Physical Chemistry Chemical Physics
Perspectives

Where Macro Meets Micro

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Abstract.

Reconciling or somehow linking the macroscopic and microscopic approaches to chemical and physical processes has been a challenge unaddressed for many years. One approach, presented here, treats the issue by examining individual phenomena well described by a macro approach that fails when applied to small systems. The key to the approach is determining the approximate system size below which the breakdown of the macro description is observable. The most developed example is the failure of the Gibbs Phase Rule for sufficiently small atomic clusters. Other examples, such as the onset, at sufficient size, of the insulator-to-metal transition, are discussed, as are some still more challenging phenomena.

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1 Introduction

1.1 The Challenge

Physical sciences describe natural phenomena in two very different ways. One, rooted in classical and quantum mechanics, approaches phenomena from the viewpoint of the behavior of the elementary components, alone, in some external environment such as a force field, and in terms of their individual interactions, one with another. The variables of the micro approach are those descriptive of the components-e.g., their mass, position, velocity, perhaps internal energy. Mechanical or, as we shall term them, micro descriptions are as time-reversible and deterministic as our choice of mechanics allows, totally in the case of classical Newtonian mechanics. The other way, appropriate for aggregates of many elementary components, uses variables characterizing entire systems such as temperature, total internal energy, pressure, and volume, with the choice of variables generally dependent on the constraints applicable to each example. Thermodynamics is perhaps the paragon of the latter mode, which we shall call the macro approach. The traditional link between the micro and macro descriptions is of course statistical mechanics, which enables us to describe the behavior of a macroscopic system in terms of the behavior of its microscopic elements through the application of probability. Describing a macro-scale system in terms of micro-level components at the detailed level of mechanics is of course far too complex a task for us to carry out (although computer simulations of ever larger aggregates are done every day), and the fluctuations away from the most probable condition grow proportionately smaller and smaller with increasing size of the system, so statistical mechanics allows us to find at least some of the micro-level properties of a macro system, properties that we might observe and use.

However there are phenomena whose macro-level descriptions, totally valid for macro-scale systems, which are not correctly described when we try to use them for portraying the behavior of small systems. The macro approach simply fails in many cases, when we try to use it for collections of only a few atoms or molecules. One of the long-outstanding challenges of the physical sciences has been to find a way to establish approximate "boundaries" which separate those systems large enough to be well described by traditional macro methods from those so small that those traditional macro methods lose their validity.

For a long time, people have recognized that small systems may have interesting properties differing from those of bulk materials of the same substances. The famous 1959 lecture by Richard Feynman, “There's Plenty of Room at the Bottom” (later reprinted) focused attention of the scientific community on the subject generally [1]. Then, in 1963, Terrill Hill published his very influential treatise on the subject [2], which laid out a systematic approach to the study of small systems.

Here, we shall review some recent approaches to the challenge of how to link the behavior and the descriptions of that behavior of macro-scale and micro-scale systems. These are based on finding answers to a general question, but one that has a different specific answer for each phenomenon that exhibits such a "boundary". The question is this: What is the approximate size of systems below which violations of or deviations from the behavior predicted by macro methods are observable? We shall formulate the approach in a bit more detail in this Section, and then go on to some specific examples, first some for which we have partial or even complete answers, and then to others that are major challenges yet to be addressed.

1.2 The Approach

To begin, we must know what the phenomenon is at the macro scale, what we would observe if we were to carry out a conventional experiment. Then we need to know at least something of how small systems deviate from what we would see in the macro experiment. And finally, we need to know something of the sensitivity of whatever experimental method we would use to study small systems, in order to observe deviations from the behavior expected from the macro description. This is enough to define our task; we must examine the particular phenomenon for small systems in a systematic way that tells us the approximate size below which those deviations would be observable to an experimentalist. Of course that determination should give us enough information to know what properties are the keys that govern that critical size region, so we can learn how the boundary size depends on the particular substance. And there may even be more than one "boundary"; some phenomena may show one kind of behavior for very small systems, another for some intermediate range of sizes and still a third for systems at a full macro scale.

One phenomenon that clearly illustrates this issue that has long been a subject of study is the metal-insulator transition. Bulk metals are of course electrical conductors, with current carried largely by electrons free to move in virtually continuous bands of partially-filled energy levels. In small clusters, the level spacings are typically wide, wide relative to typical temperatures, so many kinds of small metal clusters have filled electronic bands, a sizeable energy gap and empty higher-energy levels, and hence act as insulators. This topic has been reviewed extensively in a manner very relevant to our treatment here [3], where we use some specific phenomena to show how the general issue of the macro-micro "boundary" can be determined.

2 A First Example: The Gibbs Phase Rule

2.1 Background

One of the most universally applied concepts in the physical sciences is the Gibbs Phase Rule, given by what is probably the simplest equation describing an observable phenomenon, relating the number of degrees of freedom f, the number of different components c, and the number of phases in equilibrium together, p: $f = c - p + 2$. This is the rule that tells us that liquid water and ice can coexist in equilibrium at one atmosphere pressure at only the single temperature of 0^oC, and that the solid, liquid and vapor phases of water can coexist in equilibrium at only a single temperature and pressure, the triple point of water, also very close to 0^oC (strictly 0.01^oC) but at a pressure of only 0.006 atmospheres. That is, the vapor pressure of water at its triple point is very low indeed. (Incidentally, perhaps the single entry in the formula for the Gibbs Phase Rule that could be said to be less than obvious and perhaps even profound is the number "2". We know this number from observation; is there a way to infer or derive it from first principles?)

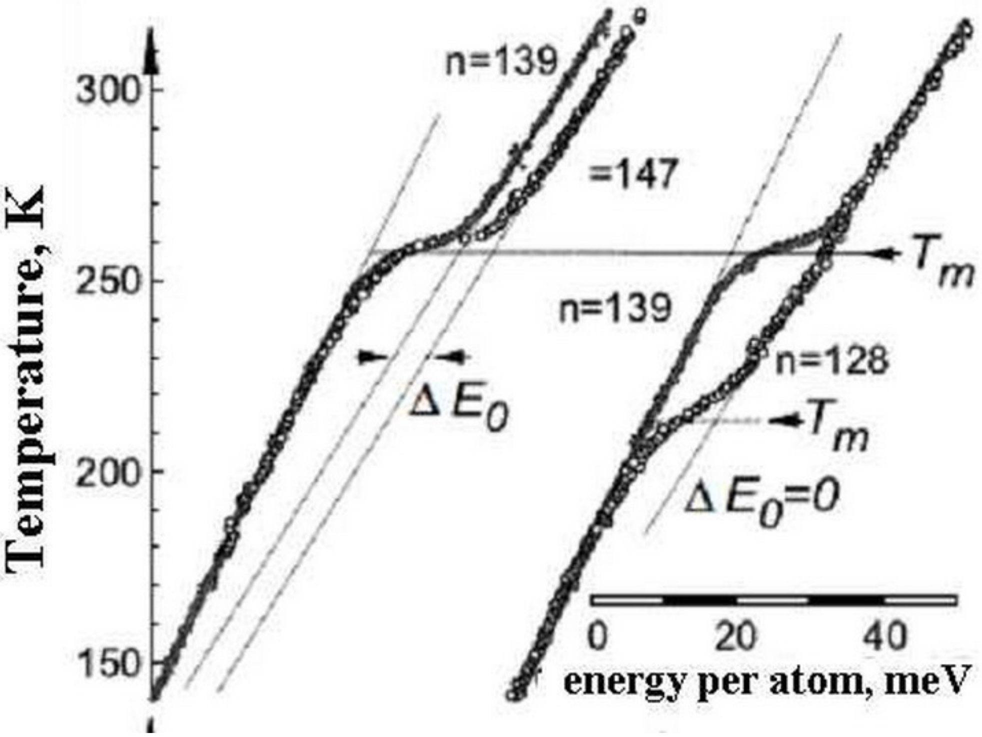

Figure 1: Caloric curves, temperature vs. energy/atom, for clusters of three sizes, Na^+_{128}, Na^+_{139}, and Na^+_{147}. The regions of more gradual slope are the regions of observable coexistence of solid and liquid phases. (From [14])

There was one clear statement, by Terrell Hill in his book [2] on small systems, that such systems should have smooth passage between phases.1 Nonetheless, The Phase Rule, long accepted as an inviolable doctrine, came abruptly into question when simulations of the melting of small atomic clusters showed that these systems could have two phases, solid and liquid, in equilibrium within a band of temperatures [4, 5, 6, 7, 8, 9, 10, 11]. It is even possible for more than two phase-like forms of some clusters to coexist [12]. Experiments proved that this can actually happen; they demonstrated coexistence of solid and liquid clusters of sodium atoms [13, 14, 15] and of sodium chloride [16] over ranges of temperature. The first of these experiments [13] probed the internal energy of thermalized Na^+_{139} clusters by photoionization, specifically by observing the fragmentation pattern, from which the internal energy of the cluster could be estimated. Fig.1, from Ref.[15], shows the gradual transition from all solid at low temperatures to all liquid at somewhat higher temperatures, for positively-charged sodium clusters of three similar sizes.

The origin of this behavior, this apparent violation of a supposedly universal rule, is actually easy to understand as soon as we look at the phenomenon in a suitable-and thermodynamically consistent-way. Let us consider the equilibrium between solid and liquid phases of a system in terms of the traditional chemical equilibrium constant K_{eq},

$$K_{eq} = \frac{w_{liq}}{w_{sol}} = \exp\left(\frac{\Delta F}{kT}\right) = \exp\left(\frac{N\Delta\mu}{kT}\right),$$

where w_{liq}, w_{sol} are the probabilities the system is found in the liquid and solid states (or the fractions in each state, in an ensemble), ΔF is the free energy difference between the phases and $\Delta\mu$ is the corresponding chemical potential difference, the difference of free energies, per particle. Suppose we are dealing with a small macroscopic system, of, say 10^{20} particles, and suppose we evaluate that equilibrium constant at a temperature just a tiny bit away from exact equality, the condition demanded by the macroscopic constraint of equilibrium of the phases; let us take, as an example, a chemical potential difference of only 10^{-10} in units of kT. Then the equilibrium constant $K_{eq} = \exp[\pm 10^{10}]$, a number so large or so small that we could not possibly detect the minority phase. If, on the other hand, we are dealing with a system for which N is, say, 10, then if $\Delta\mu/kT$ is 0.1, the equilibrium constant is e^1 and we can certainly expect to be able to observe the minority phase in thermodynamic equilibrium with the *favored phase.* This little exercise tells us that the apparent discontinuity of phase transitions is the observable consequence of a property of large numbers, that the phase change is, strictly, a continuous one but so abrupt for macroscopic systems that, for any purpose we might wish, we can treat the transition as discontinuous. However for systems of small numbers of particles, the continuous behavior can become observable, and that is exactly what the simulations and experiments with atomic clusters show.

That one does see coexisting phases over ranges of temperature, and, in principle, such coexistence within bands of temperature and pressure, and that such coexistence is entirely consistent with fundamental thermodynamics, gives us a deepened insight into the nature of phase transitions. There are limits, of course, to the ranges of coexistence. When the temperature is high enough, the local free energy minimum corresponding to the solid phase disappears. Likewise, there is a lower temperature below which the liquid has no local free energy minimum. Multiple phase coexistence is only possible under conditions that the potentially coexisting phases have local minima and hence local stability. There is an unanswered question here, of whether one could observe a limit of the stability range of a particular phase, or whether fluctuations would hide such a limit. (The possible role of fluctuations here was pointed out to one of us by Michael Fisher.)

2.2 Finding the Macro-Micro Boundary

A very natural question arises out of the observability of apparent violations of the Gibbs Phase Rule: Can we estimate the size of the largest systems for which such behavior could be observed in experiments? This turns out to be an answerable question, but of course any precise figure must depend on the sensitivity of the experiments. We can nonetheless develop the kind of answer that reveals the dependence of that "boundary size" on the properties of the specific system [17, 18, 19, 20]. We begin by making an arbitrary assumption that one could observe a minority phase if its concentration were 1/10th of that of the majority phase; this figure is of course one would choose for whatever specific experiment one is doing. This figure determines the range within which K_{eq} must lie, for observability to be possible. That is, we require that $0.1 \leq K_{eq} \leq 10$. But K_{eq} is the exponential of the free energy difference of the two forms, $K_{eq} = \exp(-\Delta F)$ with ΔF in units of kT. The ranges of observability are relatively narrow, enough that we can assume that the energy and entropy changes, ΔE and ΔS, are approximately constant within that range. Let us call T the temperature range of observable phase coexistence. Likewise, F is the observable range of free energy differences. The corresponding range of the exponent, then, is $-2.3 \leq \Delta F \leq 2.3$. (If we had chosen 1/10 as the maximum observable minority fraction, these numbers would be -2.3 and 2.3, of course.) Since $\Delta F = \Delta E/T - \Delta S$, we can evaluate $\delta F = \delta E \delta T/T^2$, but $\Delta E/T_m = \Delta S$ at the melting temperature T_m, so we find that $\delta T/T_m \sim 5/\Delta S_m$, i.e. the observable range of coexistence is inversely dependent on the entropy change in the phase transition.

To see what this means for real clusters, we can estimate the entropy change, per atom, for clusters of argon atoms in the size range of $50 - 100$ atoms. Simulations and estimates have this entropy change of about 0.8 per atom, so that for a cluster of 100 atoms, δT would be only about $0.1^o K$, assuming the $1:10$ observability criterion. However a cluster of 75 atoms would have a detectable range of close to $4^o K$ with this detectability range. Clusters of metal atoms typically have smaller entropy changes upon melting than do dielectrics such as

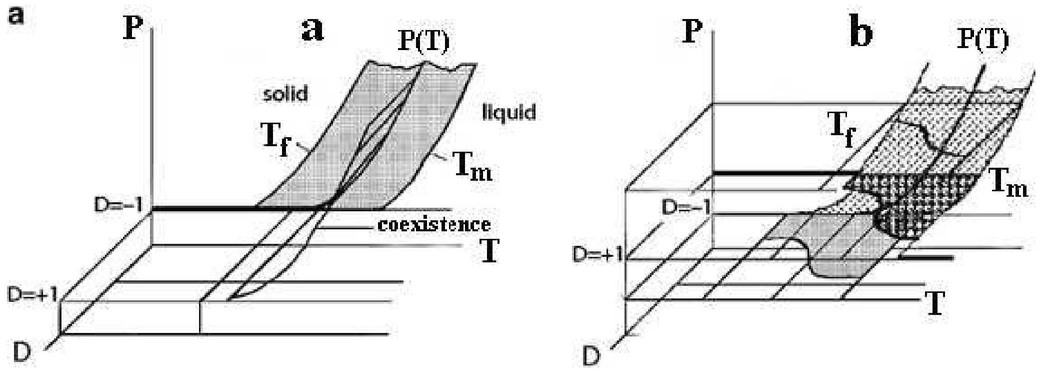

Figure 2: Phase diagrams including the variable D, the fractional difference between the amount of liquid and the amount of solid; (**a**) the diagram for a large system, for which the only observable region of coexistence is that given by the Gibbs Phase Rule; (**b**) the diagram for a small system (schematic) that can exhibit two phases in equilibrium within a range of temperature and pressure. In these figures, T_f and T_m, respectively, are the temperature limits of local stability of the liquid and solid phases, the freezing and melting limits as they have been called.

rare gases. This is because of their higher density of states in the solid phase. Consequently metal clusters may exhibit coexisting phases into the size range well above 100 atoms, as the experiments of Refs.[13, 14, 15] show.

It is perhaps useful at this point to introduce a graphical tool, a means to construct phase diagrams for these small systems for which ranges exist of coexisting phases. We can do this by defining a new coordinate, which we call D, defined as

$$D = w_{liq} - w_{sol} \tag{1}$$

with the normalization condition $w_{liq} + w_{sol} = 1$, and $D = +1$ when the system is liquid and $D = -1$ when the system is solid. This gives us a variable that allows a finite fraction of the system to be in either phase, and can be represented schematically in Fig.2, specifically Fig.2b for small systems; Fig.2a corresponds to the traditional phase diagram for a macroscopic system. The transition from solid to liquid, i.e. from $D = -1$ to $D = +1$, is so sharp as to seem discontinuous, while for the small system, D jumps from -1 to some intermediate value at a temperature at which the local free energy minimum of the liquid first appears, and then varies smoothly until it reaches a temperature at which the local free energy minimum of the solid phase disappears, and the system becomes entirely liquid.

Thus we have one way to put together the macro and micro descriptions for the first-order phase transition, the macro as represented by the Gibbs Phase Rule and the micro, by the systems that show phase coexistence in apparent violation of that rule. We have done it by determining the approximate size of those systems that are effectively at the small-system boundary of the validity of the macro description. We shall now see that this approach can be generalized to other phenomena, giving us a way to fit these two very different approaches together in a useful, meaningful way.

3 Extending to Other Phenomena

3.1 Size Dependence of Structures-Geometric and Electronic

With the example of the first-order phase transition in mind, we readily recognize other phenomena for which the macro description fails for small systems. One of the most obvious is simply the distinction between large systems whose properties vary simply and monotonically with the size of the system, and small systems, whose properties can change drastically as the number of component atoms or molecules changes. Identifying the origin of the difference here is straightforward; small systems show shell structure, for which closed-shell geometries typically exhibit greater stability than systems with fewer or more particles that yield those closed shells [21]. This example is closely related to another, namely that the stable structure of the bulk system differs from that of small aggregates. In the former example, we may ask for the approximate size above which the system's properties are monotonic with size. Alternatively, we can phrase the question to ask at what size does shell structure give over to a periodic crystal structure. In the latter case, we can try to find the smallest size at which the system takes on its stable bulk structure.

A little is known now about the boundary size above which a system exhibits its bulk crystal structure. Argon clusters of as many as $80,000$ atoms may have either the face-centered cubic (*fcc*) structure of the bulk or a hexagonal close-packed (*hcp*) structure [22]. This illustrates still another facet of the small-system challenge; some systems may take on one kind of structure at small sizes, an intermediate structure at somewhat larger sizes and eventually, for very large systems, the bulk structure. This is clearly the case with argon assemblages; they take on icosahedral structures for sizes up at least to a few hundred atoms, *hcp* structures at intermediate sizes and fcc crystal structures at the macro level. Of course it is quite possible that more than one form may exhibit long-term stability over a range of sizes. Exploring the size dependence of structural forms is currently a very open area.

Another striking example is the apparently totally anomalous melting behavior of small clusters of gallium and of tin. It has been established for over a century that small systems melt at temperatures lower than the corresponding bulk materials [23]. A typical material exhibiting this behavior is tin, whose thin films melt at temperatures below that of the bulk metal [24]. However small clusters of tin from 10 to 30 atoms melt at temperatures above the bulk [25]. Perhaps even more striking is the similar behavior of clusters of gallium, especially because this metal melts at such a low temperature, 302.9^oK, in its bulk form. Clusters, specifically Ga_{39}^+ and Ga_{40}^+ melt only at temperatures about 250^oK above the bulk melting temperature [26, 27]. This has been interpreted as a result of a significant difference between the nature of bonding in the small clusters and in the bulk metal, first for tin [28] and then for gallium[29, 30]; the origin appears to be a significant difference in the nature of the bonding in the small clusters, where it is strongly covalent, and in the bulk, where it is described as covalent-metallic.

From the perspective of this work, these findings essentially open the question, "At approximately what cluster size does the system of tin or gallium atoms change from metallic behavior to covalent, from low-melting to high-melting?" At the present time, this is one of the many open questions of this kind. We are able to ask a precise question but we do not have an easy pathway to an answer.

One kind of macro-micro boundary that is amenable to analysis now is the transition in small clusters of metal atoms from the insulator state to the metallic, conductive state. Small clusters of magnesium, for example, have a gap between the highest occupied electron levels, which are filled, and the lowest unoccupied levels, and hence do not allow electrical conduction. However, with increasing cluster size, that gap diminishes, and when it is small enough that thermal energies can excite electrons into the upper levels, the clusters can conduct (the Kubo criterion) [31]. The nature of the available levels depends sensitively on the specific material, the cluster size and the geometric structure, but the tools are available now to investigate particular systems and to determine the approximate size of the insulator-to-metal transition. For example, a cluster of about 10,000 sodium atoms has a gap of about 5^oK, i.e. should behave as a conductor at that temperature, while a cluster of only 125 atoms should be conducting at room temperature [32]. We have yet to see a systematic evaluation of the band gap for some specific elements as functions of cluster size, which would reveal the temperature at which those elements would become conductors. It would be particularly interesting to see a comparison of clusters of elements with open-shell atomic ground states, such as alkalis, with elements whose atomic ground states have filled shells, such as alkaline earth elements. Of course a related insulator-to-metal transition and its size dependence is the question of the size at which the nature of the bonding changes, notably in the gallium and tin clusters discussed above.

3.2 Reversibility vs. Thermodynamics

In one sense, irreversibility, exemplified by the Second Law of Thermodynamics, is a reflection of our having to work with incomplete information. Things happen that we cannot predict because we never know the precise state of a complex system in the full detail required to describe it via mechanics, whether classical or quantum. We cannot even do this with simulations on a computer because of the limitation on the level of precision at which we may work. A simple computer experiment demonstrated this vividly. Simulations of a cluster of atoms bound by Lennard-Jones interactions were carried out and then, at various trajectory lengths, the trajectories were reversed, to see how many forward steps could be taken and still have the system return to precisely its initial condition when "time-reversed". In the particular example, after 5000 time steps, reversing the trajectory brought the system almost but not quite back to its initial state; a single significant figure differed from those of the initial condition. When the level of precision was doubled, to carry twice the number of significant figures, the length of the trajectory at which precision began to be lost was simply doubled, to $10,000$ time steps. In other words, this experiment revealed the extent to which incomplete information necessarily leads to irreversibility.

A parallel situation occurs with real mechanical systems, such as the collisions between atoms or molecules of a gas. Suppose there is a limit to the precision of our knowledge about the impact parameters of atom-atom or molecule-molecule collisions so that the uncertainty can be estimated as $\delta\rho$. This leads to an uncertainty $\delta\theta_1 \sim \delta\rho/\rho_o$, where ρ_o is a typical distance at which the interaction potential and relative kinetic energy of the colliding species are approximately equal. Then the displacement for the next collision has an uncertainty $\Delta\rho_1 \sim \lambda\delta\rho/\rho_o^2$, where λ is the mean free path of an atom between collisions. The next collision has an uncertainty in displacement of $\Delta\rho_2 \sim \lambda\delta\theta_2 \sim \delta\rho\lambda^2/\rho_o^2$ and a velocity uncertainty of $\Delta v_2 \sim v\delta\theta_2 \sim \delta\rho\lambda/\rho_o^2$. Thus, after k collisions, the uncertainty in the displacement becomes $\Delta\rho_k \sim \delta\rho(\lambda/\rho_o)^k$ and the uncertainty in velocity, $\Delta v_k \sim v\delta\rho/\lambda(\lambda/\rho_o)^k$. Thus a succession of collisions clearly introduces a randomization, in the sense of the system being in a state about which we have virtually no micro-level information. Statistical, probabilistic approaches are the natural and virtually the only tools we have to address the microscopics of such systems. But the macro approach, via the classical concept of entropy, provides us with a different kind of variable, one that has a suitable definition in terms of macroscopic observables (quite apart from its probabilistic definition based on microstates). Statistics and probability provide the natural link between the micro and macro concepts, but are not sufficient, by themselves, to tell us where the concepts from the macro approach may lose their validity. One could approach this problem from the perspective of this paper, by asking what the largest approximate system size would be for which reversibility could be observed. Optical experiments controlling the motion of atoms in a trap might be one experimental vehicle for carrying out such experiments. The obvious variables to consider would be the size of the system (the number of atoms), and the duration of the experiment (the number of atom-atom collisions). The analytic formalism above would be the natural theoretical mode to use for making estimates of how long reversibility could be observably maintained.

Another phenomenon characteristic of many small systems is the occurrence of negative heat capacities for noncanonical, especially systems with fixed energy. This behavior occurs when the density of states of the high-potential-energy liquid form is very high, so that those states become heavily populated while there are still systems in the deep potential energy well. Under these conditions, the effective temperature, as determined by the mean kinetic energy, can decrease even when the total internal energy increases[33, 34, 35, 36, 37, 38, 39]. Typically, negative heat capacities reveal themselves as "S-bends" in caloric curves, regions of negative slope of temperature T vs. energy E. A system at least as large as Na_{147} can exhibit such a caloric curve. However nothing is known as yet about the maximum size of system for which such behavior could be observable. This is still one more challenge for finding boundary limits of the validity of results from a macro approach.

4 Clusters as objects of statistical physics

4.1 Cluster parameters near the phase transition

We have shown with some examples how macro and micro atomic systems can seem to behave as different physical objects. Macroscopic atomic systems are described on the basis of classical thermodynamics, allowing us to express the behavior of an atomic system under given conditions through thermodynamic parameters. In particular, the temperature and entropy are such parameters. Evidently, those thermodynamic parameters are not as useful, even sometimes inapplicable, for microscopic atomic systems, in that we can describe microscopic systems by the tools of mechanics, which, as we go to larger and larger systems, becomes ever more complex–and eventually unmanageable– compared with our tools for describing macroscopic systems. We will demonstrate this using the example of the phase transitions of clusters, for which coexistence of phases proceeds smoothly, in contrast to macroscopic systems for which we describe the phase transition as proceeding stepwise–despite its underlying continuity that is hidden by the effect of large numbers of particles [2]. For this we first analyze the peculiarities of microscopic atomic systems, clusters, i.e. bound systems of small finite numbers of atoms. The most relevant cluster property here is the coexistence of phases [8, 11, 40, 41, 42] near the formal point of the macroscopic phase transition. This means that a cluster can be found part of the time in one aggregate state and the rest of time, in the other aggregate state. Transitions between these states in the course of cluster evolution presumably proceed rapidly, relative to the dwell times in each phase. Some specific properties of clusters are also appropriate for characterizing macroscopic atomic systems, when they can be considered as large clusters, but some of these properties become inessential or irrelevant for large clusters. (At this point, we neglect the dynamic coexistence of more than two phases, which, as pointed out earlier, clusters may also exhibit.)

We first consider principal properties of clusters, guided by the model of clusters with pairwise atomic interactions for which these properties are readily recognizable. Moreover, to illustrate some cluster properties, we will use as a model the cluster consisting of 13 atoms, because, for clusters with pairwise interactions, this is a magic number, i.e. with this number of atoms a cluster has a closed-shell icosahedral structure. We can use this model to construct the potential energy surface (PES) for a cluster in a space of atomic coordinates. The relevant cluster property here is the multiplicity of local minima on the PES as expressed as a multidimensional function of the coordinates of the atomic constituents [43, 44, 45, 46, 47]. Each of these local minima, configurational cluster states, corresponds to a locally stable state. Therefore, the analysis of the PES landscape may be a basis for describing the cluster's behavior [48]; evolution of clusters is a result of successive transitions between neighboring configurational states. This character of cluster evolution is known as saddle-crossing dynamics [42, 49, 50, 51]. Note that the Liouville theorem, which describes the full evolution of a classical atomic system, includes coordinates and momenta of all the atoms, where, in considering cluster evolution as configurational transitions, we include only the multidimensional space of atomic position coordinates.

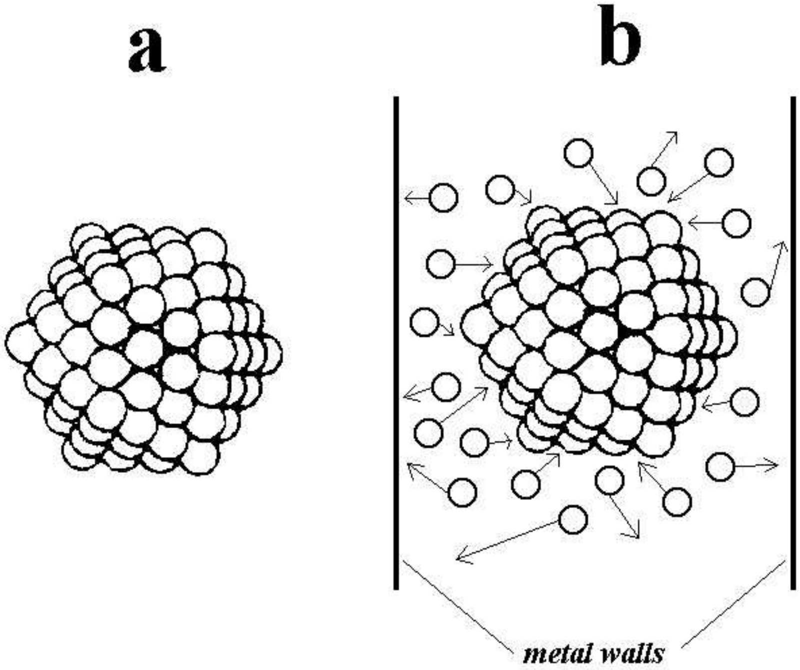

Figure 3: Two versions of cluster interaction with environment, so that a cluster is a microcanonical (a) and canonical (b) ensemble of atoms. In the case **a** a cluster is isolated and its internal energy does not vary in time, whereas in the case **b** this clusters is isothermal, in contact with a reservoir, and its temperature is conserved at the phase transition.

We consider a cluster as a system of atoms for which interactions between its atoms dominate over interactions with the environment. This requires a certain hierarchy of typical times. We now pursue this using the two-state approximation for cluster aggregate states [52]. The character of a cluster's dynamic equilibrium is determined by typical times for processes within the cluster. One can connect a typical time to establish thermal equilibrium τ_{eq} within the cluster due to interatomic interactions and the Debye frequency ω_D, that is roughly inversely proportional to a typical period of cluster oscillations ($\sim 10^{-14}s$ at room temperature). We assume that a typical dwell time of a cluster in the vicinity of any of its free energy minima τ_{ag} associated with each aggregate state is long compared with τ_{eq}

$$\tau_{eq} \ll \tau_{ag} \; , \tag{2}$$

as usually takes place. This results from the character of transitions between configurational states because passage between them requires overcoming a significant free energy barrier, an infrequent and transient event.

As follows from Fig.2, a cluster may be considered as a member of a microcanonical or canonical ensemble of atoms, depending on the character of cluster interaction with an environment [53, 54]. At this point, we consider a cluster as a member of a microcanonical ensemble, and neglect the interaction between the cluster and environment, i.e.

$$\tau_{ag} \ll \tau_{th} \ , \tag{3}$$

where τ_{th} is a typical time for 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 of observation of the cluster τ, so that

$$\tau_{ag} \ll \tau \ll \tau_{th} \ , \tag{4}$$

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, so thermal motion of atoms is described by a certain temperature [55]. If the criterion (5) holds true, this temperature is different for two aggregate states with different energy minima. Hence, for this microcanonical situation, we introduce separate effective temperatures for the solid T_{sol} and liquid T_{liq} aggregate states.

Note that we operate here with a cluster temperature that is a thermodynamical parameter, a variable associated traditionally with a macroscopic description. In thermodynamics, the temperature T of an object is connected with its internal energy E and entropy S by the relation

$$\frac{1}{T} = \frac{dS}{dE} \tag{5}$$

However this macro variable is linked to the micro approach through the usual association of temperature with the mean and distribution of kinetic energies. We likewise associate the cluster temperature with the kinetic energy of its atoms. In particular, in the Dulong-Petit limit, for which a typical atomic kinetic energy significantly exceeds the Debye temperature (in energy units), we have for the kinetic energy K of an n-atom cluster

$$K = \frac{(3n-6)T}{2}, \tag{6}$$

since three degrees of freedom relate to cluster motion as a whole, and three, to cluster rotation. We will focus on conditions of the limiting case $n >> 1$ and compare the cluster temperatures near the phase transition defined within the framework of thermodynamics (6) and statistical physics (7).

Within the framework of the approximation of two aggregate states [52], we have for the total partition function of a cluster that can be found in the solid or liquid states

$$Z = Z_{sol} + Z_{liq}, \tag{7}$$

where Z_{sol} and Z_{liq} are the partition functions for the solid and liquid cluster states, respectively. This corresponds to the situation in which the probability is small for any intermediate excited states which cannot be associated clearly with either the solid or liquid aggregate state–such as a surface-melted state. Let us introduce the parameter

$$p = \frac{Z_{liq}}{Z_{sol}} \tag{8}$$

that allows us to determine the probabilities w_{sol}, w_{liq} that the cluster be found in the solid and liquid states respectively

$$w_{sol} = \frac{1}{1+p} \ , \ w_{liq} = \frac{p}{1+p} \tag{9}$$

Hence, within the framework of statistical physics the effective cluster temperature is

$$T = w_{sol}T_{sol} + w_{liq}T_{liq}, \tag{10}$$

This value is a result of averaging over a long enough time for a cluster to have many transitions between the solid and liquid states.

In order to determine the thermodynamic cluster temperature (6), we first find its entropy for each of two aggregate states. Using the entropy definition (for example, [56]), we have

$$S = -\langle \ln w \rangle = -\sum_i w_i \ln w_i, \tag{11}$$

where w_i is the probability for an atomic system to be found in a state i and the normalization conditions gives

$$\sum_i w_i = 1$$

Let us introduce the probability X_j for the cluster to be found in the $j-$th state–the region of the $j-$th local minimum –of the solid aggregate state and the probability Y_k for the cluster to be located in the $k-$th state–the region of the $k-$th local minimum–of the liquid aggregate state, for which the following normalization conditions are fulfilled:

$$\sum_j X_j = \sum_k Y_k = 1$$

This leads to the following expression for the cluster entropy if the cluster may be found in either of two aggregate states

$$S = -w_{sol} \sum_j X_j \ln(w_{sol} X_j) - w_{liq} \sum_k Y_k \ln\left(w_{liq} Y_k\right) = w_{sol} S_{sol} + w_{liq} S_{liq} + S_{conf}, \tag{12}$$

where

$$S_{sol} = \sum_j X_j \ln X_j,\ S_{liq} = \sum_k Y_k \ln Y_k$$

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} that is given by

$$S_{conf} = -\sum_i x_i \ln x_i = -w_{sol} \ln w_{sol} - w_{liq} \ln w_{liq} = \ln(1+p) - \frac{p}{1+p} \ln p,\ \frac{dS_{conf}}{dp} = -\frac{\ln p}{(1+p)^2} \tag{13}$$

It should be noted that this expression holds true if we observe the cluster for a time long enough for many transitions to occur between aggregate states. As follows from formula (12), along with the sum of terms corresponding to the solid and liquid aggregate states, the cluster entropy includes a term that accounts for configurational excitations. But the configurational entropy part is independent of the thermal motion of atoms, and hence the cluster temperature according to formula (6) is given by formula

$$T = \frac{dE_{th}}{dS_{th}},$$

where E_{th} is the internal cluster energy that is responsible for thermal motion of atoms and is given by

$$E_{th} = w_{sol} E_{sol} + w_{liq} E_{liq} = E_{sol} + w_{liq} \Delta E \tag{14}$$

where E_{sol} and E_{liq} are the cluster internal energies for the solid and liquid aggregate states, and ΔE is the energy jump associated with the phase transition. Using the definitions for the cluster temperatures for the cluster residence in the solid or liquid states

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

we obtain for the cluster temperature in the case of phase coexistence, in which the cluster can reside in either the solid and liquid states

$$\frac{1}{T} = \frac{w_{sol}(T_{sol})}{T_{sol}} + \frac{w_{liq}(T_{liq})}{T_{liq}} \tag{15}$$

Comparing the statistical (11) and the thermodynamic (15) expressions for the cluster temperature, we find that these formulas give an identical result, if the temperature change $\Delta T = T_{sol} - T_{liq}$ is relatively small

$$\Delta T \ll T_{sol} \tag{16}$$

One can see, however, that in a general case, statistical physics, using a micro approach, and thermodynamics, the macro view, give different results for the cluster temperature in the case of phase coexistence.

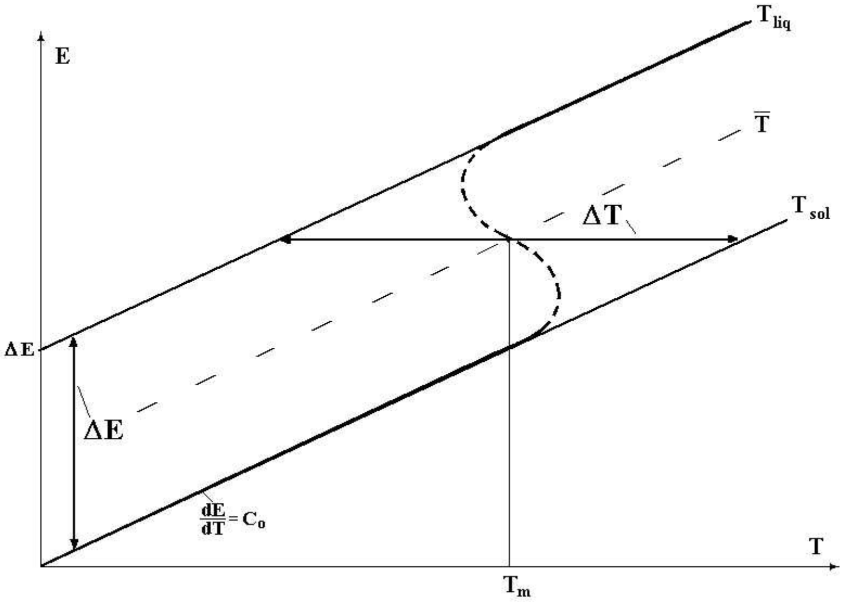

Figure 4: Caloric curve for a cluster as a member of a microcanonical ensemble in the one-temperature approach near the traditional phase transition.

We now demonstrate one more result that follows from this analysis. Let us assume that the criterion (16) holds true and find the cluster heat capacity in the one-temperature approach, describing the cluster state by one average temperature. Let us find the cluster's heat capacity within this framework. Fig.4 shows a schematic representation of the caloric curve of this cluster, i.e. the temperature dependence of its internal energy. We assume for simplicity that the cluster's heat capacities are essentially equal for the solid and liquid aggregate states throughout the region near the phase transition, i.e.

$$C_o = \frac{dE_{sol}}{dT} = \frac{dE_{liq}}{dT}$$

(This is not an assumption necessary for the argument; it is introduced only to simplify the derivation.) In addition, under these assumptions we have the following relation between parameters of the phase transition

$$\Delta T = \frac{\Delta E}{\Delta S},$$

where ΔT, ΔE and ΔS are the jumps of the corresponding quantities at the phase transition. Correspondingly, formulas (11) and (14) take the forms

$$T = T_{sol} - \Delta T w_{liq},\ E_{th} = E_{sol} + \Delta E w_{liq}$$

This gives us the cluster's thermodynamic heat capacity

$$C = \frac{dE_{th}}{dT} = \frac{C_o + \Delta E dw_{liq}/dT_{sol}}{1 - \Delta T dw_{liq}/dT_{sol}} \tag{17}$$

From this it follows that in the range of phase coexistence, where $w_{sol}\ w_{liq}$, we obtain

$$C = -\frac{\Delta E}{\Delta T} = -C_o, \tag{18}$$

i.e. the cluster's heat capacity is negative; this phenomenon is known as "an S-bend" in the caloric curve [36, 37, 57, 58, 59, 60, 61]. This cluster behavior is confirmed by experimental results [13, 14, 62, 63, 64]. Thus the criterion for the cluster's heat capacity to exhibit a range of negative values is [65]

$$\Delta E \Delta T \gg 1, \tag{19}$$

and since $\Delta E \sim n$, where n is the number of atoms in the cluster, and ΔT depends weakly on n. This criterion holds true for more than just very small clusters. We see that the cluster's heat capacity may be negative even for clusters of moderate size. One might think that the negative heat capacity contradicts laws of physics, because in this situation, transferring energy to a physical object leads to its cooling. In fact, the result does not contradict traditional physical laws, because we are dealing here with systems at constant energy, not at constant temperature, and we are ascribing effective temperatures to each phase and then using their average to associate a single temperature to the system. Raising the total energy of an ensemble of such systems moves them from regions of low potential energy and hence of high kinetic energy, into regions of high potential and low kinetic energy, where the density of states is higher than in the regions of local minima.

This analysis shows how we can use thermodynamics under specific but perhaps unconventional conditions, in this case, at a micro level. In the case under consideration of a cluster near its phase transition, the configurational changes make an important contribution to the cluster's thermodynamic parameters. Therefore describing it within the framework of thermodynamics, we reduce this object to the thermodynamic model with an effective common temperature. This operation may lead to contradiction. Hence, it is necessary to be careful in applying thermodynamics to specific physical objects or conditions, especially for micro objects.

4.2 Demonstration of cluster properties: the 13-atom Lennard-Jones cluster

Classical thermodynamics is appropriate and useful, and effectively has a universal character for describing macroscopic systems. However some thermodynamic concepts lose their applicability when we try to use them for microscopic atomic systems. Instead, we must use statistical mechanics, for example to analyze the behavior of a cluster of several atoms, even hundreds or thousands. In particular, we can best use the concept of the Gibbsian ensemble, a large, idealized collection of many, many systems, all subject to the constraints we wish to apply to our specific system [66, 67]. As defined by Gibbs, the aggregate state or phase of a macroscopic atomic system is a uniform spatial distribution of atoms restricted by a boundary, and the phase transition is a transition between two such aggregate states. Transferring this concept to clusters, we must modify this definition. Specifically, if we consider configurational states as stable cluster states, one can formulate an aggregate state as one or a set of configurational states with similar energies that can exist in dynamic equilibrium together [68]. It is clear intuitively that the phase or aggregate state as a sum of configurational states may be separated from other sets of configurational states if the density of such states in the energy space and their statistical weights are sufficient. Therefore, although we ascribe existence of aggregate states for macroscopic systems based on observations, we cannot to do this for small clusters and must use another method. As an example of this, Fig.5 demonstrates existence of the solid and liquid aggregate states for the

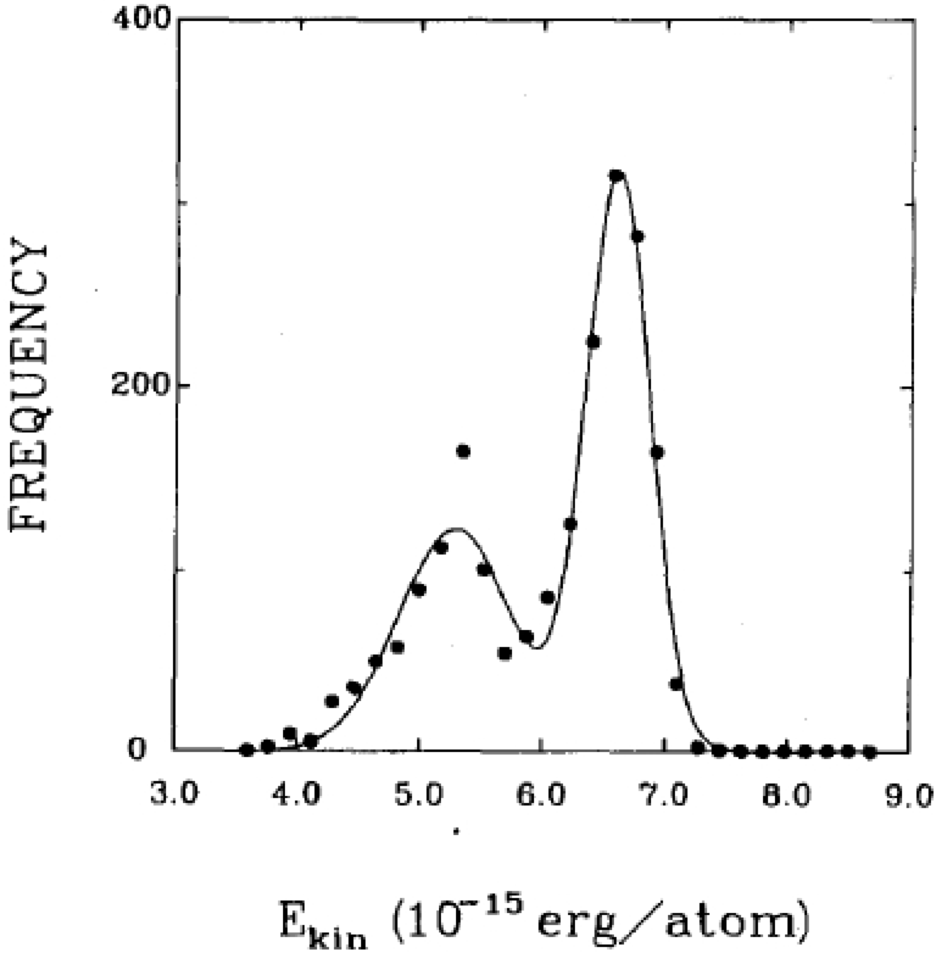

Figure 5: The distribution function over the total kinetic energies of atoms of an isolated 13-atom Lennard-Jones cluster [8]. Here the energy of cluster excitation from the global minimum is $-4.04x10^{-14}$ erg/atom, and E_{kin} is the total kinetic energy of the cluster atoms. The bimodal distribution with peaks of different areas reveals the coexistence of two phases in equilibrium but in unequal amounts.

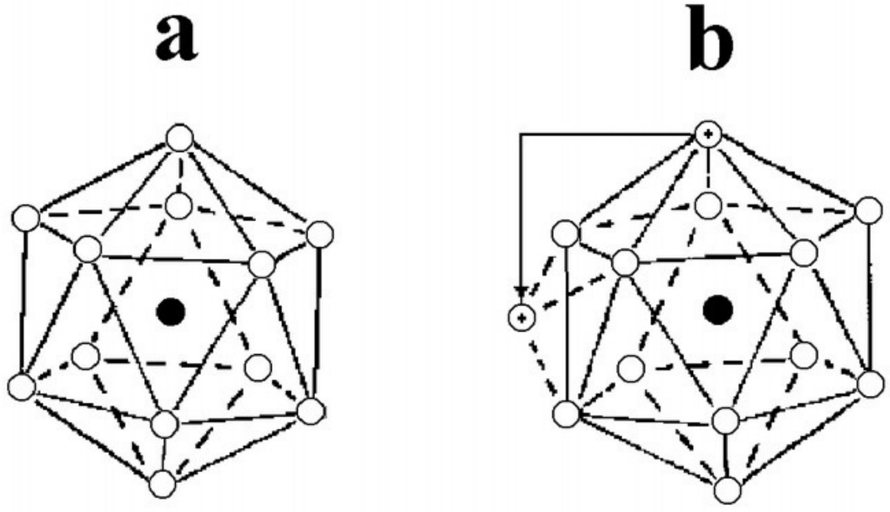

Figure 6: Structure of the 13-atom cluster with pairwise atomic interaction for which interaction between nearest neighbors dominates. Left (a) the cluster structure for the solid aggregate ground state with its icosahedral structure, and right (b) the structure of the lowest configuration assignable to the liquid aggregate state, in which one atom is promoted onto the cluster surface where it exhibits lability [68].

13-atom Lennard-Jones cluster. In this case the distribution function of the total kinetic energies of the cluster atoms exhibits two maxima which correspond to the solid and liquid aggregate states.

Let us analyze the structure of the 13-atom cluster with pairwise interaction between atoms. The ground configurational state is a regular icosahedron (see Fig.6a). This symmetric structure is characterized by a central atom and 12 surface atoms. If we join atoms of the cluster surface with nearest neighbors, the cluster surface would consist of 20 regular triangles, giving 42 bonds between nearest neighbors for this cluster. A corresponding 13-atom fcc (cuboctahedron) or hexagonal (hexahedron) structure would have only 36 bonds between nearest neighbors; hence the icosahedral structure dominates for this and other clusters in this size range. The lowest configurationally excited cluster states correspond to promotion of one atom from the outer shell to the cluster surface (Fig.6b). At zero temperature, this state is separated in energy from other, higher excited configurations and is characterized by a statistical weight $g = 12 \cdot 15 = 180$, corresponding to the 12 positions in the cluster shell and 15 positions on the cluster surface when these positions do not border. This gives an entropy jump ΔS for the configurational change, which would be that of the phase transition between these states, if the phase transition were to occur at zero temperature.

Fig.7 shows the energy parameters for configurational transitions of the 13-atom Lennard- Jones cluster [69]. Note the large energy barrier between the lowest state and the “single-particle promoted” states. As Fig.6b shows, an atom can transfer from the surface shell to the cluster surface by a rotation around an axis joining two nearest neighbors of this atom. This transfer requires crossing the potential barrier for this transition, a value approximately equal to the energy of one bond. This is indicated schematically in Fig.7. Let us consider a state as liquid if a single atom is relatively free to move about the surface and to exchange with any other atom in the surface; then we can determine the melting point T_m for the 13-atom Lennard-Jones cluster with the assumption that the entropy jump ΔS and the excitation energy ΔE to the set of configurational states that comprise that liquid state are independent of the temperature. Taking these values at zero temperature $\Delta S = \ln 180 =$ and $\Delta E = 2.89 \pm 0.04$, we obtain for the melting point of this cluster

$$T_m = \frac{\Delta E}{\Delta S} = 0.56, \tag{20}$$

where the melting point is expressed in energy units, with the energy of one bond as the energy unit.

In reality, the entropy jump of the phase transition varies with cluster excitation or its temperature. Fig.8 shows the entropy jump for the 13-atom Lennard-Jones cluster. The data of this Figure were obtained from computer simulations [8, 9] under both microcanonical and canonical conditions. The entropy jump is slightly

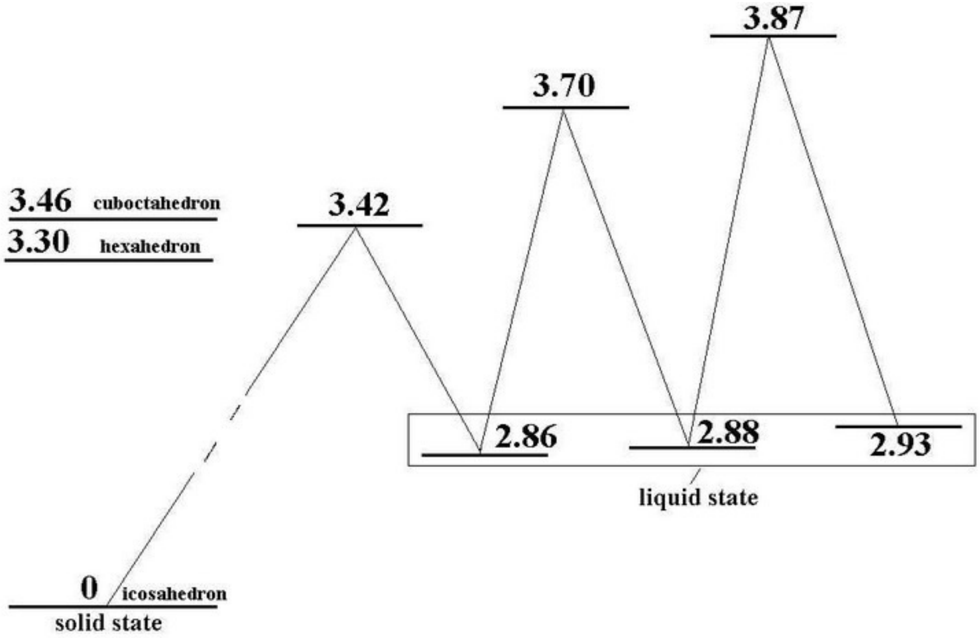

Figure 7: Energies of the lowest configurational states of the 13-atom Lennard-Jones cluster [69] at zero temperature. The energy of breaking one bond is taken as the energy unit. At moderate temperatures, transitions between configurationally excited states indicated in this Figure become effective, so that these states together define the liquid aggregate state of this cluster. Note that the vertical scale is only a qualitative indication, so the excited states are much closer to the saddles that separate them than is the ground state from the excited states.

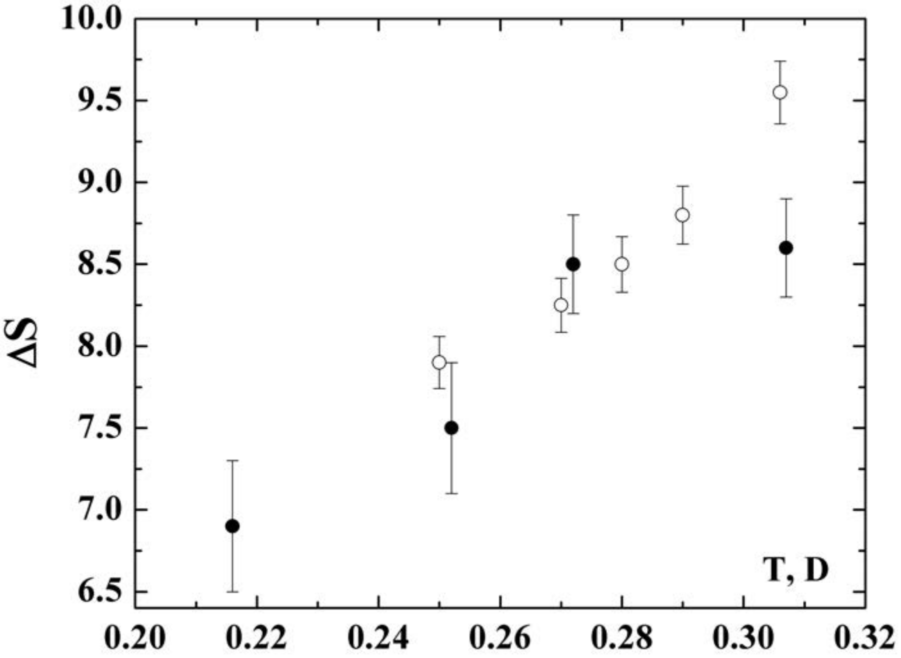

Figure 8: The entropy jump for the phase transition in the 13-atom Lennard-Jones isothermal cluster [18, 70].

lower for the isothermal case, the canonical ensemble. One can divide the entropy jump ΔS into two parts, one due to the configurational transition ΔS_o which is the entropy jump at zero temperature, and the other, to the contribution of thermal vibrations, especially of the liquid state. The latter includes a significant contribution from anharmonic motions. We can thus account for the temperature variation of the energy change ΔE and the entropy jump ΔS; at the classical melting point these values are [68] $\Delta E_m = 2.49 \pm 0.05$, $\Delta S_m = 8.5 \pm 0.5$, and this determines the melting point T_m

$$T_m = \frac{\Delta E_m}{\Delta S_m} = 0.29 \pm 0.02; \tag{21}$$

the values are measured in the units of one bond strength. Comparing this with formula (20), one can conclude that ignoring the temperature dependence of the parameters of the phase transition leads to an error of a factor of two for the melting point.

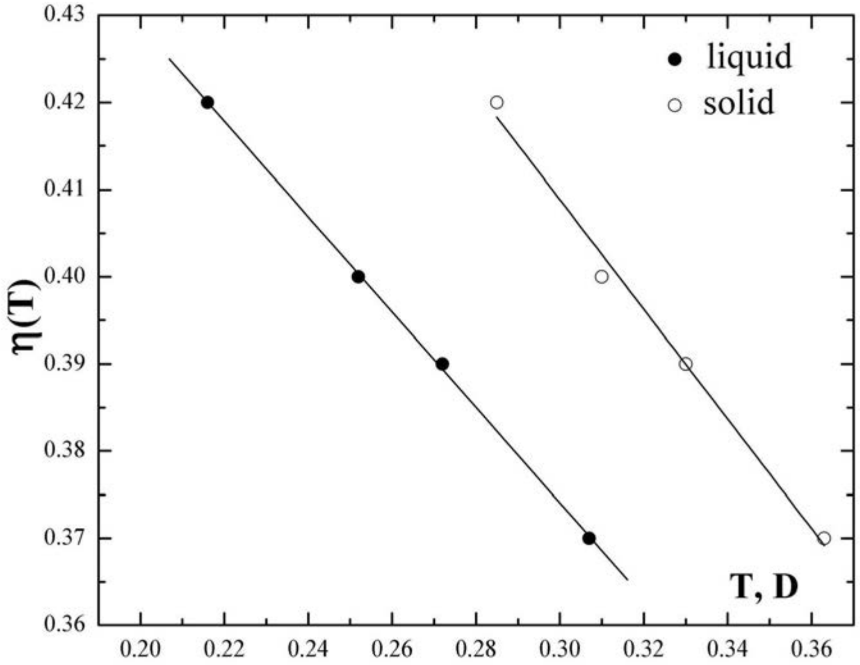

Figure 9: Anharmonic coefficient for the solid and liquid aggregate states of the 13-atom Lennard-Jones cluster [68, 71].

In order to analyze the temperature dependence of parameters of the phase transition, we introduce the anharmonic coefficient η for each aggregate state

$$\eta_{sol} = \frac{K_{sol}}{E_{sol}}, \; \eta_{liq} = \frac{K_{liq}}{E_{liq}}, \tag{22}$$

corresponding to thermal atomic motion in the solid and liquid state, respectively. Fig.9 shows the temperature dependence of the anharmonic coefficients $\eta(T)$ for both solid and liquid states. The lines $\eta_{sol}(T)$ and η_{liq} are shifted with respect to one another, and approximately we have

$$\eta_{sol}(T) \approx \eta_{liq}(T - \Delta T), \tag{23}$$

where ΔT is the temperature change in the phase transition of the isolated 13-atom Lennard-Jones cluster.

Let us return to formula (10) for the probabilities of the solid w_{sol} and the liquid w_{liq} states

$$w_{sol} = \frac{1}{1+p} \; , \; w_{liq} = \frac{p}{1+p};$$

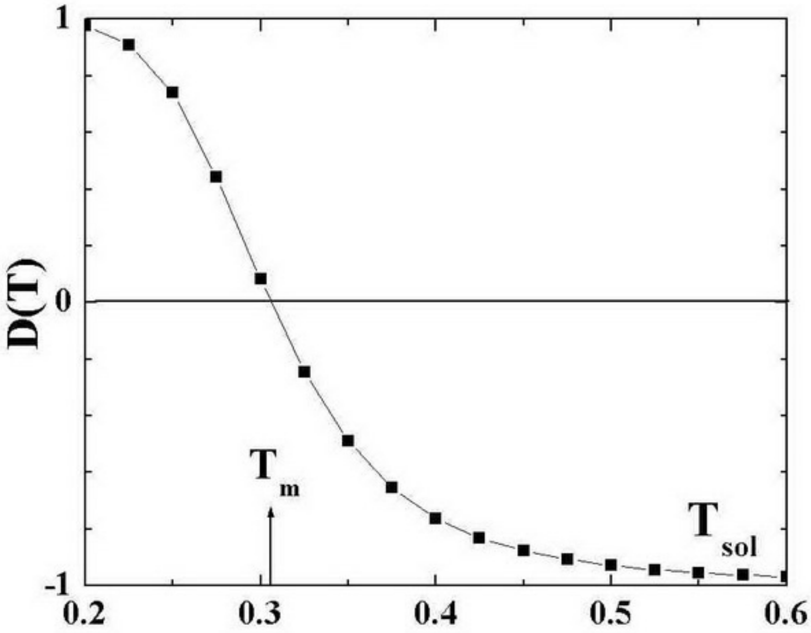

Figure 10: The parameter of phase coexistence for the 13-atom Lennard-Jones cluster given by formula (1).

expressing the ratio of these probabilities in thermodynamic terms as the classical equilibrium constant,

$$p = \frac{Z_{liq}}{Z_{sol}} = \exp\left(-\frac{\Delta E}{T_{con}} + \Delta S\right). \tag{24}$$

In this manner we introduce the effective configurational temperature T_{con}. Let us determine this temperature for an isolated cluster in the two-temperature approach. We use the principle of detailed balance for this transition [72, 73]

$$w_{sol}\nu_{sl}(T_{sol}) = w_{liq}\nu_{ls}(T_{liq}), \tag{25}$$

where ν_{sl} is the rate of transition from the solid to the liquid state, ν_{ls} is the rate of the reciprocal transition, and we take into account that these rates are determined by the temperature of the initial state. If these temperatures are identical, we have from the principle of detailed balance

$$\frac{\nu_{sol}(T)}{\nu_{liq}(T)} = g\exp\left(-\frac{\Delta E}{T}\right) = g\exp\left(\Delta S - \frac{\Delta E}{T}\right), \tag{26}$$

where g is the ratio of statistical weights for the liquid and solid aggregate states, so that the transition entropy is $\Delta S = \ln g$, and ΔE is the energy of this transition. Since the phase transition has an activation energy, the transition rates are given by

$$\nu_{sl}(T) \sim \exp\left(-\frac{\Delta E}{T} - \frac{E_b}{T}\right),\ \nu_{ls}(T) \sim \exp\left(-\frac{E_b}{T}\right),$$

where E_b is the barrier energy. On the basis of formulas (24), (25) and (26) we obtain for the configurational temperature given by formula (24)

$$T_{con} = \frac{T_{sol}}{1 + \frac{E_b}{\Delta E}\frac{\Delta T}{T_{liq}}}\ , \tag{27}$$

where $\Delta T = T_{sol} - T_{liq}$. In considering the isolated 13-atom Lennard-Jones cluster, we take the barrier height at zero temperature $E_b = 0.56$ according to Fig.7 and the above values of other parameters, we reduce formula (27) to the form

$$T_{con} = \frac{T_{sol}}{1 + \frac{0.013}{T_{liq}}} , \tag{28}$$

so that the effective configurational temperature is close to the solid temperature. Using this formula, we give in Fig.10 the temperature dependence $D(T_{sol}$ for the parameter D which is defined by formula (1) and characterizes the contribution of the solid or liquid aggregate state in phase coexistence.

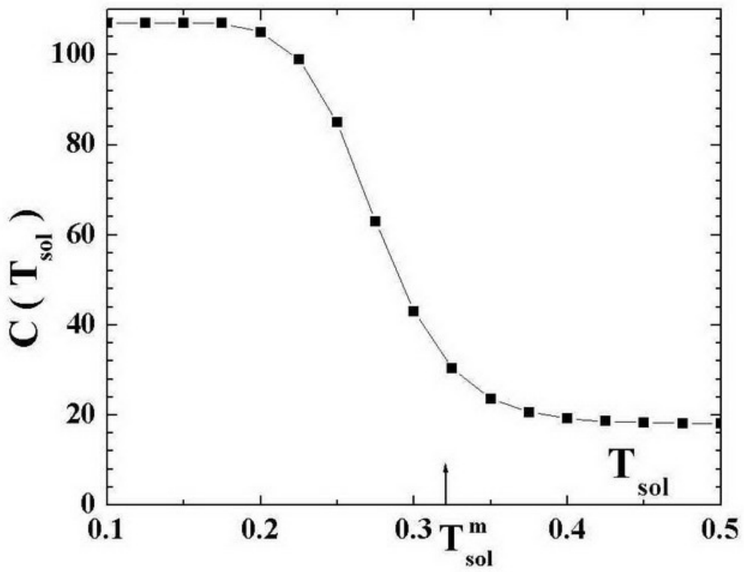

Figure 11: Heat capacity of the 13-atom Lennard-Jones cluster as a microcanonical ensemble of atoms according to formula (30). The energy of breaking of one bond is taken as the energy unit, the melting point where $p(T^m_{sol} = 1$ is indicated by an arrow.

We also determine the heat capacity of the 13-atom Lennard-Jones cluster under microcanonical conditions that, according to formula (17) and accounting for formulas (11) and (14) is given by

$$C = \frac{\Delta E_{th}}{dT} = \frac{dE_{sol} + \Delta E dw_{liq}}{dT_{sol} - \Delta T dw_{liq}} \tag{29}$$

On the basis of formula (24) we have

$$dw_{liq} = \frac{\Delta E dT_{con}}{T^2_{con}(1+p)^2}$$

From this we have for the heat capacity of an isolated cluster

$$C = \left[C_o + \left(\frac{\Delta E}{T_{con}} \right)^2 \frac{dT_{con}}{dT_{sol}} \frac{1}{(1+p)^2} \right] \left[1 - \frac{\Delta E \Delta T}{(1+p)^2} \frac{dT_{con}}{dT_{sol}} \right]^{-1} \tag{30}$$

We apply formula (30) to the 13-atom Lennard-Jones cluster. Parameters of formula (30) for this cluster are $T^m_{sol} = 1.05 T^m_{con} = 0.315 \pm 0.03$ and $\Delta E = 2.49 \pm 0.05$; the anharmonic coefficient is $\eta_m = 0.4$, the cluster excitation energy at the melting point is $E^m_{ex} = 13.9 \pm 0.2$, $C_o = 18 \pm 1$, and $\Delta T \approx 0.06$ [68]. Fig.11 gives the

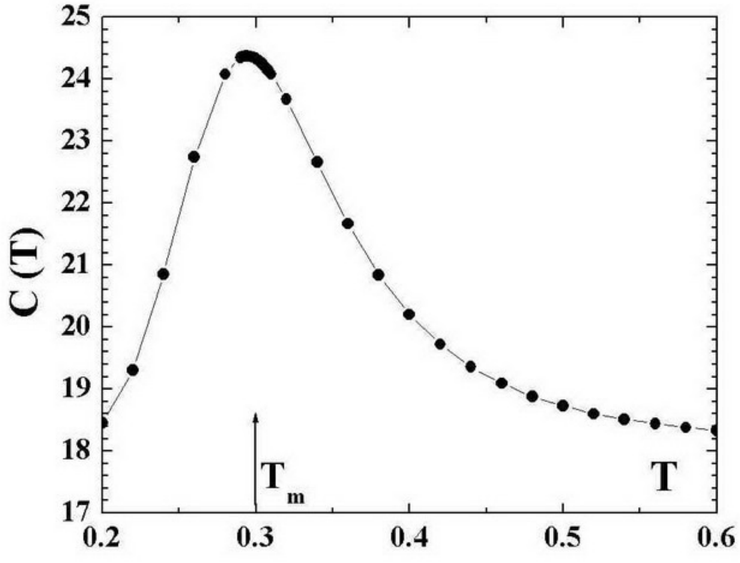

Figure 12: Heat capacity of the 13-atom Lennard-Jones isothermal cluster (a canonical ensemble of atoms) according to formula (30). The energy of breaking one bond is again taken as the energy unit, the melting point where $p(T^m_{sol}) = 1$ is indicated by an arrow.

temperature dependence for the heat capacity of this cluster. We see that in this case, the criterion (19) does not hold, and the heat capacity of this cluster cannot take on negative values.

We also present the heat capacity of the isothermal cluster; close to the melting point, this is given by [68]

$$C(T) = C_o + \Delta S_m(2\Delta S_m - \Delta S_o)\frac{p}{(1+p)^2}, \tag{31}$$

where ΔS_m and $DeltaS_o$ are the entropy jump at the melting point and at zero temperature, and the parameter (9) is determined by formula (24) with the configurational temperature T_{con} which is equal to the cluster temperature T ($T_{con} = T$). For the 13-atom Lennard-Jones cluster we have $\Delta s_o = 5.2$ and $\Delta S_m = 8.5 \pm 0.5$. The results are given in Fig.12.

5 Conclusion

Here we have presented an overview, with examples, of a way we can bridge between macroscopic approaches to describing nature and microscopic methods rooted in our concepts of the elements from which our world is built. The central key to this bridge is recognizing that there are some descriptions of phenomena at the macro scale that break down when we try to apply them to small systems, systems of a size that easily accommodates a micro approach. The focus and tool for making that bridge and reconciliation is finding the system size, for any specific phenomenon, below which the macro description loses its validity. This has been carried out for some phenomena now, but there are others, some very important, that stand as challenges for us now.

6 Acknowledgment

RSB would like to acknowledge the hospitality of the Aspen Center for Physics, where some of this work was done. The Center supports its participants with the assistance of NSF Grant 1066293.

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