

## AGRÉGATS COMME PRÉCURSEURS DES NANO-OBJETS CLUSTERS AS PRECURSORS OF NANO-OBJECTS

# The amazing phases of small systems

R. Stephen Berry

The University of Chicago, Department of Chemistry, Chicago, IL 60637, USA

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### Abstract

Small systems, notably clusters of tens or hundreds of atoms or molecules, exhibit forms almost precisely analogous to the phases of bulk systems. However their small sizes make these systems behave in ways quite different from their bulk counterparts. These differences can be elucidated and related to the behavior of bulk systems. Understanding these relationships gives us new insights into the traditional, classical bulk phase transitions, and shows us some unique properties of phases and phase equilibrium of nanoscale systems. *To cite this article: R.S. Berry, C. R. Physique 3 (2002) 319–326.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

nanoscale systems / phase equilibrium

### Les phases surprenantes des petits systèmes

### Résumé

Les petits systèmes, et plus particulièrement les agrégats de quelques dizaines ou de quelques centaines d'atomes ou de molécules, présentent des formes sensiblement proches des celles que l'on rencontre dans les systèmes macroscopiques. Cependant leur petite taille confèrent à ces systèmes des comportements tout à fait différents de ceux du solide massif correspondant. Ces différences peuvent être comprises et reliées au comportement de ce solide. La compréhension de ces liens donne un nouvel éclairage sur les traditionnelles transitions de phase dans les solides et montre bien les propriétés uniques des phases et de l'équilibre entre phases dans ces systèmes nanoscopiques. *Pour citer cet article : R.S. Berry, C. R. Physique 3 (2002) 319–326.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

systèmes nanoscopiques / équilibre entre phases

## 1. Introduction

Phases of bulk matter became a central subject of thermodynamics during the nineteenth century, perhaps culminating with the famous Phase Rule of J.W. Gibbs: the number  $f$  of degrees of (macroscopic) degrees of freedom for a system in equilibrium is determined by the number  $c$  of components and the number  $p$  of phases that are present in equilibrium:  $f = c - p + 2$ , where the deepest part of the insight in this equation is the number 2! Each component provides a variable, and each phase requires its own equation of state, which

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*E-mail address:* berry@uchicago.edu (R.S. Berry).

acts as a constraint. Hence a pure substance, with  $c = 1$ , may exist in states controlled by two independent variables, e.g. pressure and temperature, but if we require two phases to be in equilibrium, then only one of those variables can be independent. We can thus represent the region of stability of a single phase as a region in a plane, e.g. in  $p$ – $T$  space, but the region of coexistence of two phases must be only a curve in that space. The phases of bulk matter are homogeneous, macroscopic regions with uniform physical properties satisfying an equation of state. Moreover they are essentially static, permanent constituents of the overall system, so long as the conditions are constant. The description of bulk phases in equilibrium can be said to be one of the completed parts of classical thermodynamics. (The kinetics of nucleation and changes of phase are, of course, only partly understood [1,2].)

Here we review a closely related but remarkably different kind of phase behavior, that of very small systems, nanoscale particles composed of tens, hundreds or thousands of atoms or molecules. We shall see that many of these systems exhibit forms we can readily identify with well-known phases of bulk matter, but that they undergo changes from one phase to another in ways different from those described by the Gibbs phase rule. Small particles can exhibit two or more phases in equilibrium over ranges of temperature and pressure; distinctions between first-order and second-order transitions blur; and small systems can exhibit phases—in equilibrium—that cannot possibly be observed for macroscopic systems. We shall see how all these phenomena come about and how they are closely related to phase behavior of bulk matter. (A recent review related to this work is available [3], and contains extensive references to original material.)

## 2. Dynamics and thermodynamics of phase equilibrium

The essential condition underlying *local* stability of any form of matter, however small or large its stage of aggregation, is the occurrence of a local minimum in the free energy, for fixed external variables, usually intensive, with respect to some suitable order parameter. A local minimum not only assures the stability of the global minimum state, that state with the lowest free energy for those conditions; it also assures the possibility of other kinds of stability, such as the metastability of superheated or supercooled (undercooled) water. This condition applies for stability of forms of clusters just as it does for bulk matter.

The other essential relationship on which we call is the one that determines the relative proportions of locally stable forms with different free energies. This is the ubiquitous relationship that governs the relative amounts of different chemical isomers  $A$  and  $B$ , for example, the expression for the equilibrium constant  $K(T)$ :  $K(T) = [A]/[B] = \exp(-\Delta F(T)/k_B T)$ , where  $\Delta F(T)$  is the difference in free energy of species  $A$  and  $B$  at temperature  $T$ . The free energy can be written in terms of the mean chemical potential difference  $\Delta\mu(T)$  and the number  $N$  of particles in the system,  $\Delta F(T) = N\Delta\mu(T)$ .

Suppose that *phases*  $A$  and  $B$  are locally stable forms of a macroscopic sample of material. Then in an *ensemble* of such samples, the ratio one would observe of the two forms would be precisely  $[A]/[B] = \exp(-N\Delta\mu(T)/k_B T)$ . Let us measure the free energy and mean chemical potential in units of  $k_B T$ . Traditional thermodynamics tells us that these two phases may coexist in equilibrium only when  $\Delta\mu = 0$ . Why? Suppose that the difference  $\Delta\mu$  is nonzero but very tiny in these units, e.g.  $\pm 10^{-10}$ . This might suggest that we could find observable amounts of both the more stable, favored form and the unfavored form in the ensemble. However we must remember that  $N$  is a number of order  $10^{20}$ , so that the equilibrium ratio  $[A]/[B]$  is of order  $\exp(\pm 10^{10})$ ! Even a tiny difference in free energies is enough to make the favored phase so much more favored than the unfavored phase that the latter is simply unobservable. Hence the only conditions under which we can expect to see phase coexistence is the condition of equal chemical potentials.

When we deal with systems of tens, hundreds or thousands of particles, the situation is completely different. There, with  $N$  of order 10 to 1000 or even 100 000, the equilibrium ratio of the two species may well lie within a range of perhaps  $10^{-4}$  to  $10^4$  over a temperature range of a controllable fraction of a degree, or even over several degrees  $K$ , at a fixed pressure. This means that we can expect to observe both phases in our ensemble of *nanoscale* particles over a range of temperatures, not just at a single temperature!

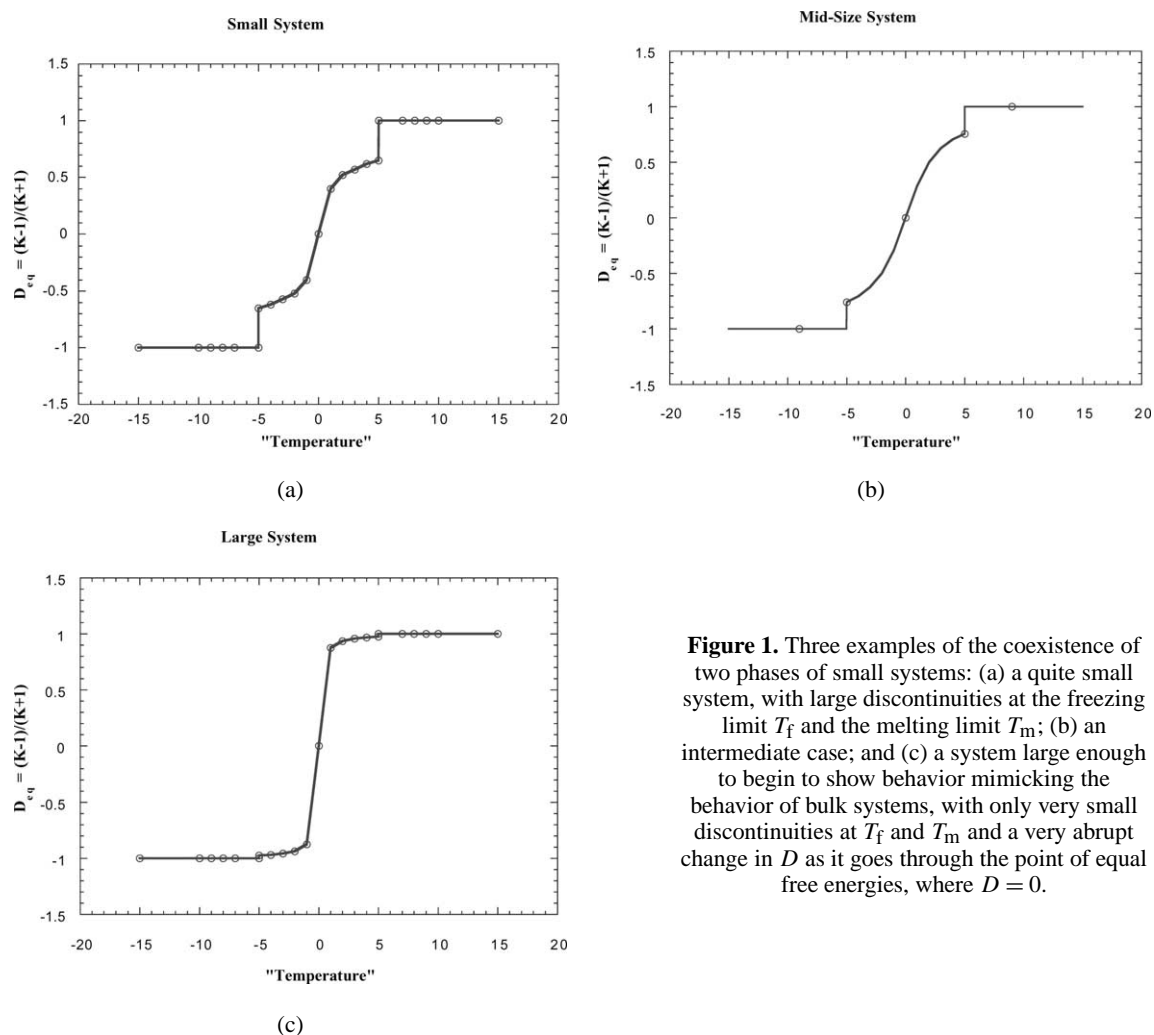
What sets the limits within which such coexistence is possible? It is simply the range within which the first condition, of the occurrence of a local minimum in the free energy for the phase. Consider, for example, the situation of a single solid phase *A* and a liquid phase *B*. At sufficiently low temperatures, the system has too low a mean energy to have any minimum in the free energy except that determined by the low enthalpy of the solid phase, when regarded as a function of the order parameter  $\gamma$  measuring the rigidity of the system. However, the density of states of the higher-energy liquid form increases with energy considerably faster than the density of solid-like states. This density of states naturally contributes to the entropy of the liquid form, so that at some temperature  $T_f$ , which we call the ‘freezing limit,’ a point appears in the curve of  $F(T, \gamma)$  versus  $\gamma$  (at fixed  $T$ , of course) where the slope is zero and  $\gamma$  is well in the liquid range. At temperatures above  $T_f$ , the curve of  $F(T, \gamma)$  has two minima, not just one. These two minima persist up to a temperature  $T_m$ , the ‘melting limit,’ at which the minimum in the solid-like region of  $\gamma$  turns into a single point where the slope is zero. Above  $T_m$ , the free energy has only a single minimum, in the liquid range, so only the liquid phase is stable there. Coexistence in equilibrium occurs at all temperatures between  $T_f$  and  $T_m$ . These two temperatures are of course functions of pressure, but the coexistence is possible so long as the two minima appear in the free energy. Incidentally, because of the difference between the behavior of bulk and small systems, and the long tradition and vast literature on phase transformations of bulk matter, we choose to reserve the term ‘phase transition’ for bulk matter, and the term ‘phase change’ for the more general behavior of small systems as well as bulk phase transitions. The way size affects the coexistence of two phases has been discussed by Wales and Doye [4].

The behavior of systems of three sizes—a small number of particles per cluster, an intermediate number and a large number—are illustrated schematically in Fig. 1, (a)–(c). These are expressed in terms not of the equilibrium ratio  $K = [A]/[B]$ , which may vary between zero and infinity, but in terms of a more convenient transformation of  $K$ . We define the distribution  $D = (K - 1)/(K + 1) = ([A] - [B])/([A] + [B])$ , the fractional difference between the two concentrations. For example, if *A* is the liquid phase and *B* is a solid phase, then  $D$  is the amount of liquid minus the amount of solid, divided by the total amount of material. Consequently the distribution  $D$  varies from  $-1$  for a system consisting only of phase *B* to  $+1$  to a phase consisting entirely of phase *A*. The figures show that below  $T_f$ ,  $D = -1$  corresponding to the system being entirely solid; likewise, above  $T_m$ ,  $D = +1$ , corresponding to a pure liquid. At the transition temperatures, we can expect discontinuities in  $D$ . However, these discontinuities become smaller and smaller as the number of particles comprising the clusters increases.

For large clusters, above the discontinuity at  $T_f$  and below that at  $T_m$ , the values of  $D$  remain very close to  $-1$  and  $+1$ , respectively, up to very close to the point where  $D = 0$ . There, the change of value of  $D$  becomes more and more abrupt as the size of the clusters increases. For macroscopic systems, that (continuous but abrupt) change is, in effect, the discontinuity we associate with a first-order phase transition.

It is possible to estimate the conditions for solid–liquid phase changes and phase coexistence of clusters, using two essential and fairly general properties of clusters. Both are rooted in examining the configurational behavior associated with these two forms. In the solid, most particles have the maximum number of nearest neighbors associated with the solid’s structure. In the liquid phase, there are defects that reduce the number of neighbors and hence reduce the binding energy. At the same time, the density of configurational states with defects increases with the number of defects. Thus the binding energy decreases as the configurational entropy increases. Combinatorics provides the tool to estimate these, and hence to provide an approximate description of the phase behavior of clusters [5].

The difference between small systems and bulk matter is simply a consequence of the magnitude of  $N$ . But there are other important consequences of this difference, beyond just the existence of finite bands of conditions for coexistence of two phases of small systems, instead of a single, sharp curve. Because only hundreds or thousands of particles interact to determine the phase of a small system, the time scale for its ergodic exploration of its available phase space is vastly shorter than the time scale for the macroscopic system to do its counterpart exploration [6,7]. The latter time scales are so long that we consider phases of bulk matter as static, permanent forms; clusters of tens or hundreds of particles may pass from one phase to



**Figure 1.** Three examples of the coexistence of two phases of small systems: (a) a quite small system, with large discontinuities at the freezing limit  $T_f$  and the melting limit  $T_m$ ; (b) an intermediate case; and (c) a system large enough to begin to show behavior mimicking the behavior of bulk systems, with only very small discontinuities at  $T_f$  and  $T_m$  and a very abrupt change in  $D$  as it goes through the point of equal free energies, where  $D = 0$ .

another on a time scale of picoseconds or hundreds of picoseconds, just as molecules of tens or hundreds of atoms can pass from one isomeric form to another on such a time scale. In fact, we see here *the loss of the distinction between components and phases* when we consider matter at the nanoscale. This loss of distinction means that the Gibbs Phase Rule loses its significance for particles so small that components and phases can transform themselves on roughly the same time scale. One of the fascinating open questions regarding the phases of nanoscale matter is “At approximately what size of particle does a phase of a nanoscale particle endure long enough to make it significantly more persistent and ‘permanent’ than an isomerizing component?” This is very likely the kind of question that can only be answered by specifying the kind of observation one would use, and the time scale for such a measurement.

Because small clusters do pass rapidly between phases, it is important to recognize that what we observe of their behavior may depend very much on the time scale of the observation we use. If our measurement is slow, e.g. requiring hundreds of nanoseconds, and the passage between phases of our clusters occurs on a scale of hundreds of picoseconds, we can observe only the average behavior of our ensemble or our single system moving through time. If, however, our observation takes only tens of picoseconds, then we can observe distinct phases. That is, we can observe distinct phases provided another time-scale consideration

is met. The systems must remain in each phase long enough to develop the properties we associate with that phase in equilibrium properties such as a well-defined mean square displacement as a function of time (whose slope is essentially the diffusion coefficient), a well-defined relative root-mean-square deviation of the particle displacements or interparticle distances (the ‘Lindemann criterion’), a well-defined pair distribution function, the properties we use to determine existence of a specific phase. Many clusters, even as small as six or seven particles, do appear, from simulations, to show such persistence. However other clusters, typically in a size range of tens of particles, pass too rapidly between a solid-like region of their multidimensional potential surface and a liquid-like region on the same surface to develop those equilibrium properties. This behavior is very dependent on the specific number of particles comprising the cluster, and is not simply monotonic with  $N$ . For example, Ar<sub>7</sub>, Ar<sub>13</sub> and Ar<sub>19</sub> show persistent solid and liquid forms, while Ar<sub>15</sub> and Ar<sub>17</sub> pass too rapidly between solid and liquid to develop those equilibrium properties [8].

Still another important difference between phase behavior of bulk matter and small systems is a consequence of the coexistence phenomenon and the loss of distinction between component and phase. There is nothing that prevents the free energy of a small system (or a bulk system, for that matter) from having several local minima as a function of a single order parameter or of two or more order parameters. The influence of a very large  $N$  for bulk systems dictates that only the most favored of these phases is stable in observable amounts, unless the free energies of two phases are equal, as we have seen; that *three* phases (of a system of a single component) could have equal free energies can be expected only at a single point, the well-known *triple point*. Small systems, in contrast, with equilibrium concentration ratios lying in observable ranges over bands of temperature and pressure, may exhibit any number of coexisting phases in observable quantities [9]. There is nothing to prevent three or more phases of a homogeneous cluster from being present in observable quantities over some finite band of conditions. An example is the Ar<sub>55</sub> cluster, for which simulations predict that the solid phase, the liquid phase and an intermediate ‘surface-melted’ phase should all coexist over a narrow range of conditions. Just outside that range, on the low-temperature side, the solid and ‘surface-melted’ forms should coexist, and on the high-temperature side, the liquid and ‘surface-melted’ forms should coexist [10,11]. At still lower and higher temperatures, of course only the solid and liquid forms should be stable.

The last of the special phase properties of small systems that we point out here is the possibility for a phase of a nanoscale particle to be quite stable and observable in equilibrium and yet have no counterpart in bulk matter. This may happen for at least two reasons. One is simply the structural consideration; a system with a large fraction of its particles at its surface may have very different structures than one that is essentially infinite, insofar as so few of its particles are on its surface that they cannot affect the energetic considerations that determine what structure is stable. The best known examples of this behavior are of course the polyhedral rare gas clusters, mostly icosahedral or based on icosahedral structures, that are more stable than their close-packed counterparts that characterize the bulk solids of these substances. The other reason for a phase to be observable at the nanoscale but not in bulk matter is that it corresponds to a local minimum in the free energy that is *under no conditions the lowest free energy minimum* of the system. An ensemble of nanoscale particles may be prepared so that it exhibits such a phase in equilibrium but the same phase becomes so unfavored, thermodynamically, in bulk systems that it is simply never observable except as a metastable form, at best.

While researchers have found a variety of sufficient conditions for coexistence of two or more phases, only one demonstration of *necessary* conditions has been given [12]. As yet, there has been no statement of necessary and sufficient conditions.

### 3. Phase changes of differing order

Up to this point, the discussion has focused on phase changes that involve passage of a system from one locally stable state to another. Small systems accomplish this passage as a gradual shift in the equilibrium populations from one state to another, a passage we express as a shift of population from one local free

energy minimum to another. Bulk systems exhibit the same kind of shift but, as we have seen, the shift is extremely abrupt because of the leverage of a very large value of  $N$  on the equilibrium ratio. This is precisely the traditional first-order or discontinuous phase transition of bulk matter. Now we turn our attention to the small-system analogues of second-order or continuous phase transitions.

The classic second-order phase transition has no energy or enthalpy associated with the phase change but does have a discontinuity in the derivative of the energy with respect to the variable, usually intensive, whose change reveals the transition. Hence heat capacities show discontinuities at second-order transitions. A more microscopic characterization of second-order transitions associated them with a shift in the value of an order parameter that fixes the stable state of minimum free energy. The free energy of a system showing a continuous transition has only one minimum, but that minimum falls at different values of the order parameter on the two sides of the transition.

How do small systems behave as they go through their counterparts of second-order transitions? This question has not been studied nearly as much as the small-system counterparts of first-order transitions, and the subject is currently only partly explored. Structural phase changes of molecular clusters have now been investigated, but, for example, very little has been done on small-system analogues of magnetic transitions. Hence we shall concentrate here on what has been learned about structural phase changes and what the implications of these results are for second-order phase changes of small and bulk systems.

The most-studied structural phase changes of molecular clusters appear to be those of clusters of octahedral hexafluoride molecules, particularly of  $\text{SF}_6$  and  $\text{TeF}_6$ . These have been subjects of both experimental [13,14] and theoretical investigations [15–19]. The tellurium compound appeared for a long time to exhibit more complex phase behavior than did sulfur hexafluoride, but that picture has changed recently, and they do seem to be very similar, as one might expect.

At sufficiently high temperatures, of course, clusters of  $\text{TeF}_6$  molecules are liquid. Cooled, they form a solid with body-centered cubic structure, and with the molecular orientations completely disordered. Cooled further, the clusters take on a monoclinic structure with ordering of the molecular orientations around only one axis. Cooled still further, they remain monoclinic but change to a completely orientationally ordered phase. Experiments have demonstrated the existence of these three phases for clusters of various sizes, but the only information now available about phase changes and coexistence of these phases comes from simulations and analytic theory. Bulk  $\text{TeF}_6$  exhibits a transition thought to be second-order, between disordered body-centered cubic and ordered monoclinic.

Careful simulations, isoergic and isothermal molecular dynamics and isothermal Monte Carlo, have shown that there is a narrow band of temperature (at constant pressure of zero) in which the body-centered cubic and partially ordered monoclinic phases of clusters of 59 or more  $\text{TeF}_6$  molecules coexist. This is a demonstration that such a system behaves as the analogue of a *first-order* transition of the bulk material. However, the coexistence range for these two forms becomes narrower as the number of molecules in the cluster increases. These results indicate that the two minima of the free energy, corresponding to the two phases, either approach one another or that temperature bounds for existence of the intermediate phase approach each other, or both. In any case, here is an example of a system whose second-order bulk transition, if one exists, emerges from a small-system phase change that has the character of an analogue of a bulk first-order transition.

The lower-temperature phase change is different. There is no indication at all that the partially orientationally ordered and completely ordered phases ever coexist. This phase change appears to be one involving a single minimum in the free energy, with respect to the order parameter, and is thus precisely like its bulk second-order counterpart.

These two results imply that there are two kinds of bulk second-order phase transitions: those whose small-system counterparts have only a single minimum in free energy, and those whose small-system counterparts have two minima that converge as the clusters become larger. This also suggests that weak first-order transitions are like the second variety, but for them, the convergence is not complete, but that the two minima still just barely remain, when the cluster size reaches macroscopic dimensions.

In the case of the tellurium hexafluoride clusters, the distinction between the two kinds of phase changes has proved amenable to an analytic, symmetry-based interpretation [19]. The higher-temperature structural change involves a symmetry change that requires coupling vibrational and rotational motion, and a breaking of lattice symmetry. The lower-temperature phase change requires only couplings of molecular rotation, and no change of lattice symmetry.

Experiments with clusters of sulfur hexafluoride molecules have not shown the intermediate, partially ordered phase. However recent simulations have demonstrated the presence of this phase and its coexistence with the body-centered cubic phase. This coexistence lies only within a very narrow temperature band, a fraction of a degree K for clusters in the range of 50 to several hundred particles. The reason for such a fragile coexistence is that the intermolecular potential for SF<sub>6</sub> clusters is considerably weaker and softer than that for TeF<sub>6</sub> clusters.

An interesting set of questions still very open ask how the convergence of the two minima occur for phase changes such as the higher-temperature structural change of these molecular clusters. Do the minima converge at some finite  $N$ , or as  $N$  goes to infinity, or, perhaps, do they only come to some small finite separation as  $N$  becomes arbitrarily large? Or do all three cases occur with different systems? This is by no means a completed subject.

#### 4. Phase diagrams for small systems

A common and powerful device to represent the phase transitions and phase behavior of bulk materials has long been the phase diagram, essentially a map of the curves of coexistence of phases in a space of convenient variables, most commonly pressure  $p$  and temperature  $T$ . Another useful representation is the locus of extremal values of the partition function as a function of one or more order parameters and one thermodynamic variable, e.g. temperature, for a system at constant pressure. Both of these phase diagrams can be extended to small systems, at least to show some of the essential characteristics of these systems [3,10,11]. Here, we shall illustrate only the former, the extension of the conventional phase diagram.

The traditional phase diagram is inadequate for small systems because two or more phases may coexist over bands of temperature and pressure. Hence a phase diagram, even for just two coexisting phases of clusters, must reveal both the bounds of such a region, and the relative amounts of the two phases. This can be done by adding a single dimension to the traditional  $p$ – $T$  plot. One might think of using the equilibrium ratio  $K = [A]/[B]$ , but because this varies between zero and infinity, it is far more convenient to return to the distribution  $D = (K - 1)/(K + 1)$  that we introduced previously.

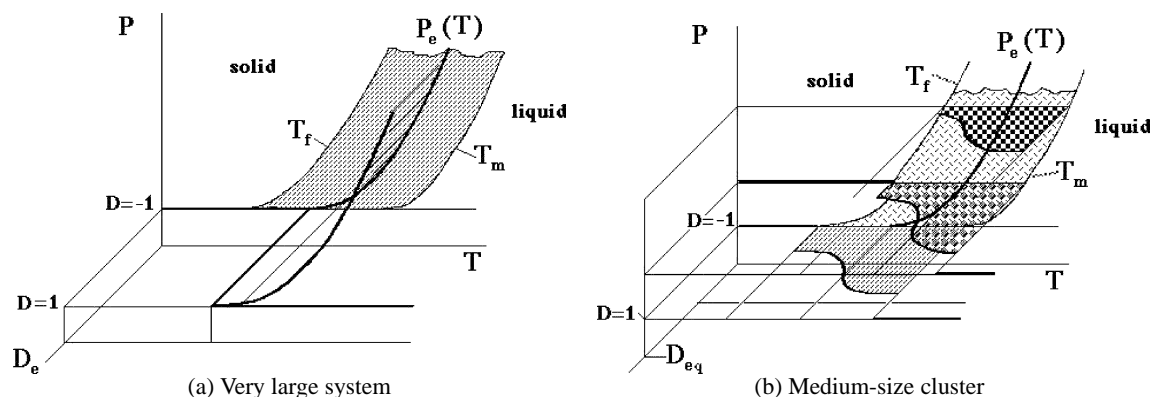
A large system can be described by a traditional phase diagram because every state on one side of the coexistence curve lies essentially in the plane of  $D = -1$  and every state on the other side of that curve lies in the plane of  $D = +1$ . The dimension associated with  $D$  is superfluous for such systems, as Fig. 2(a) indicates. However a smaller system exhibits intermediate values of  $D$  at temperatures between  $T_f$  and  $T_m$ . This situation is shown schematically in Fig. 2(b).

Actual phase diagrams for clusters are only now being constructed from simulations. We have yet to see libraries of these to guide our preparation of nanoscale materials, but we can expect that they will become as standard in that field as traditional phase diagrams have been for preparation of desired forms of bulk matter.

#### 5. Conclusion and future directions

We have outlined the current state of understanding of how and why the phase changes of small systems differ from traditional phase transitions of bulk matter. These are, in a sense, all traceable to the leverage of the number  $N$  of particles comprising each system in a Gibbsian thermodynamic ensemble. However they range from essentially thermodynamic considerations to time-scale issues.

Some of the open questions have been stated, e.g. the question of how the two minima may converge (or not) for a system that has two minima in its free energy if the clusters are small, but apparently only one if



**Figure 2.** Two examples of the extension of the traditional  $p$ - $T$  phase diagram to describe small systems, for which  $D$  may take on intermediate values between  $-1$  and  $+1$  in the coexistence range: (a) schematic representation of the extended phase diagram for a very large system, so all points not on the coexistence curve are virtually in either the plane of  $D = -1$  or the plane of  $D = +1$ ; (b) schematic representation of a smaller system, for which intermediate values of  $D$  would be observable over a measurable range of pressure and temperature.

the system is very large. Other questions have been indicated only in passing, e.g. there is no fundamental understanding of the nucleation and kinetics of phase changes of small systems, although one can see the process occurring in simulations. Finally, there are larger questions that we have not discussed here because we have very little understanding of them. Perhaps the most prominent are questions about precisely how size and nature of the system governs the conditions under which phase changes and phase coexistence may occur. We do not, for example, understand how the change of stable structures with size occurs even in rare-gas nanoparticles: how does the change of stability happen, that makes small clusters of most sizes icosahedral and larger systems face-centered, close-packed cubic? The subject remains full of challenges.

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