature of a cluster, solid or liquid, can be defined in either of two ways. One is the mean kinetic energy per degree of freedom; the other is the derivative of the internal energy with respect to the microcanonical entropy at constant volume. While these are equivalent for a canonical ensemble of macroscopic systems (with the conventional canonical entropy), they are not necessarily equivalent for microcanonical ensembles, particularly of small systems. Defined in terms of kinetic energy, the effective temperature of the solid is necessarily higher than that of a liquid at the same energy. Hence, increasing the energy in the zone of coexistence of the solid and the liquid (i.e., in the transition region)

can lead to an effective temperature decrease. In what follows, we consider this problem in terms of two aggregate states, with the additional simplifying assumptions that the separate caloric curves for the solid and liquid states are parallel straight lines, i.e., the transition energy is independent of the temperature, and that the difference of the solid and liquid temperatures is relatively small. These simplifications allow us to understand the cluster properties near the melting point in a simple way. (We use the term «melting point» to mean the temperature at which the free energies of the solid and liquid clusters are equal. There is, of course, no sharp melting point for small clusters.)

Under these conditions, when equilibrium is established at each new cluster energy, each small increase of that energy near the melting point goes in part to excitation of thermal (vibrational) motion, and in part to configuration excitation. Consequently, the heat capacity of an isolated cluster changes near the melting point. If the temperature is defined as the entropy derivative of the internal energy, then the heat capacity almost certainly remains positive and typically increases as more degrees of freedom absorb energy¹. But if the mean potential energy of the liquid form is significantly higher than that of the solid, and the temperature is defined in terms of mean kinetic energy per degree of freedom, then the system may exhibit a negative heat capacity and a region of a negative slope, an «S-bend», in its caloric curve. This behavior of cluster heating has been found for clusters on the basis of theoretical [17–22] and experimental studies [23–28]. Below, we consider this problem in detail.

2. HIEARCHY OF CLUSTER TIMES

We first analyze the character of equilibrium in a cluster. We use the two-state approximation for cluster aggregate states [8], which extends the thermodynamic concept of the aggregate states from bulk to clusters, and we assume the existence — local stability and thermal equilibration — of two aggregate states, solid and liquid. Although clusters may exhibit several aggregate states in equilibrium, for example associated with melting of different cluster shells [13, 14], the model that we use here involves the assumption that in a given range of parameters, the cluster can be found only in two aggregate states. The character of cluster equilibrium

¹ Only if the available phase space were to decrease with the energy for some pathological system could its caloric curve show a negative slope with this definition of temperature. Such a situation is logically possible, but physically almost unimaginable.

is determined by typical times for processes within the cluster. A typical time to establish thermal equilibrium τ_{eq} between bound atoms is of the order of magnitude

$$\tau_{eq} \sim \frac{1}{\omega_D}, \quad (1)$$

where ω_D is the Debye frequency, roughly inversely proportional to the period of cluster oscillations ($\sim 10^{-14}$ s at room temperature). A typical dwell time of a cluster in the vicinity of the free energy minimum τ_{ag} associated with each aggregate state is long compared with τ_{eq} ,

$$\tau_{eq} \ll \tau_{ag}, \quad (2)$$

because transitions between aggregate states require that the cluster overcome a significant free energy barrier. We consider a cluster of bound atoms as a member of a microcanonical ensemble, and neglect the interaction between the cluster and environment, i.e.,

$$\tau_{ag} \ll \tau_{th}, \quad (3)$$

where τ_{th} is a typical time for the exchange of energy between the cluster and its environment; for shorter times, the cluster can be considered as an isolated particle. We introduce a typical time τ of cluster observation such that

$$\tau_{ag} \ll \tau \ll \tau_{th}. \quad (4)$$

This hierarchy of cluster times leads to a particular pattern of cluster behavior. Indeed, during τ_{eq} , thermal equilibrium is established for the vibrational motion of the cluster atoms, and the thermal motion of atoms can then be characterized by a temperature [16]. Because of criterion (2), this temperature is different for the two aggregate states. We therefore introduce separate temperatures of atoms for the solid T_{sol} and liquid T_{liq} aggregate states. In particular, in the Dulong–Petit limit, the cluster energy is given by

$$E = (3n - 6)T_{sol} = \Delta E + (3n - 6)T_{liq}, \quad (5)$$

where n is the number of cluster atoms and ΔE is the fusion energy. This implies that

$$\Delta T = T_{sol} - T_{liq} = \frac{\Delta E}{3n - 6}. \quad (6)$$

Along with these temperatures, one can introduce a general cluster temperature T for a large time of the order of τ , which can be expressed in terms of an average energy of an individual cluster atom if the average is taken for a time of the order of τ long enough for the cluster to change its aggregate state many times.

3. TWO-AGGREGATE APPROACH

Considering the approximation of two aggregate states [8], we express the total partition function of a cluster as

$$Z = Z_{sol} + Z_{liq}, \quad (7)$$

where Z_{sol} and Z_{liq} , the partition functions for the solid and liquid cluster states respectively, are related by

$$p(T) = \frac{Z_{liq}}{Z_{sol}}. \quad (8)$$

The respective probabilities w_{sol} and w_{liq} that the cluster is found in the solid and liquid states are

$$w_{sol} = \frac{1}{1+p}, \quad w_{liq} = \frac{p}{1+p}. \quad (9)$$

From the thermodynamic relation, we have

$$\begin{aligned} p &= \exp \left[-\frac{\Delta E}{T} + S_{liq}(T_{liq}) - S_{sol}(T_{sol}) \right] = \\ &= \exp \left[-\frac{\Delta E}{T} + \Delta S \right]. \end{aligned} \quad (10)$$

where $S_{sol}(T)$ and $S_{liq}(T)$ are the entropies of the solid and liquid states at the given temperature, T is an effective temperature that characterizes the rates of transitions between the solid and liquid states, and ΔE and ΔS are the changes of the thermodynamic variables at the phase transition.

Although clusters exhibit bands of coexistence rather than the sharp melting points of bulk systems, we can, as mentioned above, define the melting point of a cluster by analogy with that of the bulk as the temperature of equal free energies of the two phases. In this way, the precise definition is that of the «equality» temperature T_{eq} such that

$$p(T_{eq}) = 1, \quad (11)$$

and hence

$$w_{sol}(T_{eq}) = w_{liq}(T_{eq}) = 1/2.$$

As the general cluster temperature, the effective cluster temperature T tends to T_{sol} as $p \rightarrow 0$ ($w_{sol} = 1$), and tends to T_{liq} in the limit as $p \rightarrow \infty$, or when $w_{liq} = 1$. (It is sometimes convenient to use the quantity $(w_{liq} - w_{sol})/(w_{liq} + w_{sol})$ simply because it varies only between -1 and $+1$ [13, 14].)

4. ENTROPY OF AN ISOLATED CLUSTER IN THE TWO-STATE APPROACH

When a cluster does not interact with its environment, a thermodynamic equilibrium is established. In

addition to the temperatures of the solid T_{sol} and liquid T_{liq} aggregate cluster states, this allows us to introduce the general cluster temperature from the thermodynamical relation

$$dE = T dS, \quad (12)$$

where E and S are the cluster energy and entropy. This definition can be used for the two aggregate states separately or for the long-time average over both aggregate states. Here, we use the latter option and evaluate the entropy S of a cluster in a long-term equilibrium (with or without the environment) between two aggregate states. Basing this analysis on a general entropy formula [29], we have

$$S = -\langle \ln w \rangle = -\sum_i w_i \ln w_i, \quad (13)$$

where i is a cluster state and w_i is the probability that the cluster is found in this state ($\sum_i w_i = 1$). Along with w_{sol} and w_{liq} in Eq. (9), we introduce the probability X_j for the cluster to be in the j th state if the cluster is first found in the solid aggregate state, and the probability Y_k for the cluster to be in k th state if it is initially in the liquid aggregate state. That is, we introduce a kind of conditional probability. According to the definition, we have

$$w_{sol} + w_{liq} = 1, \quad \sum_j X_j = \sum_k Y_k = 1. \quad (14)$$

From this, we obtain the cluster entropy

$$\begin{aligned} S &= -w_{sol} \sum_j X_j \ln(w_{sol} X_j) - w_{liq} \sum_k Y_k \ln(w_{liq} Y_k) = \\ &= w_{sol} S_{sol} + w_{liq} S_{liq} + S_{conf}, \end{aligned} \quad (15)$$

where

$$S_{sol} = \sum_j X_j \ln X_j, \quad S_{liq} = \sum_k Y_k \ln Y_k \quad (16)$$

are the entropies of the corresponding aggregate states. We thus express the entropy of a cluster with two aggregate states through entropies of each aggregate state and the entropy of the cluster configuration state S_{conf} , equal to

$$\begin{aligned} S_{conf} &= -\sum_i x_i \ln x_i = -w_{sol} \ln w_{sol} - w_{liq} \ln w_{liq} = \\ &= \ln(1+p) - \frac{p}{1+p} \ln p, \end{aligned} \quad (17a)$$

$$\frac{dS_{conf}}{dp} = -\frac{\ln p}{(1+p)^2}, \quad (17b)$$

where x_i is the probability for the cluster to be in a given aggregate state, and we use Eqs. (9). We note that this expression is valid under the assumption that the cluster is observed in a long-term equilibrium, i.e., can be located many times in each aggregate state during the observation time. Thus, expression (15) for the cluster entropy is a sum of terms corresponding to the solid and liquid aggregate states, and also of the term that accounts for configurational excitation.

5. TEMPERATURE OF A CLUSTER AS A MICROCANONICAL ENSEMBLE OF ATOMS

It follows from the above discussion that an isolated cluster with two aggregate states can be considered in the two-temperature approach if criterion (2) is satisfied, i.e., a typical time τ_{eq} for thermodynamic equilibration of the atomic thermal motion in each aggregate state is short compared with the dwell time τ_{ag} of the cluster in each aggregate state. When we observe a cluster during a time long compared with τ_{ag} , we can model the cluster with two aggregate states by a cluster with one aggregate state, and thus introduce a single average cluster temperature T . For this purpose, we can use the connection between the kinetic energy of cluster atoms and their temperature. Connecting the mean kinetic energy of cluster atoms averaged over a time long enough to reflect the kinetic energies of atoms in both aggregate states, we then define the (long-term) cluster temperature as

$$T = w_{sol} T_{sol} + w_{liq} T_{liq}. \quad (18)$$

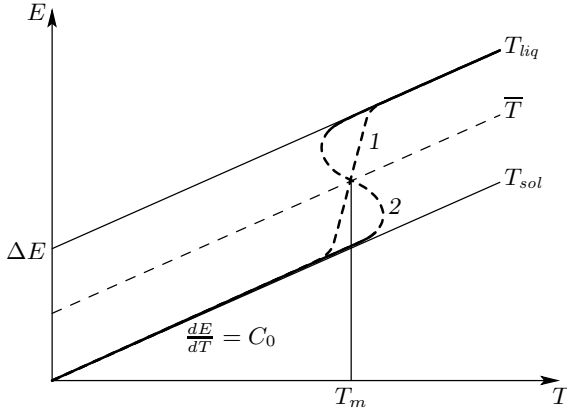
This definition of temperature is to be used in the context of traditional statistical physics, i.e., on the basis of a very long-time average. This remains a useful and valid approach, but the availability of measurements fast enough to enable us to observe the individual aggregate states justifies the extension of the conceptual framework to describe each aggregate state by itself, to supplement our long-time average description.

Turning to the two-temperature approach for a cluster, we assume the cluster heat capacity to be independent of the temperature in the range of phase coexistence; in other words, the caloric curves for the solid and liquid states are straight lines, as shown in the Figure. We use the parameters of this curve

$$\bar{T} = \frac{T_{sol} + T_{liq}}{2}, \quad \Delta T = T_{sol} - T_{liq}, \quad (19a)$$

and for simplicity assume that

$$\Delta T \ll \bar{T}. \quad (19b)$$



Caloric curves of an isolated cluster with two aggregate states in the one-temperature approach: 1 — the case of a positive heat capacity; 2 — the case of a negative heat capacity near the melting point

In accordance with Eq. (18), the statistical temperature T is expressed through these parameters as

$$T = \bar{T} + \frac{\Delta T}{2} \frac{1-p}{1+p}. \quad (20)$$

Evidently, within the framework of the general temperature, it follows from (10) that

$$p = \exp \left[-\frac{\Delta E}{T} + \Delta S \right]. \quad (21)$$

For simplicity, we assume that the entropy jump ΔS at the phase transition and the transition energy ΔE are independent of the temperature. In addition, we have for the cluster energy E under our assumptions (see the Figure)

$$E = C_0 \bar{T}, \quad \Delta E = C_0 \Delta T, \quad (22)$$

where C_0 is the cluster heat capacity far from the melting point.

We now use Eq. (12) as the thermodynamic definition of the cluster temperature T ,

$$\frac{1}{T} = \left[\frac{dS}{dE} \right]_V. \quad (23)$$

That is, we use the entropy–energy definition, rather than the mean kinetic energy definition for temperature. Because this formula is also valid for each aggregate state, we have the relations

$$\frac{1}{T_{sol}} = \frac{dS_{sol}}{dE}, \quad \frac{1}{T_{liq}} = \frac{dS_{liq}}{dE}$$

for the cluster temperature of a given aggregate state. On the basis of these formulas and formula (17) for the

entropy of a cluster with two aggregate states, we then express the cluster temperature as

$$\begin{aligned} \frac{1}{T} &= \frac{w_{sol}(T_{sol})}{T_{sol}} + \frac{w_{liq}(T_{liq})}{T_{liq}} + \frac{dS_{conf}}{dE} = \\ &= \frac{1}{(1+p)T_{sol}} + \frac{p}{(1+p)T_{liq}} - \frac{\ln p}{(1+p)^2} \frac{dp}{dE}, \end{aligned} \quad (24)$$

where

$$\frac{dS_{conf}}{dE} = -\frac{\ln p}{(1+p)^2} \frac{dp}{dE} \quad (25)$$

in accordance with Eqs. (17). It can be seen that the statistical and thermodynamic temperature definitions (20) and (23) are different. But the difference between them is small in the present case because we have imposed criterion (19b). In particular, at the equality point ($p = 1$), we have $T_{eq} = \bar{T}$ in accordance with (20), and Eq. (24) then gives

$$T_{eq} = \frac{2T_{sol}T_{liq}}{T_{sol} + T_{liq}} = \bar{T} \left(1 - \frac{\Delta T^2}{4\bar{T}^2} \right). \quad (26)$$

Thus, although the definitions of the cluster temperature are different, under assumption (19b) this difference is only of the second order in terms of the expansion in the small parameter $\Delta T/\bar{T}$.

6. HEAT CAPACITY OF A CLUSTER AS A MICROCANONICAL ENSEMBLE OF ATOMS

We now construct caloric curves for a large cluster, supposing that the caloric curves for the solid and liquid aggregate states are parallel straight lines and the distance between these lines satisfies criterion (19b). The cluster state corresponds to the solid caloric curve at low temperatures below the equality point, and to the liquid caloric curve at high temperatures above that temperature, T_{eq} . An intermediate part of the caloric curve near the melting point can have two forms, as shown in the Figure; in case 1, the cluster heat capacity is positive at any temperature, and in case 2, it is negative near T_{eq} . In principle, both cases are possible. Based on their experimental study of sodium clusters of hundreds of atoms, Haberland [30, 31] et al. infer that the case of a negative cluster heat capacity near T_{eq} is more representative. Initially, the accuracy of the experimental data [23–26] left some possibility to question that inference, but more recent, independent measurements have made the case for some microcanonical negative heat capacities much more plausible [27, 28]. All these experiments, in effect, base the evaluation of temperature on the kinetic energy of the atoms of the

clusters, consistent with this definition being the one that allows negative heat capacities. Below, we analyze this problem using the above approach. Within the framework of statistical and thermodynamical considerations, we introduce the general temperature for an isolated cluster that can be found in both the solid and liquid states.

We evaluate the heat capacity C of a cluster of bound atoms as a member of a microcanonical ensemble near the melting or equality point. When we introduce one cluster temperature T , its heat capacities are

$$C = \frac{dE}{dT}, \quad C_0 = \frac{dE}{d\bar{T}} = \frac{dE}{dT_{sol}} = \frac{dE}{dT_{liq}},$$

where E is the internal cluster energy and \bar{T} is given by Eq. (19a). We assume in the discussion here that T_{sol} and T_{liq} are almost equal; hence, we are not dealing with the general case. Relation (21) is valid under our assumption and gives

$$\frac{dp}{dE} = \frac{p\Delta E}{T^2 C}. \quad (27)$$

For simplicity, we assume here that the cluster parameters ΔE and ΔS are independent of the cluster temperature T . Under these conditions, for the statistical definition of the temperature, we have, taking the differential of (20) and using Eq. (22),

$$\frac{1}{C} = \frac{1}{C_0} - \frac{\Delta T}{(1+p)^2} \frac{p\Delta E}{T^2 C}.$$

This implies that

$$C = C_0(1 + Z), \quad Z = \frac{p}{(1+p)^2} \frac{\Delta T \Delta E}{T^2}. \quad (28)$$

We now consider the case of the thermodynamic definition of the cluster temperature when a cluster with two aggregate states is modeled by the cluster with one average aggregate state. Taking the differential of (24) and expanding it in a small parameter $\Delta T/\bar{T}$, we then have

$$-\frac{dT}{T^2} = -\frac{d\bar{T}}{\bar{T}^2} + \frac{\Delta T d\bar{T}}{\bar{T}^3} \frac{1-p}{1+p} + \frac{\Delta T dp}{\bar{T}^2 (1+p)^2} + d\left(\frac{\ln p}{(1+p)^2} \frac{dp}{dE}\right).$$

Ignoring the second term in the right-hand side of this equation in comparison with the first one because of (19b), we then obtain

$$-\frac{1}{CT^2} = -\frac{1}{C_0\bar{T}^2} + \frac{\Delta T}{\bar{T}^2(1+p)^2} \frac{dp}{dE} + \frac{d}{dE} \left(\frac{\ln p}{(1+p)^2} \frac{dp}{dE} \right). \quad (29)$$

Because the maximum heat capacity of the cluster corresponds to the equality or melting point (if its value is positive), we consider Eq. (29) at T_{eq} , where $p = 1$, $T = \bar{T} = T_{eq}$, and therefore

$$\frac{1}{C} = \frac{1}{C_0} - \frac{Z}{C} - \frac{ZC_0}{C^2}. \quad (30)$$

We note that Eq. (28) follows from this if we ignore the last term, i.e., if we neglect the configurational part S_{conf} in expression (15) for the cluster entropy. The physical solution of Eq. (30) is given by

$$C = C_0 \left[\frac{1+Z}{2} + \sqrt{\left(\frac{1+Z}{2}\right)^2 + Z} \right]. \quad (31)$$

Formulas (28) and (31) for the cluster heat capacity, based on the two different definitions of the cluster temperature, lead to identical results in the limiting cases $Z = 0$ and $Z = \infty$. The maximum ratio of the heat capacities according to formulas (31) and (28) corresponds to $Z = 1$ and is $(1 + \sqrt{2})/2 \approx 1.2$. Thus, if an isolated cluster with two aggregate states is modeled by a cluster with one temperature, the values of its heat capacity depend on the definition of the cluster temperature. But for the statistical and thermodynamical definitions of the cluster temperatures, the values of the cluster heat capacity coincide within the limits of 20% in the cases considered here.

We now analyze the character of consumption of energy that is transferred to an isolated cluster very slowly, such that equilibrium is established for each input of energy. We divide the total energy of the ensemble of bound atoms into the kinetic energy of atoms, the potential energy of the interaction between atoms, and the energy of configurational excitation. For simplicity, we take the ratio between the kinetic and potential energy to be governed by the virial relation; this ratio is therefore independent of excitation. Moreover, these excitations involve sufficiently low energies such that they can be supposed to be harmonic oscillations. Therefore, the excitation energy can be thought to be consumed in two channels, thermal motion of atoms and configurational excitation. It is clear that the cluster total heat capacity must be greater than if configuration excitation were absent, because only a part of the input energy is consumed by the thermal motion of atoms. A significant part must go into increasing

excitation of «new» degrees of freedom that are unexcited at lower temperatures, but are fully excited at higher temperatures. Hence, in the range of the phase change, the heat capacity exceeds that in the temperature ranges far from the phase change.

The configurational and vibrational contributions may nonetheless be strongly linked in the following way. If the configurational excitations bring the cluster to a region of high potential energy, and thus to a region of low kinetic energy, then during those intervals in which the configurational excitation is high, the kinetic temperature is necessarily low. This situation does not conform to our assumption above that T_{sol} and T_{liq} are almost equal. In accordance with this assumption, configurational excitation requires relatively little energy. Consequently, we can suppose that clusters of sizes far from the «magic number» or closed-shell sizes are likely to conform to the assumption used above, but that the «magic number» or closed-shell clusters are least likely to satisfy that assumption.

If the configurational excitation energy requires a significant part of the cluster internal energy, the heat capacity may become negative because an increase of the total cluster energy leads to a decrease of its thermal (or vibrational) energy. Just this situation is proposed by Haberland [30, 31] for sodium clusters consisting of a hundred and more atoms. Evidently, the conditions favorable for clusters to have a negative heat capacity apply to those systems. Based as it is on Eqs. (28) and (31), the analysis here, with its strong assumptions, leads to a positive cluster heat capacity at any cluster temperature. We can therefore interpret the assumptions leading to this conclusion as sufficient conditions for a positive heat capacity. This should not be interpreted to imply that negative heat capacities cannot occur in microcanonical systems; they certainly can occur if the kinetic definition of temperature is used. In fact, we can now say that the next challenge in this field is finding sufficient conditions for a negative heat capacity, in terms of the relative energies and phase space volumes of the solid and liquid phases, and then finding what classes of systems best satisfy those conditions — or those for strictly positive heat capacities.

Equations (28) and (31) characterize the increase of the cluster heat capacity near the melting point. We now consider this increase for a large cluster with $Z \gg 1$. Because for a large cluster $C_0 \sim n$, where n is the number of atoms forming the cluster, criterion (19b) becomes

$$\left(\frac{T_m}{\Delta T}\right)^2 \ll n, \tag{32}$$

The parameters of the isolated Lennard–Jones cluster consisting of 13 atoms at the melting point. The data are obtained on the basis of [10].

Parameter	Value
E_m	13.6
ΔE	2.46
$\eta(E_m)$	0.39
T_{sol}	0.32
T_{liq}	0.26
T_m	0.29
$Z(T_m)$	0.46
$\frac{C_{max}}{C_0}, (28)$	1.46
$\frac{C_{max}}{C_0}, (31)$	1.73

such that the increase of the heat capacity for such large clusters is strong. In this limit, Eqs. (28) and (31) give the maximum heat capacity that corresponds to the equality or melting point

$$C_{max} = C_0 Z = \frac{\Delta E^2}{4T_{eq}^2}. \tag{33}$$

This expression also involves the assumption that the transition thermodynamic parameters ΔE and ΔS are independent of the temperature. The maximum heat capacity has the same value in the case of isothermal heating [8].

We now apply Eq. (30) to the Lennard–Jones cluster of 13 atoms, taking its parameters from the computer modeling [10] of this cluster. Assuming the Dulong–Petit law to be valid at melting, we have the heat capacity of this cluster $C_0 = 3n - 6 = 33$. The temperatures of the solid T_{sol} and liquid T_{liq} states are

$$T_{sol} = \frac{2\eta E}{C_0}, \quad T_{liq} = \frac{2\eta(E - \Delta E)}{C_0}, \tag{34}$$

where η is the part of the cluster excitation energy E that is transformed into kinetic energy of the atoms. Thus, we express the temperature of cluster atoms through the total kinetic energy. Parameters in the Table refer to the equality or melting point ($p(E_m) = 1$, $T = T_{eq}$), and we use reduced energy units with the energy unit given by the binding energy per bond.

The data in the Table, based on cluster computer simulation [10], show the validity of criterion (19b); the small parameter $\Delta T/T_{eq}$ used above is equal to 0.2 for the Lennard–Jones cluster of 13 atoms. This small parameter determines the accuracy of using one cluster temperature. We note that the increase of the heat capacity near the melting point is not strong for this cluster, and the heat capacity is positive at any temperature. This does not agree with the supposition of a negative heat capacity of clusters near T_{eq} [30, 31] of the sort inferred from experiments with sodium clusters [23–26]. A more exacting test with Lennard–Jones clusters would require examining the behavior of a larger system, e.g., a closed-shell icosahedral structure of 55 or 137 atoms.

7. CONCLUSIONS

It follows from the above analysis that the behavior of a real isolated cluster with two aggregate states can be described using either one aggregate state with a general temperature or two aggregate states with two temperatures. The latter requires that the vibrational modes of the cluster equilibrate rapidly compared with the rate of passage between aggregate states, such that temperatures of those states can be well defined. In reality, such thermodynamical equilibrium is established for many kinds of clusters and other small systems during the time the system resides in each aggregate state. The single-temperature description requires that during an observation time, a cluster changes its aggregate state many times. Although the statistical and thermodynamical definitions of the temperature lead to different temperatures and heat capacities, the differences between these values are not large under the assumptions used in this work. In addition, under these assumptions, the maximum heat capacities of a large cluster at the melting point coincide for the adiabatic and isothermal regimes of energy input, and in the case of the adiabatic regime (or for an isolated cluster), the heat capacities of a large cluster coincide for the statistical and thermodynamic definitions of temperature. A system satisfying the conditions invoked here does not exhibit a negative heat capacity of the type reported for an isolated cluster [30, 31]. The analysis provides sufficient conditions that the heat capacity of an isolated cluster in a microcanonical ensemble with two aggregate states is positive at any size and temperature. The question is now open to find comparable general conditions that produce the negative heat ca-

pacities that have been seen in experiment and theory.

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