

## Coexistence in Finite Systems

David J. Wales

*University Chemical Laboratories, Lensfield Road, Cambridge, CB2 1EW, United Kingdom*

R. Stephen Berry

*Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637*

(Received 27 January 1994)

We derive necessary conditions for finite systems to exhibit two locally stable states with respect to fluctuations in the microcanonical and canonical ensembles. The requirements are, respectively, that there be two inflections in the logarithm of the probability distribution of the energy or the number of particles in the canonical or grand canonical ensembles. The thermodynamics associated with the whole phase space may be related to quantities averaged over regions of phase space and are consistent with van Hove's theorem.

PACS numbers: 64.60.-i, 05.20.-y, 36.40.+d

The embryonic first-order melting transition in finite systems has been the subject of considerable study. It is now clear that clusters of atoms or molecules can exhibit two or more stable states corresponding to liquidlike and solidlike forms or, under suitable circumstances, to other forms such as soft solids or surface-melted solids [1]. Convincing evidence has recently been obtained from simulations in which the energy density of states is calculated and used to compute a range of thermodynamic properties [2-4]. These results confirm the conclusions of a number of theoretical studies, starting from the earliest arguments based upon the quantum density of states in rigid and "floppy" systems [5]. The latter work indicated the existence of minima in the Helmholtz free energy for both solidlike and liquidlike forms of a cluster over a finite range of temperature [5], and hence observable coexistence of both forms, like isomers, whether their free energies were equal or only moderately different. Reiss *et al.* subsequently used classical capillarity theory to infer the existence of a Gibbs free energy barrier between local minima corresponding to solidlike and liquidlike clusters [6]. Honeycutt and Andersen contrasted results obtained by simulations in the canonical and microcanonical ensembles for a range of cluster sizes [7]. Bixon and Jortner invoked idealized partition functions and distributions of local energy minima to study coexistence in both the canonical and microcanonical ensembles [8]. Good agreement with simulation has also been obtained for a specific cluster when anharmonicity is included in a model analytic partition function [9]. In fact, coexistence may be identified in thermodynamic functions calculated with model densities of states using only a representative sample of local minima and their normal mode frequencies [10,11]. Separate limits for the thermodynamic stability of solidlike and liquidlike clusters have also been found from a simple model partition function based upon a defect model for nonrigidity [12].

Such studies show that sufficient conditions for coexistence can arise in several ways. In the present Letter we

derive the *necessary* conditions in terms of van der Waals loops or *S* bends, for coexistence to occur, conditions on statistical distributions, themselves based on microscopic properties of the system. Explicitly, the conditions state that there must be two inflections in the logarithms of the probability distributions  $\mathcal{P}(E)$ ,  $\mathcal{P}(N)$ , or  $\mathcal{P}(X)$ , of energy, number, or other extensive variable in an ensemble based, respectively, on a constant intensive variable  $T$ ,  $\mu$ , or, in general,  $I$ . This condition is of course weaker than conditions such as the traditional *S*-bend (sufficiency) criterion of van der Waals theory, which take segments of isotherms to have negative slopes. We then explain how these are related to short time averages and to van Hove's theorem [13], which states that the thermodynamic variables of *infinite* systems cannot exhibit any regions of instability with respect to fluctuations when those variables are computed from global phase space (or infinite time) averages.

First, we consider the conditions for stability with respect to fluctuations in thermodynamic variables [10,14]. In the microcanonical ensemble, the entropy must be a maximum, and we have a stable state with respect to energy fluctuations, when  $(\partial T/\partial E)_{N,V} > 0$  and instability for the opposite sign. The same is true in this ensemble for the derivative  $(\partial \mu/\partial N)_{V,E}$  and fluctuations in  $N$ , while the opposite signs apply to the derivative  $(\partial P/\partial V)_{N,E}$  and fluctuations in  $V$ , i.e.,  $S$  is a maximum when  $(\partial P/\partial V)_{N,E} < 0$ . In the canonical ensemble the last two conditions define a minimum in the Helmholtz free energy and a stable state, except that constant  $E$  is replaced by constant  $T$ .

The microcanonical  $T(E)$  curve may exhibit a van der Waals loop or "*S* bend" (Fig. 1) for a finite system. Here, the two branches of the curve with positive slope correspond to local stability, and the connecting branch with negative slope corresponds to instability. The existence of a loop implies that there is a range of temperature for which two stable states of the system are possible. Such loops have now been found in calculations based upon

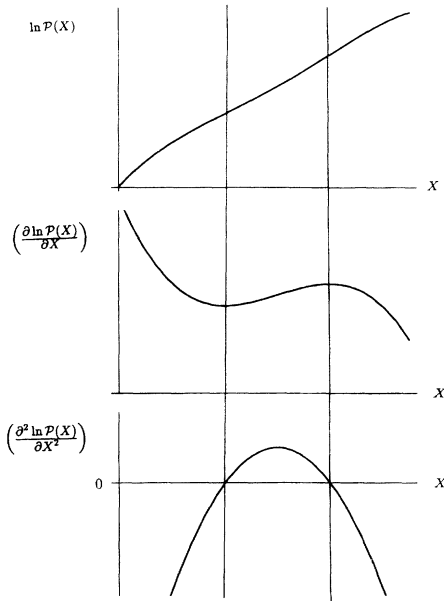


FIG. 1. Relationships between a probability distribution  $\mathcal{P}(X)$  and its derivatives. Top:  $\ln \mathcal{P}(X)$  showing two inflections; middle,  $\partial \ln \mathcal{P}(X)/\partial X$  showing a loop; bottom,  $\partial^2 \ln \mathcal{P}(X)/\partial X^2$  crosses the zero axis twice. The vertical lines show how the inflection points in  $\ln \mathcal{P}(X)$  become turning points and then zeros in the first and second derivatives. An explicit example identifies  $X$  with the energy  $E$ ,  $\partial \ln \mathcal{P}(X)/\partial X$  with  $1/kT$ , and  $\partial^2 \ln \mathcal{P}(X)/\partial X^2$  with  $-(\partial T/\partial E)_{N,V}/kT^2$ , where  $T$  is the microcanonical temperature.

densities of states found at constant pressure and constant volume from both simulations and model partition functions, with very good agreement between the two [15,16]. (In microcanonical simulations the mean temperature is derived from the mean kinetic energy per degree of freedom. This follows from the generalized equipartition theorem [17], which is correct to order [18]  $1/N$ , and from the well-substantiated supposition of ergodicity on the time scale of several vibrational periods.)

In the microcanonical ensemble, the energy is fixed and there is a unique temperature if we average over all of phase space in a simulation. However, we may also calculate a short-time-averaged temperature [19], and for some clusters this quantity exhibits a bimodal (or multimodal) distribution which, in an ergodic system, corresponds to an equilibrium between species passing between two (or more) regions of phase space that have their own characteristic temperatures [20]. The time scale for which short-time averaging produces multimodal distributions is typically several vibrational periods. Whether an experiment will resolve the two characteristic temperatures or see an average therefore depends upon the time scale of the observation.

To clarify the physical meaning of an  $S$  bend consider the behavior of an ensemble of clusters prepared under conditions in which  $C_v \equiv (dE/dT)_{N,V} < 0$ . If the constraints

on the ensemble are relaxed to allow exchange of energy among the clusters, while the total energy remains fixed, then the stable state of the ensemble consists of some clusters with lower energy and some with higher energy. In other words, the initial ensemble is unstable with respect to energy fluctuations among the clusters. This kind of behavior may be identified for a single cluster in a microcanonical simulation if and only if the system is ergodic, i.e., an average over a large ensemble of clusters at any instant gives the same value of any equilibrium property as a long-time average over the history of a single system. When short-time averages of quantities such as the kinetic energy are taken, it is often possible to identify two or more distinct species corresponding to liquidlike and solidlike behavior [20]. The different species may in turn be related to distinct regions of the potential energy surface, and so this dynamical coexistence is analogous to the fluctuation between two geometrical isomers of a molecule which would have their own characteristic temperatures in the microcanonical ensemble. Hence, in the present context, *coexistence* does not refer to coexistence of two distinct phases in static physical contact, but rather to dynamical coexistence of two (or more) phaselike forms. Nevertheless, this dynamic coexistence is related to the static equilibrium of bulk phases and to the stability limits of superheated and supercooled systems [12]. In practice, the ergodicity condition means that the energy must be high enough for the cluster to pass among minima in the liquidlike region and between solidlike and liquidlike regions on relevant, observable time scales, whether for experiment or simulation.

We first deduce the *necessary* conditions for an  $S$  bend to occur for the variation of temperature with energy in the microcanonical ensemble and the variation of chemical potential with the number of atoms in the canonical ensemble, where all quantities are calculated as complete phase space averages. The probability distribution function of the energy  $\mathcal{P}(E)$  for particular, fixed  $N$ ,  $V$ , and  $T$  in the canonical ensemble is

$$\mathcal{P}(E) = \Omega(N, V, E) e^{-\beta E} / Q(N, V, T), \quad (1)$$

where  $\beta = 1/kT$ , and  $\Omega$  and  $Q$  are the microcanonical and canonical partition functions. Now  $S = k \ln \Omega(N, V, E)$  and  $T = 1/(\partial S/\partial E)_{N,V}$ , so we have

$$\left( \frac{\partial^2 \ln \mathcal{P}(E)}{\partial E^2} \right)_{N,V} = -\frac{1}{kT^2} \left( \frac{\partial T}{\partial E} \right)_{N,V}. \quad (2)$$

Hence, to see a loop in the microcanonical  $T(E)$  function the right-hand side must change sign twice as  $E$  increases. The second derivative of  $\ln \mathcal{P}(E)$  must therefore go through zero twice, and hence  $\ln \mathcal{P}(E)$  must have two inflections as a function of energy. The correspondence between these curves and their derivatives is shown in Fig. 1. The necessary condition for a loop in the microcanonical caloric curve  $T(E)$  is therefore that the logarithm of the canonical energy distribution function

should have two inflections. One way in which two such inflections can arise, i.e., one sufficient condition, is that  $\mathcal{P}(E)$  be the sum of two contributions that are centered on different values of  $E$ . This suggests that we might be able to partition phase space into regions identifiable by some order parameter [5,12,21].

To analyze  $\mu(N)$  in the canonical ensemble we consider the distribution function for the number of atoms in the grand canonical ensemble for particular  $\mu, V, T$ :

$$\mathcal{P}(N) = Q(N, V, T) e^{\beta\mu N} / \Xi(\mu, V, T), \quad (3)$$

where  $\Xi$  is the grand canonical partition function. In this case,  $A = -kT \ln Q(N, V, T)$  and  $\mu = (\partial A / \partial N)_{V, T}$ , so that

$$\left( \frac{\partial^2 \ln \mathcal{P}(N)}{\partial N^2} \right)_{V, T} = -\beta \left( \frac{\partial \mu}{\partial N} \right)_{V, T}. \quad (4)$$

Therefore, the necessary condition for a loop in the canonical chemical potential as a function of the number of atoms is that the logarithm of the grand canonical distribution function  $\mathcal{P}(N)$  has two inflections. In fact, Hill [22] noted some time ago that a loop will result if  $\mathcal{P}(N)$  is bimodal; the requirement of two inflections in  $\ln \mathcal{P}(N)$  is less restrictive. Absence of a loop in, e.g., the microcanonical  $T(E)$  does not preclude the presence of a loop in, e.g.,  $P(V)$ . Thermodynamic stability therefore depends upon which sort of fluctuation is in question.

It is not difficult to generalize this analysis. Let  $X$  and  $I$  represent conjugate thermodynamic extensive and intensive variables, respectively, e.g.,  $E$  and  $1/T$ . The other two thermodynamic variables which are needed to define the state of the system are arbitrary and will be omitted hereafter. We consider a thermodynamic function  $B$ , which is a natural function of  $X$ , so that  $dB$  contains a term in  $I dX$ , and  $B$  is related to a partition function  $Z(X)$  by  $B \propto \ln Z(X)$ . Then the function  $B'$ , which is the Legendre transform  $B' = B - IX$  of  $B$ , is related to a partition function  $Z'(I)$  by  $B' \propto \ln Z'(I)$ , and the differential  $dB'$  contains a term in  $-X dI$ .

$B$  and  $B'$  are the natural thermodynamic functions for ensembles with  $X$  and  $I$  fixed, respectively. When the extensive variable  $X$  is free to vary, an extra constraint term is needed in setting up the usual constrained maximization problem which defines the probability distribution in the given ensemble. The net result is that  $Z'(I) = \sum_X Z(X) \exp(-IX)$ , where the sum becomes an integral if  $X$  is continuous. The probability distribution of  $X$  for a particular, fixed value of  $I$  is therefore

$$\mathcal{P}(X) = Z(X) e^{-XI} / Z'(I), \quad (5)$$

and a loop may occur for the average value of  $I$  as a function of  $X$  in the unprimed ensemble if  $\ln \mathcal{P}(X)$  has two inflections. Furthermore, no loop is possible in the primed ensemble, because the derivative of the average value of  $X$  is proportional to the mean square fluctuation of  $X$ :

$$\left( \frac{\partial \langle X \rangle}{\partial I} \right) = -\langle (X - \langle X \rangle)^2 \rangle < 0, \quad (6)$$

and so  $\langle X \rangle$  is a monotonic function of  $I$ . Familiar examples should be the energy in the canonical ensemble  $[(\partial \langle E \rangle / \partial \beta)_{N, V} = -\langle (E - \langle E \rangle)^2 \rangle]$  and the number of particles in the grand canonical ensemble (GCE)  $[(\partial \langle N \rangle / \partial \mu)_{N, V} = \beta \langle (N - \langle N \rangle)^2 \rangle]$ .

We now show how the above conditions are related to short-time-averaged properties, or, more rigorously, averages restricted to certain regions of phase space. This assumes that a suitable order parameter exists by which the forms, 1 and 2 say, can be recognized [21]; the rigidity parameter, discussed in earlier work [5,12], is one such possibility. Then we may write

$$S(E) = k \ln \Omega(N, V, E) = k \ln [\Omega_1(N, V, E) + \Omega_2(N, V, E)], \quad (7)$$

which we abbreviate for convenience as  $S = k \ln(\Omega_1 + \Omega_2)$ . Hence,

$$\begin{aligned} \left( \frac{\partial S}{\partial E} \right)_{N, V} &= \frac{1}{T} = k \left[ \left( \frac{\partial \Omega_1}{\partial E} \right)_{N, V} + \left( \frac{\partial \Omega_2}{\partial E} \right)_{N, V} \right] / \Omega \\ &= k \frac{\Omega_1}{\Omega} \left( \frac{\partial \ln \Omega_1}{\partial E} \right)_{N, V} + k \frac{\Omega_2}{\Omega} \left( \frac{\partial \ln \Omega_2}{\partial E} \right)_{N, V} \\ &= p_1 / T_1 + p_2 / T_2, \end{aligned} \quad (8)$$

where  $p_1(N, V, E)$  is the probability of finding the system in region 1 ( $p_1 + p_2 = 1$ ), and  $1/T_1 = k[\partial \times \ln \Omega_1(N, V, E) / \partial E]_{N, V}$  defines  $T_1$ , etc. It is now easy to show that

$$\begin{aligned} \left( \frac{\partial T}{\partial E} \right)_{N, V} &= T^2 \left( \frac{\partial p_1}{\partial E} \right)_{N, V} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\ &+ T^2 \left[ \frac{p_1}{T_1^2} \left( \frac{\partial T_1}{\partial E} \right)_{N, V} + \frac{p_2}{T_2^2} \left( \frac{\partial T_2}{\partial E} \right)_{N, V} \right], \end{aligned} \quad (9)$$

where we normally expect the first term to be negative and the second to be positive. For example, suppose 1  $\equiv$  solidlike and 2  $\equiv$  liquidlike and that the liquidlike form appears at higher energies or temperatures than the solidlike form. Then the liquidlike form exhibits a relative increase of entropy with energy so that  $(\partial p_1 / \partial E)_{N, V} < 0$  and at a given total energy  $T_1 > T_2$ , because the solidlike region has lower potential energy. Hence, stability conditions require that the second term be positive. The condition for an  $S$  bend in  $T(E)$  is that  $(\partial T / \partial E)_{N, V}$  must change from positive to negative and back again. In fact, writing  $\mathcal{P}(E) = [\Omega_1(N, V, E) + \Omega_2(N, V, E)] e^{-\beta E} / Q(N, V, T)$  it is easy to reach precisely the same expression for  $(\partial T / \partial E)_{N, V}$  using Eq. (2). Some useful results can be derived from this framework, as shown elsewhere [16].

So, should we say that a cluster exhibits "coexistence" when we see a double inflection in a globally averaged property, or when distinctive regions of phase space can be identified by separate averaging? Such regions certainly exist for the thirteen-atom Lennard-Jones cluster

(LJ<sub>13</sub>) but its microcanonical  $T(E)$  has an inflection rather than an  $S$  bend, because the relative difference in heat capacities between the solidlike and liquidlike regions is small by comparison, for example, with that of LJ<sub>55</sub>. Could one see an  $S$  bend or double inflection without finding a multimodal distribution for short-time averaging? This really depends upon our ability to find an appropriate order parameter [21]. In general, we expect to see a feature indicating two phaselike forms in globally averaged thermodynamic properties of a finite system if its phase space has distinctively ordered regions and an observable time scale for the duration of each form. However, the prominence of the feature depends upon how different these forms are.

Finally, we comment upon the relation of the present work to van Hove's theorem [13], which states that the region of negative slope associated with an  $S$  bend in a thermodynamic function is forbidden in the bulk limit. This is the source of the textbook assertion that such features are the result of "approximate theories." However, finite systems can certainly exhibit  $S$  bends with stability limits which we associate with superheating and supercooling, as for the bulk [12]. The two-state model considered above does not provide a link to the bulk limit, because it does not allow for phase separation for which more complicated models are necessary [1].

We have now deduced the necessary conditions for two separate phaselike forms of a finite system to occur and coexist and have related these to short-time averaging or, more formally, to averages over distinct regions of phase space [21]. Taken together with previous work which establishes various sufficient conditions for multiple phaselike forms to occur, we now have a reasonably coherent understanding of coexistence of two phases in finite systems. The extension of these necessary conditions to the coexistence of multiple phases may also be within our grasp [1]. Finally, it should now be possible to predict from estimates of densities of states which cluster sizes will exhibit coexisting phaselike forms and which will not.

We are grateful to NATO and the Royal Society (D.J.W.) for financial support. D.J.W. thanks Prof. R. Zwanzig for first drawing his attention to the van Hove theorem, and Dr. R.M. Lynden-Bell for helpful discussions.

- [1] H.-P. Cheng and R.S. Berry, *Phys. Rev. A* **45**, 7969 (1992); R. Kunz and R.S. Berry, *Phys. Rev. Lett.* **71**, 3987 (1993); R. Kunz and R.S. Berry, *Phys. Rev. E* **49**, 1895 (1994).
- [2] P. Labastie and R.L. Whetten, *Phys. Rev. Lett.* **65**, 1567 (1990).
- [3] H.-P. Cheng, X. Li, R.L. Whetten, and R.S. Berry, *Phys. Rev. A* **46**, 791 (1992).
- [4] S. Weerasinghe and F.G. Amar, *J. Chem. Phys.* **98**, 4967 (1993).
- [5] G. Natanson, F. Amar, and R.S. Berry, *J. Chem. Phys.* **78**, 399 (1983); R.S. Berry, J. Jellinek, and G. Natanson, *Phys. Rev. A* **30**, 7241 (1984).
- [6] H. Reiss, P. Mirabel, and R.L. Whetten, *J. Phys. Chem.* **92**, 7241 (1988).
- [7] J.D. Honeycutt and H.C. Andersen, *J. Phys. Chem.* **91**, 4590 (1987).
- [8] M. Bixon and J. Jortner, *J. Chem. Phys.* **91**, 1631 (1989).
- [9] S.F. Chekmarev and I.H. Umirzakov, *Z. Phys. D* **26**, 373 (1993).
- [10] D.J. Wales, *Mol. Phys.* **78**, 151 (1993).
- [11] D.J. Wales and I. Ohmine, *J. Chem. Phys.* **98**, 7245 (1993).
- [12] R.S. Berry and D.J. Wales, *Phys. Rev. Lett.* **63**, 1156 (1989); D.J. Wales and R.S. Berry, *J. Chem. Phys.* **92**, 4308 (1990).
- [13] L. van Hove, *Physica (Utrecht)* **15**, 951 (1949); T.L. Hill, *J. Phys. Chem.* **57**, 324 (1953).
- [14] See, e.g., D. Chandler, *Introduction to Modern Statistical Thermodynamics* (Oxford University Press, Oxford, 1987), p. 35.
- [15] J.P. Rose and R.S. Berry, *J. Chem. Phys.* **98**, 3246 (1993).
- [16] J.P.K. Doye and D.J. Wales (to be published).
- [17] M. Allen and D.J. Tildesley, *The Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987), p. 46.
- [18] A. Münster, *Statistical Thermodynamics* (Springer, Berlin, 1969).
- [19] C.L. Briant and J.J. Burton, *J. Chem. Phys.* **63**, 2045 (1975).
- [20] J. Jellinek, T.L. Beck, and R.S. Berry, *J. Chem. Phys.* **84**, 2783 (1986); T.L. Beck, J. Jellinek, and R.S. Berry, *J. Chem. Phys.* **87**, 545 (1987); T.L. Beck and R.S. Berry, *J. Chem. Phys.* **88**, 3910 (1988); D.J. Wales and R.S. Berry, *J. Chem. Phys.* **92**, 4283 (1990).
- [21] R.M. Lynden-Bell and D.J. Wales, *J. Chem. Phys.* **101**, 1460 (1994).
- [22] T.L. Hill, *J. Chem. Phys.* **23**, 812 (1955).