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Bridging the macro and micro

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ABSTRACT

A long-standing but rarely addressed challenge to physical sciences is reconciling or bridging between the macroscopic approach, exemplified by thermodynamics, continuum and infinite models, and the microscopic approach built from individual elements. Here, we show an approach to finding the boundary size region below which a microscopic approach is mandatory, and above which, one can use the macroscopic approach's tools. We illustrate how to estimate this boundary size using examples from atomic clusters. The first reviews the boundary size above which the Gibbs Phase Rule is valid, but below, is inapplicable. Then we show how to find boundary sizes for other properties.

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1. Introduction

Much of physical science uses a macroscopic approach to express concepts and relationships, an approach whose variables are collective, involving average properties of systems such as temperature, pressure and mean energy. At the same time, we use a microscopic approach to deal with atomistic phenomena, for which the variables are typically properties of individual particles and their explicit interactions. Occasionally, we encounter a situation in which some well-known and presumably well-understood macroscopic kind of behavior seems to be violated at the microscopic level. Typically, this is a consequence of the macroscopic behavior being due in some way to the very large number of elementary, microscopic components that make up the macro system. The deviation from our macro expectations are a result of the fact that the small system that seems to violate our macro-based concepts simply shows detectable variability that disappears when the number of component elements is very large. One long-standing but usually tacit challenge for dealing with this is finding a way to reconcile the macro and micro approaches by finding where we are justified in making the crossover. At what approximate size can we begin to rely on a macro approach to describe some phenomenon?

Here, we address this question at two levels. First, we examine one specific phenomenon for which we have been able to develop an explicit solution. This is the melting–freezing behavior of atomic clusters and, of course, of bulk matter. Then we go on to provide a general formulation that can be applied to determining the crossover for other phenomena, yet to be explored explicitly.

Of course the boundary between the micro and macro is not a precise, sharp one. We shall introduce a precise transition size for purposes of illustrating the method, but the appropriate criterion in any particular case must depend on the specific experimental probe and its capabilities to detect deviations from the macro expectation for that particular phenomenon. It will be apparent how one would set the criterion for observability of micro behavior, when we treat the explicit example in the next section.

2. A specific illustration: melting and freezing

Small atomic clusters display a kind of behavior in their melting and freezing that came as a dramatic surprise when it was first observed in simulations [1–8], and was eventually confirmed by experiment [9]. Specifically, these systems simply do not obey the Gibbs Phase Rule, relating the number of degrees of freedom, f, to the number of components, c, and the number of coexisting phases, p: $f = c - p + 2$. The first examples, simulated clusters of argon atoms, display bands of temperature and pressure in which solid and liquid phases coexist in dynamic equilibrium, much like chemical isomers can coexist. The Gibbs Phase Rule, perhaps the simplest mathematical relation in all of physical science, is part of the basic doctrine of thermodynamics; how can it be that these simple systems can violate it? Actually, the violation goes even further; small clusters can exhibit coexistence of more than two phases in dynamic equilibrium, over ranges of temperature and pressure!

The explanation and reconciliation with fundamental thermodynamics of this apparent violation is actually straightforward and even 'forehead-slapping' obvious when one looks at the problem in a suitable way. One can write the equilibrium between two forms of any substance in terms of a traditional equilibrium constant, K_{eq}, although it is hardly customary to do that for solid and

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liquid phases. Nonetheless it is the key to understanding how small clusters behave. We can write

$$K_{eq} = [liquid]/[solid] = \exp(-\Delta G/kT) \tag{1}$$

where ΔG is the difference between the Gibbs free energies (at constant temperature T and pressure p). But $\Delta G = n\Delta\mu$, where n is the number of atomic particles in the system and μ is the chemical potential, *per atom*, in the system. Suppose we are dealing with a small macroscopic system of, say, 10^{20} particles.

And suppose that we consider a system very, very slightly away from the condition of equal free energy, the condition at which the macroscopic solid and liquid exhibit traditional equilibrium. To be explicit, suppose that $\Delta\mu/kT$ is $\pm 10^{-10}$. Then, at this condition, a tiny bit away from equilibrium, $K_{eq} = \exp(\pm 10^{10})$. This obviously tells us that the unfavored phase is present is such a tiny amount that it would be totally undetectable.

Now let us examine the same expression but with a very few atomic particles, say 10. Then since $\Delta G = 10\Delta\mu$, the chemical potential difference $\Delta\mu$ can easily be a moderate, nonzero fraction of kT so that K_{eq} can be a number of order 1, well away from the point of equal free energies for the two phases. This means that the two forms, favored and unfavored, can be present *in observable amounts in thermal equilibrium* under conditions of unequal free energies. Thus we are led to the realization that, while basic thermodynamics retains its validity for ensembles in equilibrium, at least one of the widely accepted consequences of that general theory is really not as general as the basic theory, but rather, is valid only when we deal with large numbers of particles.

The same reasoning holds also for coexistence of multiple phases. If the free energy differences among those phases are nonzero but relatively small, then the phases can coexist in thermodynamic equilibrium over a range of temperature and pressure. Examples are clusters of roughly 50 argon atoms, which can exhibit solid, liquid and surface-melted forms in coexistence [10].

That small systems do not conform to the Gibbs Phase Rule, and that this striking behavior has a simple explanation completely consistent with the fundamentals of thermodynamics, stimulates a new question, which, as we shall see, leads to a broad, very general counterpart. Here, we are led to ask, 'How can we determine *the boundary size range* below which systems can be expected to violate the Phase Rule, and above which, they should obey it?' This turns out to be a question we can address in a very straightforward way.

There is, however, an element of arbitrariness in the precise value we determine. This is simply because there is an arbitrariness in the minimum fraction of the minority phase that we consider observable. Hence, to apply this analytic tool to guide any specific experimental investigation, one should know what that minimum observable fraction is. Here, to illustrate and apply the approach, we set that fraction at 10%, but it is completely straightforward to choose any other fraction and redo the calculation.

The question we ask now becomes this: at what values of N, the number of particles comprising the system, does the equilibrium constant (1) take the values of 10 and 0.1? Or, rephrased, at what values of N is $N\Delta\mu/kT$ equal to ln(10) and ln(0.1)? More specifically, for what N does the detectable coexistence range $\delta F = N\Delta\mu/kT$ lie between -2.3 and $+2.3$? (We can change those limits to fit whatever experiments can show.) [11,12].

Expressing the free energy in units of kT, we have $\Delta F = \Delta E/T - \Delta S$. We can write this as $(\partial F/\partial T)\delta T = \Delta E_m \delta T/T_m^2$ where the subscript 'm' indicates the values at the melting point. We assume that ΔE_m and ΔS_m are nearly constant within the range of interest. But $\Delta E_m/T_m = \Delta S_m$, so $\delta T/T_m = \delta F/\Delta S_m$ or, the quantity we want, δT, is $T_m \delta F/\Delta S_m$ and we have arbitrarily chosen 4.6 as our acceptable value for δF; we can round this off to say $\delta T = 5T_m/\Delta S_m$. Hence we see that

the observable range of coexistence depends only on the melting temperature and, inversely, on the entropy change in the phase transition. Simulations enable us to estimate the entropy change per particle that occurs with melting. Thus we have arrived at a criterion for the system size that is the effective boundary between bulk and small-system behavior for the coexistence of phases.

Applying this criterion to rare gas clusters, we find that for a cluster of 100 argon atoms, for which the entropy change on melting is large, δT is approximately 0.1 K, so we can expect bulk-like behavior and conformity to the Gibbs Phase Rule for clusters of about 100 or more particles. However metal clusters have significantly smaller entropy changes, per atom, on melting, so their observable ranges of bands of coexisting phases extends to several hundred atoms. Positively charged sodium clusters of 139 atoms were the first to be observed exhibiting this coexistence [9].

3. Generalizing to other properties

Now we generalize, in order to indicate a procedure by which the particle size for 'small-to-large' or 'micro-to-macro' can be estimated. The essence, like that in the melting-freezing example above, is determining the size range in which the free energy difference between favored and unfavored forms is small enough to make the fraction of unfavorable form detectable. We may think of such properties as the coexistence of multiple structures for small systems [13], or regions of negative heat capacity for microcanonical ensembles [14–16], or occurrence of a form of bonding that only small systems exhibit, as in the high-melting clusters of gallium and tin [17,18]. The gallium clusters, for example, show wide variations in melting behavior with size, very different from the monotonic size dependence that classical models would indicate [19]. The cause of this behavior in terms of electronic behavior is still an unsettled issue [20,21].

The essence of a general approach to 'finding the boundary' is identifying the dominant specific property that reveals how small systems deviate from the expected behavior of macroscopic systems. In the case of the multiplicity of structures, especially non-lattice structures, that small systems frequently exhibit, it is simply the energetic accessibility of those stable structures. This tells us that we need to determine the size dependence of the free energy or chemical potential for the form or behavior pattern that we are trying to investigate. In the case of the coexistence of solid and liquid forms, or of multiple phases, we could assume that the principle contribution to the variation in the chemical potential is that of the entropy. To determine the approximate size at which the bulk structure must dominate, the energies of the competing structures provide the dominant size-dependent properties, since the entropies of the solids are necessarily relatively similar and are not likely to be very size-dependent.

Thus, the general approach consists of establishing a range of values of the appropriate free energy within which the minority phase would be present in detectable amounts. In the previous example, our range was $-2.3 \leqslant \Delta G/kT \leqslant +2.3$. Then we simply need to write $\Delta G/kT = N\Delta\mu/kT$ and estimate the N-dependence of $\Delta\mu$. Suppose we consider the structural problem in terms of the observable coexistence of multiple structures. Then the question is one of the size dependence of the energy gap $\Delta\varepsilon$ between the lowest-energy structure and the next higher one. Or we may want to know the approximate size at which the bulk crystalline structure becomes the most stable, or at which it is present in detectable amounts. That requires computing the size dependence of the energy of clusters having the same structure as the bulk, and comparing that with the energy of the most stable structure. When $N\Delta\mu/kT$ or, taking all the structural variation as energetic, $N\Delta\varepsilon/kT$,

is small enough to fall just within that range ±2.3, we have found the value of N that is, in effect, the boundary size.

At present, we do not yet have a clear enough understanding of the cause of the anomalously high melting temperatures of gallium and tin clusters, so we cannot yet carry out an *ab initio* estimation of the cluster size at which bulk behavior begins. However it may be possible from measurements of the latent heats of melting and the corresponding free energy changes to find empirically the size dependence of the free energy change for these systems, and, from those data, to estimate the maximum size at which the anomalously high melting temperature occurs.

We must recognize that the transition from microparticles to macroparticles takes place at different particle sizes depending on the property under consideration. Let us consider some examples of this. An important, characteristic property of clusters, i.e. systems of a finite number of bound atoms, is that clusters have properties associated with magic numbers [22]. Magic numbers correspond either to completed, closed-shell structures of atoms or to closed electron shells. Here, we focus on structural magic numbers. Typically, a cluster with a magic number of atoms has a higher binding energy of a surface atom, a higher ionization potential, and a higher electron affinity than clusters composed of one more or fewer atoms. For macroscopic particles magic numbers are irrelevant because of variation of configurations of surface atoms due to fluctuations and because their surface energy is a small fraction of their total binding energy. In experiments, magic numbers of clusters are observed up to 20000 atoms [23]. One more parameter which characterizes a macroscopic particle is its high ratio of the number of surface atoms to the total number of atoms; moreover the surface atoms typically make significant contributions to some cluster parameters, such as entropy. The role of surface atoms in relatively small clusters may influence their structure and properties. Therefore transitions to the cluster size above which the cluster behaves in the same way as a macroscopic system may be considered as the transition to the macroparticle. For example, solid clusters with Lennard–Jones interaction potentials between atoms or with another interaction potential for which interaction between nearest atoms dominates largely have icosahedral structures up to sizes of hundreds of atoms. Solid clusters of inert gases follow this relation, and they have the icosahedral structures for cluster sizes into the hundreds [24]. The corresponding macroscopic systems, including condensed inert gases, have face-centered cubic structures [25]. The transition between these structures at zero temperature proceeds if the number of cluster atoms is thousands [26]. It is possible in principle to compute estimates of the free energies of various locally-stable geometric structures, including both the lattice structure characteristic of the bulk and the more stable other structures. Because the transition to bulk structures seems to take place at such large cluster sizes, this could be a burdensome computation, but is within current computing capabilities.

Still another property showing a micro-to-macro change is sometimes the electronic structure. Even if a macroscopic system of atoms behaves as a metal, small clusters of the same material may be dielectrics. In particle, this takes place for mercury, for which a cluster takes on metallic properties if the number of its atoms exceeds 400 [27]. Determining the micro–macro boundary for such systems will require computations of electronic structures for ground and low-lying excited states, to find the cluster size at which a zero-gap conduction band state takes on the lowest energy.

Thus, study of various cluster properties gives some experience about transition from microparticle to macroparticle that takes place at different cluster sizes depending on the property under consideration. Moreover, in some range of sizes, a cluster belongs to the class of microscopic systems for some properties and to that of macroscopic systems for other properties. For example, clusters consisting of tens or hundreds of atoms, which are microscopic systems of atoms according to their structure in the solid state, are nevertheless subject to thermodynamic laws and their ensembles can be described by such parameters as temperature, entropy etc.

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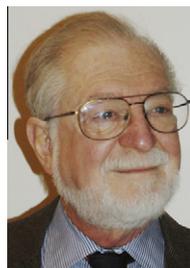
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