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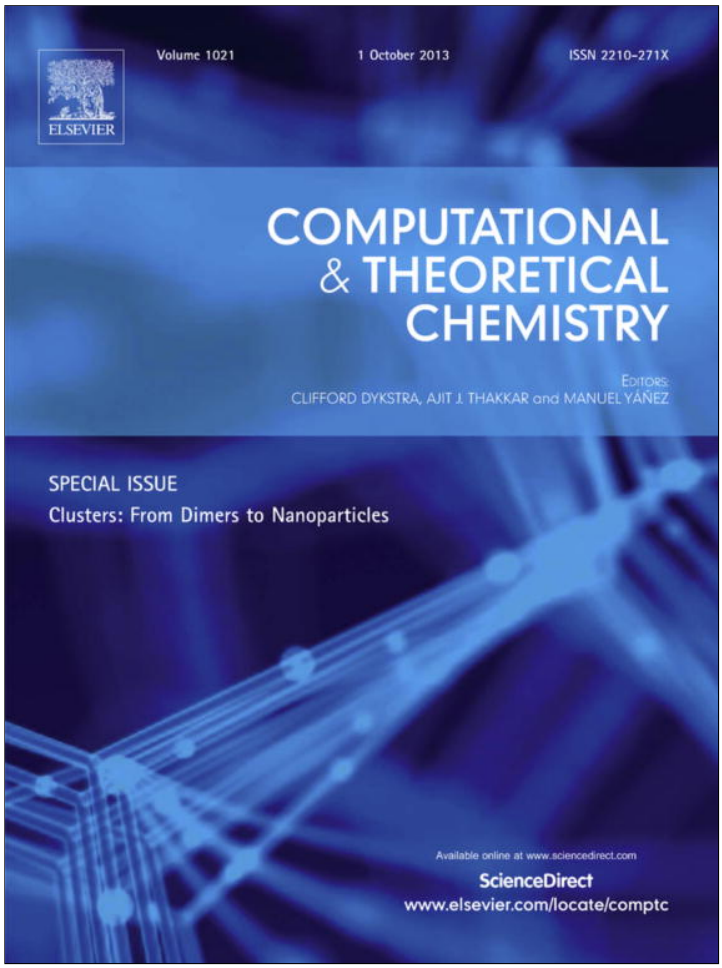

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Viewpoint article

Clusters as tools to link macro and micro approaches

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ABSTRACT

Physical sciences have two distinct approaches, the macroscopic as exemplified by thermodynamics, and the microscopic, based on the behavior and interactions of individual atoms and molecules. These two have coexisted with virtually no links to join or bridge between them. This paper outlines an approach that achieves one kind of bridge, specifically by offering a way to determine the upper size limit of individual systems that do not conform to the macroscopic description of a chosen property or phenomenon. Despite the random motion of the atoms, extending macroscopic methods to clusters requires additional information because of their size-specific and structure-specific properties.

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1. Introduction

Macroscopic approaches to describing the behavior of systems, such as the application of traditional thermodynamics, the assumption of infinite size or of continuous structure, have proved very powerful for many kinds of phenomena. One example is the Gibbs Phase Rule [1], relating the number of degrees of freedom f of a macroscopic system to the number c of independent components and the number p of phases present in equilibrium: $f = c - p + 2$, perhaps the simplest formula in all of physical science. This rule shows that two phases of a single substance can exist in equilibrium at only one temperature for any chosen pressure, for example. However it is now well established that small atomic clusters do not conform to that rule. Computer simulations [2–11] and experiments [12,13] have demonstrated that solid and liquid clusters can coexist in equilibrium over bands of temperature and pressure, and that more than two phase-like forms can coexist.

The reason for this apparent violation of a fundamental thermodynamic principle is in fact not difficult to understand. The Gibbs Phase Rule [1] is actually a consequence of the thermodynamic behavior of a system of a very large number of particles. The same thermodynamics applied to systems of only a small number of atoms or molecules does not yield the Gibbs Phase Rule at all. Specifically, if one thinks of solid–liquid equilibrium in terms of the traditional equilibrium constant, the ratio of the two species K_{eq} = [liquid]/[solid], this quantity is the exponential of the difference in free energies of the two forms, $\exp[-\Delta F/kT] = \exp[-N\Delta\mu/kT]$, where μ is the chemical potential, the free energy per particle. This tells us that if N is very large, e.g. $\sim 10^{20}$, then although the two species can both be present when their chemical potentials are equal, even a very tiny difference in their chemical potentials will make the amount of the unfavored species so tiny as to be unobservable. However if the number N is, say, ~10, then the equilibrium constant can be of the magnitude of unity over a moderate range of temperatures. This implies that the unfavored phase can easily be present as a minority species in observable amounts, so long as it is locally stable. Hence if the minority phase of a small system has a local free energy minimum, it is quite consistent with fundamental thermodynamics for that system to violate the Gibbs Phase Rule [14].

The next step, pursuing this approach, is to ask whether and how one can determine an approximate boundary that separates the systems large enough that the macro rules of behavior describe them from the small systems that violate macro-scale rules, even while obeying the fundamental underlying laws. This is precisely the question we address in this discussion. Presumably one must find a different answer for each phenomenon, but, as we shall see, it is now within reach to get those answers.

The first thing one must do is estimate, for any given choice of phenomenon, what the minimum observable deviation from the macroscopic limit would be. For example, in the solid–liquid equilibrium case, one may suppose that if 10% or more of a sample is in the minority phase, and the temperature band within which that 10% or more coexists with the majority phase is, say, 0.5 K, then that minority phase could be detected. With that estimate in hand, one can then ask the next question: "How wide is the temperature band within which the solid–liquid equilibrium constant is between 0.1 and 10, as a function of the number of particles comprising the system?" The maximum number N_{max} for which the minority phase represents at least 10% of the population is the primary criterion that fixes the macro–micro boundary. In this case, however, if the temperature band for coexistence were much less than 0.5 K at the value

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of N_{max}, then the boundary would be determined by the value of N at which the coexistence band is only 0.5 K wide. In reality, for the clusters that have been investigated in this way until now, the population criterion, rather than the latter temperature band criterion, has proven to be the appropriate one.

2. A solved example: cluster solid–liquid equilibria

We briefly review the one example of solid–liquid equilibria of small clusters for which a full, explicit solution now exists [14–16]. The equilibrium constant for solid–liquid equilibrium at a fixed temperature, as given above, is the governing quantity. If we set the observable limit as just described at 10% of the minority species, then we must find the conditions for which K_{eq} lies between 0.1 and 10, or $\ln K_{eq} = -N\Delta\mu/kT$ lies between −2.3 and +2.3. At the classical melting point, of course $\Delta F = 0$, or $E_m/T = \Delta S_m$, where the subscript "m" indicates the quantity's value at that point. We assume that both ΔE and ΔS in the vicinity of the classical melting point retain almost the same values as those at that point, so we can determine a range δF and a corresponding temperature range δT just from the temperature derivative of $\delta F = \Delta E_m \delta T/T_m^2$. We replace $\Delta E_m/T_m$ with its equivalent, ΔS_m, so we have $\delta F = \delta T(\Delta S_m/T_m)$. But we have just determined that we have chosen δF to be 4.6. Hence, approximating this as 5, we find the temperature range of observable deviation from the Gibbs Phase Rule depends just on the classical melting temperature (for the cluster, of course, not that of the bulk material), and, inversely, on the entropy change in the melting transition:

$$\delta T \sim \frac{5T_m}{\Delta S_m} \tag{2.1}$$

For rare gas clusters, we make an assumption that the entropy change, per atom, found from simulations of a 55-atom cluster's melting can be used to estimate corresponding entropy change for a range of cluster sizes. The value one obtains, 0.82 per particle, yields a range δT of ca. 0.1 K for clusters of about 100 atoms which satisfy the arbitrary condition we have set on the free energy range. Thus we can take 100 atoms as the effective boundary, the lower limit of the size to which macroscopic treatment is adequately accurate. For a cluster of 75 argon atoms, the temperature range is almost 4 K. For metal clusters, for which the entropy changes are somewhat smaller, the effective size boundary is in the range of several hundred atoms.

3. Extending to other phenomena

A small step toward extending this approach-finding the boundary by determining the particle size below which the macro description fails-has just been made [17]. Here, we carry the process a step further. Let us list a few phenomena for which establishing such boundaries may give us useful insights. First, since we know that small systems have, as their most stable structures, geometries typically different from the bulk crystalline structures. At what particle number does the system take on the structure of the bulk? Closely related to that is the non-monotonic behavior of several properties, not only the form of the most stale structure but also the binding energy and the ionization potential-and with that, the relatively unexplored matter of spectra of atomic clusters. This brings us to the electronic properties. The small sizes of clusters of course implies that the energy levels are discrete, so there are no analogs of the conduction bands, sets of levels so closely spaced, so numerous and so interlinked that they form continuous rather than discrete over ranges of energy and extending throughout entire systems. This means that small clusters of metal atoms are effectively nonmetals, dielectrics, insulators or possibly semiconductors. Then there are examples for which the nature of bonding in clusters must be different from that of the corresponding bulk system. The most egregious examples of this are clusters of gallium and of tin, whose melting points are well above the melting points of the bulk materials [18–21]. This is clearly a violation of the rule, long established, that small systems must melt at temperatures lower than their bulk counterparts, simply because of their much larger surface-to-volume ratios [22,23]. The explanation of this dramatic deviation from traditional expectations is a consequence of the difference of the nature of the chemical bonding in clusters and bulk [20,21]; in the clusters that have been investigated in these studies, the atoms are bound covalently.

These phenomena have all been studied for specific clusters. The question we raise here forces us to look more systematically at the size dependence of the phenomena. At what size, for example, do clusters of copper atoms become metallic conductors? At what size does the binding of gallium or of tin become that of the bulk metal? At what size do clusters of argon atoms take on the close-packed lattice structure of bulk solid argon? At what size does the behavior, e.g. the particle binding energy, become constant, rather than varying considerably with small changes in the number of particles in the cluster? We can attribute the nonmonotonic behavior to the geometric and electronic structure of finite systems, specifically to their tendency to form closed shells of atoms or of electrons when the number of particles takes on a "magic number" [24]. Hence the answer to the monotonicity issue is closely linked to the question of attainment of the bulk structure. Simulations indicate, for example, that a cluster of 55 Ag atoms assigned initially to the bulk face-centered cubic (FCC) structure transforms spontaneously to an icosahedron at room temperature [25] so the FCC structure clearly does not become the most stable until the cluster size is well above 55 atoms.

Related to that last issue is a pervasive one that we encounter with virtually every phenomenon that exhibits different behavior with small and macroscopic systems. That is the question of the size above which behavior is monotonic with size. Small systems behavior is frequently a result of and often predictable from shell structure, either atomic or electronic. Because of the special stability of closed shells, of whichever sort, we encounter nonmonotonic behavior of finite systems, sometimes to surprisingly large sizes [24].

Perhaps the easiest of these questions to address is that of determining the approximate size above which clusters of metal atoms can be expected to behave as metals. One important thing to keep in mind here is the role that the system boundary plays in conductivity. Because metal clusters are of nanoscale or subnanoscale diameters, direct-current or low-frequency conductivity measurements are dominated by the effects of any conducting electrons colliding with the system boundaries. Hence the appropriate test of metallic conductivity in a cluster must be done as a measurement of sufficiently high-frequency conductivity that the current-carrying electrons (or holes) are not strongly influenced by the system boundaries. We can assume that the electronic wave functions in the highest occupied orbitals, those primarily responsible for binding the metal atoms together, overlap fairly strongly from one atom to its neighbors, so that we need not consider tunneling through barriers as contributing to nonmetallic behavior. Rather, the dominant issue here is almost certainly the magnitude of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). We use as our model here systems in which the HOMO is filled, so that the electrons cannot move, except to show some polarization, in the presence of an external field; they cannot conduct unless some are promoted to the LUMO. Thus such clusters begin to behave as metals when the cluster is large enough that the energy gap between HOMO and LUMO is comparable to the ambient kT. Under those conditions, there are enough electrons promoted by thermal excitation to enable the cluster to be conductive, in the sense that

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those electrons can move through the cluster unimpeded except by scattering off of atomic cores. While we will present no specific computational results of the size dependence of the HOMO–LUMO band gaps for metal clusters, the methods for doing such calculations are well known. One may use empirical effective potentials such as the Gupta [26] or Sutton-Chen [27], or Density Functional Theory (DFT) [20,28]. It is simply a matter of finding the cluster size (and perhaps geometric structure) above which that energy gap is comparable to or smaller than the reference temperature one chooses. It is possible that some clusters of metal atoms may have different electronic properties in different structures, which would of course be a phenomenon requiring micro-scale treatment.

The question of the size above which the bulk structure is that of the finite system is still quite open. Argon clusters would be the natural first system to test, and this was done by simulation and experiment in 2000 [29]. The results of that study indicate that even clusters of 80,000 atoms show no clear preference for the bulk face-centered cubic (fcc) structure over the hexagonal close-packed (hcp) form, and that the clusters may have mixtures of both structures. Whether those results are a consequence of the conditions under which the clusters were formed or of there being no clear free energy difference between the different forms (including mixtures of the two) are unanswered questions. It may be necessary to carry out very large-scale simulations in order to find answers. In contrast, some metal clusters, notably platinum and aluminum, may take on bulk structure even in relatively small clusters, but the actual structures even of small clusters, e.g. of aluminum, are not yet well-known, because different effective potentials give different patterns of structure [30]. The status of knowledge of aluminum clusters, for example, is extensively discussed in a recent review, which, among other things, shows extensive examples of non-monotonic behavior with size, particularly regarding melting processes [31]. Determining the "crossover size" above which any given substance takes on its limiting bulk structure may prove to be a very great challenge.

An equally great challenge will be that for systems whose bonding is different for small clusters than for the bulk systems. That certain gallium and tin clusters exhibit covalent rather than metallic bonding seems established [20,21] but it will be a major undertaking to determine the cluster size above which these substances behave as they do in their macro forms, as metals. It is not even clear now whether it will be better to pursue this question via experiment or by theoretical calculations. Pursuing the latter might give insight if one were to compare results of electronic structure calculations from isolated clusters with those from calculations based on periodic boundary conditions. Certainly, systematic calculations for clusters of many sizes, especially rather large sizes, does not appear to be an efficient approach, although it might prove necessary.

4. Randomization in clusters

When we use thermodynamic parameters to describe a cluster, we implicitly consider it as a member of a Gibbsian ensemble, so, in that sense, thermodynamics is appropriate. However, because a cluster is typically a system of a relatively small number of bound atoms, we must use care when we apply generalizations that are valid because the individual systems they represent are themselves very large. Even though we have in mind a random character for cluster evolution, rather than a deterministic one in which we can specify the positions and velocities of all the atoms (if we use classical mechanics to prescribe the trajectories), in that context, we still retain time reversibility. This follows from the reversibility of the laws of classical and quantum mechanics, or the Newton or Schrödinger equations with respect to time reversibility. On contrary, in a traditional statistical description, we assume the atomic system to be random in a manner that does not preserve time reversibility.

A clear illustration of the difference between the idealized statistical picture with time-reversible but random motion and a situation in which the particle behavior is random but must be treated as non-time-reversible is simply simulation of cluster evolution by computer simulation, e.g. by molecular dynamics (MD). A simple MD calculation, forward and then backward, showed that time reversibility for a simple Lennard–Jones cluster was retained up to about 5000 time steps, but beyond that, a single significant figure was lost when trajectories were reversed and followed "backward" to what was supposed to be the initial state. Moreover if the precision of the calculation was doubled, so that twice as many significant figures were kept, the length of the trajectory that retained reversibility went up only to 10,000 time steps. Evidently, a small random force or bit of noise may lead to randomization of an atomic system within a reasonably short time interval. This illustrates randomization in the way we carry out our analysis of the system.

Next, we consider how randomization develops when we have incomplete knowledge of the mechanical variables of a several-particle or many-particle system, which of course is always the case. We demonstrate this kind of transition to a nonreversible random system using as our example an ensemble of classical atoms in a specified volume. We treat the atomic gas as a collection of particles that move on straight trajectories except when they collide with other atoms. This means that each collision induces a sharp change in the velocities of the colliding atoms, both in magnitude and direction. We assume the region of strong interatomic interaction as small compared to a typical length of the collision-free segments. Thus, we have a gas of classical atoms moving freely but the rare collisions between atoms leads to variation of their trajectories. Let us follow the trajectory of a test atom and introduce a small random force that changes this trajectory. It will be shown that the Poincaré instability makes this trajectory random after several collisions.

Let a test classical atom move along a certain trajectory in a gas until it collides with other atoms with some mean frequency and impact parameters ρ that turn the trajectory of the test atom by certain angles. Let us introduce a small random force that leads to a displacement $\delta\rho$ in the impact parameter of first collision. According to the Poincaré instability, this uncertainty in the impact parameter increases in further collisions. Indeed, a variation of the scattering angle in the first collision is $\delta\theta_1 \sim \delta\rho/\rho_o$, where ρ_o is a typical size of the region of atomic interaction where the interaction potential between atoms is comparable with their kinetic energy. From this we find the test atom's trajectory displacement before the second collision and, respectively, the variation of the impact parameter for the second collision $\Delta\rho_1 \sim \lambda\delta\theta_1 \sim \delta\rho\lambda/\rho_o$, where $\lambda$is the mean free path of a test atom, and the variation of the atom velocity is $\Delta v_1 \sim v\delta\theta_1 \sim \delta\rho/\rho_o$. This leads to the displacement of the scattering angle in the second collision to be $\delta\theta_2 \sim \Delta\rho_1/\rho_o \sim \delta\rho\lambda/\rho_o^2$. From this we find the displacement of the particle trajectory after the second collision is $\Delta\rho_2 \sim \lambda\delta\theta_2 \sim \delta\rho\lambda^2/\rho_o^2$ and for the velocity deviation after the second collision, $\Delta v_2 \sim v\delta\theta_2 \sim \delta\rho\lambda/\rho_o^2$. Continuing this operation, we obtain for the net deviation after k collisions

$$\Delta\rho_k \sim \delta\rho\left(\frac{\lambda}{\rho_o}\right)^k, \quad \Delta v_k \sim v\frac{\delta\rho}{\lambda}\left(\frac{\lambda}{\rho_o}\right)^k \tag{4.1}$$

Evidently, randomization proceeds after k collisions if $\Delta\rho_k \sim \rho_o$. From this we find the number of collisions for randomization of this system is

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$$k = \frac{\ln \frac{\lambda}{\delta\rho}}{\ln \frac{\lambda}{\rho_o}} \tag{4.2}$$

and a typical randomization time is $t_r = k\lambda/v$ with

$$t_r = \frac{\lambda}{v} \frac{\ln \frac{\lambda}{\delta\rho}}{\ln \frac{\lambda}{\rho_o}} \tag{4.3}$$

These results require that the following criterion be satisfied:

$$\delta\rho \ll \rho_o \ll \lambda \tag{4.4}$$

To illustrate, we take $\delta\rho/\rho_o = 10^{-8}$ and $\lambda/\rho_o = 100$, and obtain $k = 5$. Because of the weak (logarithmic) dependence of the number of collisions on the problem's parameters, we find that randomization of our model gaseous atomic system occurs through several collisions of a test atom with others.

Thus, according to the Poincaré instability criterion, small uncertainties are amplified in a system of interacting atoms. Although we have demonstrated this for a gaseous atomic system, it is clear that fast randomization is inevitable for almost any ensemble of bound atoms because this phenomenon results from atomic interactions for which we have imperfect knowledge. An exception could be a perfectly harmonic lattice of atoms with no other interactions, effectively an idealized case which implicitly supposed complete knowledge.

Of course, this kind of randomization is greater for an atomic quantum system, whose states are represented as combination of wave packets, and randomization results partially by shifts of phases for these wave packets as they interact. In other words, randomization is inevitably a fast process in a system whose atomic eigenstates interfere, leading to significant transitions among them due to the interatomic interactions. One can see that randomization is typical for atomic systems, even for systems of just a few atoms. Therefore we describe clusters using statistical methods including thermodynamic parameters, but do not invoke temporal reversibility in our descriptions.

Note that in our analysis we have not specified the size of the clusters; randomization is typical for any cluster sizes. In reality, a tacit assumption is made that a cluster is characterized by a continuous spectrum and that transitions between its states proceed efficiently.

5. Cluster entropy near a phase transition

Thus, treating clusters of several atoms by statistical and thermodynamic methods is justified if done with full realization of the extent to which tacit assumptions based on a very large *system size* must be avoided. Of course the notion of a large-size ensemble is justified however small the individual systems are. As an example of such a description, here we evaluate the entropy of an isolated cluster near the solid–liquid phase transition where both aggregate states coexist in thermodynamic equilibrium [32,33]. This dynamic coexistence of phases means that during some time the cluster resides in one phase-like state, and the rest of the time, it is in the other state. These conditions correspond to the following relations between typical times

$$\tau_{eq} \ll \tau_{ag} \ll \tau \ll \tau_{th}, \tag{5.1}$$

where $\tau_{eq} \sim 1/\omega_D$ is the time for establishing (vibrational) thermodynamic equilibrium within the cluster, ω_D is the Debye frequency, $\sim 10^{-14}$ s at room temperature, τ_{ag} is a typical dwell time of the cluster in each aggregate state, τ is a typical observaton time of the cluster, and τ_{th} is a typical time for exchange of energy between the cluster and its environment. Of course an isolated cluster does not exchange energy with an environment, i.e. we conceive of it as a member of a microcanonical ensemble. Because the time scale criterion (5.1) ensures that thermodynamic equilibrium is established within each aggregate state, the solid and liquid, in a microcanonical ensemble, these states are characterized by different temperatures, T_{sol} and T_{liq}. In particular, using the kinetic definition of the temperature of atoms T through the total kinetic energy of atoms K, i.e. $K = (3N - 6)T$, and approximating the atomic motion as a sum of harmonic oscillators, we have

$$T_{sol} - T_{liq} = \frac{\Delta E}{3N - 6}, \tag{5.2}$$

where N is the number of atoms in the cluster, and ΔE is the energy of the phase transition.

Using the two-state approach for cluster aggregate states [34], which extends the thermodynamic concept of the aggregate states from bulk to clusters, the probabilities of cluster to be in the solid w_{sol} and liquid w_{liq} states, with $K_{eq} = w_{sol}/w_{liq}$, are

$$w_{sol} = \frac{1}{1 + K_{eq}}, \quad w_{liq} = \frac{K_{eq}}{1 + K_{eq}}, \tag{5.3}$$

where $K_{eq} = \exp[-N\Delta\mu/kT]$ is the equilibrium constant for the solid and liquid state. Let us consider a cluster as a thermodynamic system. We then characterize it by some temperature T which corresponds to an average over a long time τ in accordance with (5.1) during which the cluster changes its aggregate state many times. If we connect this temperature with the average kinetic energy of the atoms, we obtain an effective overall value

$$T = w_{sol}T_{sol} + w_{liq}T_{liq} \tag{5.4}$$

There are, of course, two different definitions for entropy, those from thermodynamics and from statistical physics, and we compare them. In considering a cluster as a thermodynamic object, we ignore the contribution to the enthalpy from the mechanical energy because for inert gases at their triple point this contribution is only 2×10^{-4} [35]. This gives the connection between the internal cluster energy E and its entropy S

$$dS = \frac{dE}{T} \tag{5.5}$$

Evidently, one can write the same relation for each aggregate state of the cluster:

$$\frac{1}{T_{sol}} = \frac{dS_{sol}}{dE}, \quad \frac{1}{T_{liq}} = \frac{dS_{liq}}{dE} \tag{5.6}$$

Taking the cluster entropy S as an additive function of entropies of the solid S_{sol} and liquid S_{liq} states, we have

$$S = w_{sol}S_{sol} + w_{liq}S_{liq}, \tag{5.7}$$

and from formulas (5.5) and (5.6) we get for the effective cluster temperature

$$\frac{1}{T} = \frac{w_{sol}}{T_{sol}} + \frac{w_{liq}}{T_{liq}} \tag{5.8}$$

One can see a contradiction between formulas (5.4) and (5.8) although they do give the same effective thermodynamic temperature if the difference between the solid and liquid temperatures is small.

One can remove this contradiction, if we include in formula (5.6) the entropy contribution due to the configurational transition [36]. This example shows that as a system consisting of a finite number atoms, a cluster has some specific properties associated with its small finite size. In particular, we also point out that, in a microcanonical ensemble, a cluster's heat capacity may be negative in the vicinity of the phase transition [37,38]. Hence, we have another illustration of why it is necessary to be careful in application the methods of macrophysics to clusters and other small systems.

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6. Conclusions

One way to think of the bridge between macro and micro approaches is to determine the size of systems below which a macro description of some chosen property is inadequate or inaccurate. What that boundary size is, depends very much on the property and the substance, but the basic approach may be applied to a variety of phenomena. The boundary for breakdown of the Gibbs Phase Rule is the one example for which we have an explicit answer. We can see a pathway to getting an answer to the boundary for clusters of metal atoms to become metallic. Other phenomena, the onset of monotonic behavior of properties with size, the establishment of the bulk geometric structure as that of finite systems, and of the electronic structure characteristic of the bulk system, seem to pose greater challenges, but do not appear insoluble at this time. One can add to this that although a cluster, being a system of a finite number of atoms becomes random in a rather brief time, nevertheless, the specifics of clusters as microsystems requires caution in using macro methods for their analysis.

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