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NUCLEATION THEORY AND SMALL SYSTEM THERMODYNAMICS

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Abstract. The exact treatment of first-order phase transition is an important topic in thermodynamics. This topic exists as an exact branch of thermodynamics, only by virtue of the occurrence of sharp discontinuities in properties of macroscopic systems. In small systems, instead of such discontinities, there are more or less gradual changes which approach discontinuities more closely as the system becomes larger. Metastable macroscopic systems below a critical temperature show nucleation phenomena and depending on the saturation degree the number of constitutive elements that form the evolving nuclei may vary from a couple of tens to hundreds of thousands. In Classical Nucleation Theory specific corrections done on Gibbs' surface tension term take care of small size effects and theoretical predictions are in fair agreement with early experimental data. However results obtained by experimental techniques developed in the last decade revealed systematic deviations from the classical theory. Nuclei that evolve into the new phase may contain only a few of tens of molecules and continuum thermodynamics does not apply to such situations. Statistical mechanical methods rely on complex interaction potentials and the generality of thermodynamic predictions is lost. However clever modifications introduced in continuum thermodynamics extend its applicability to small systems even in cases where the thermodynamic limit is not valid anymore. In all those treatments the grand canonical potential is of central importance and the driving force for nucleation is the entropy, whatever the nucleation process maybe.

1. INTRODUCTION

Experimental observations reflect the fact that there are kinetic barriers to first order phase transitions with metastable phases persisting over large periods of time. Small fluctuations of the new (stable) phase tend to disappear while large fluctuations tend to grow. The critical nucleus is that fluctuation which lies at the barrier between shrinking and growing regions of the new phase. The nucleation rate (i.e. the rate of appearance of critical nuclei) then determines the time it takes for a phase transition to occur, as the growth beyond the critical nucleus is generally fast compared to its formation rate. As an activated process its rate depends exponentially on the height of the barrier represented by the work of formation of the critical nucleus and the calculation of this value is central in theories of nucleation.

Through most of this century, the study of nucleation has been dominated by the classical capilarity approximation [1-3]. In this approach, the free energy change to form a small cluster of a new phase (surrounded by the old phase) is taken to be the sum of a bulk and a surface contribution, proportional, respectively, to the volume and the surface area of the cluster. Classical Nucleation Theory (CNT) is a simple approach that has provided experimentalists with a standart of comparison for their data, but it cannot be used as a starting point for more systematic microscopic theories. CNT builds on the continuum thermodynamics according to which small droplets are considered to have the same properties as bulk condensed phases, with bulk surface properties. This continuum assumption has been viewed with suspicion, and other models have been proposed which introduce more microscopic fea-

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tures. [4-7]. However CNT compares well with these others in accounting for experimental data. Oxtoby [8] showed that, the qualitatively reasonable but quantitatively incorrect agreement of CNT results for condensation of samples of single-component nonpolar fluids in overall order of magnitude of rates, is “largely fortuitous”. The reasons for this qualitative success could be traced to a cancellation of errors, due to two critical physical features of nucleation omitted by CNT: the surface tension dependence on curvature and the vanishing of the nucleation barrier at the spinodal. Oxtoby [8] argues that these two errors accidentally cancel at some temperature, often within the experimental accessible region, but together give rise to the systematically incorrect temperature dependence of CNT.

In order to investigate the failings of CNT it is necessary to question the underlying approach, namely the application of continuum thermodynamics to small clusters of molecules. This problem was addressed by Bowles *et al.* [9]. They presented a proof for the Nucleation Theorem (NT) that applies to any system having an equilibrium nonuniform distribution of density induced by an external field and not only to the cluster that constitutes the nucleus of CNT. This proof shows that the NT extends rigorously down to nonuniformities of molecular dimensions.

Also, Hill [10] as long as 1962, derived the same result in the context of his development of the Thermodynamics of Small Systems (TSS). His insight was that even though the methods of continuum thermodynamics cannot be used to analyse a small cluster, they are valid at treating a large ensemble of such systems. The thermodynamic relations which emerge are in terms of averages of system thermodynamic quantities over the ensemble. These relations can differ from those expected for large systems, although in the continuum limit they concide . Furthermore the questionable introduction of a well defined cluster surface area can be avoided.

Mokross [11,12] in analogy to the treatment of Cahn and Hilliard [13] developed an Entropic Nucleation Theory (ENT) in which entropy is the driving force for nucleation instead of the difference in Gibbs free energy. The nucleation process is described as the result of fluctuations which induce inhomogeneities in the enthalpy that eventually evolve into a critical nucleus. The entropy is maximized relatively to these inhomogenities and the work of formation of a critical nucleus is obtained by multiplying this entropy by the temperature. This model as discussed [12] is independent of the conditions (adiabatic, isothermic, etc.) under which nucleation takes place and is valid for nuclei of any size.

In Section 2 we review the derivation of the work to form a nucleus (any size) by CNT taking the change in the grand canonical potential as the driving force. This development establishes contact with Bowles’ [9] method used to derive the NT, with SST and with fluctuation theory as will be seen later. In Section 3 we present Bowles’ method for the calculation of the work necessary to form a critical nucleus. In Section 4 this is redone in the entropy representation [14] showing that the driving force necessary to form an inhomogeneous nucleus is the variation of the grand canonical potential in the entropic representation. This driving force is an exact differential as in ENT [12] and corresponds to an entropy variation. In Section 5 and 6 we present a summary of the SST method and of the ENT. Conclusions from this work are given in Section 7.

2. CLASSICAL NUCLEATION THEORY – THE GIBBS METHOD

According to Gibbs treatment the condensate and vapor can be modelled as though they were homogeneous bulk phases with extensive internal energies and entropies, proportional to the number of molecules in each. An additional surface phase is introduced with an excess free energy which carries the non-linear terms. This is defined on an arbitrary dividing surface separating the condensed and vapor phases. The Tolman prediction [15] of the size dependence of the surface tension emerges from this formalism. The Gibbs treatment is reasonable for large clusters, where the thermodynamic limit applies, but it is a poor approximation to real clusters when the number of molecules is small.

In this teatment a spherical condensed phase droplet is considered within a homogeneous vapor phase, with total system volume V, and in contact with particle and heat reservoirs. The temperature, T, and chemical potential, μ, are constant throughout. The internal energy, number of molecules and entropy, U, N and S respectively, characterizing the whole system, are divided into contributions associated with the condensate and vapor separately (considered to be occupying volumes V_l and V_v with $V=V_l+V_v$, and pressures p_l and p_v respectively) and a third phase defined on a notional dividing surface of area A separating the two. A condition for the position of the dividing surface must also be chosen.

For a change in entropy, volume and molecular content, the first law of thermodynamics gives the associated changes in internal energy of the liquid and vapor phases as

(2.1)

where the indexation l,ν refers to liquid phase, l or to vapor phase, ν. The continuum assumption presumes that the internal energy, entropy and volume of each phase are proportional to the number of molecules in each phase and which fails for small systems. Then Eq. (2.1) integrates according to Euler's theorem to

(2.2)

The thermodynamic properties of the surface are then assigned using

(2.3)

where X may refer to U, S or N, with the suffix s denoting surface terms, and we may write a relation similar to Eq. (2.2) for surface properties, i.e.,

(2.4)

which can be considered a definition of the surface tension, σ.

The work required to form the cluster from a uniform vapor phase is given by the change in internal energy of the system in going from a vapor system to the critical droplet plus vapor sate just considered, with the total number of molecules, volume and entropy all constant. This can be written as the change in grand potential in going from a bulk vapor state to the droplet plus vapor state at constant T, V and μ [16]

(2.5)

where $\Omega_0=-p_\nu V$ is the grand potential for the system containing a uniform vapor phase. Summing Eqs. (2.2) and (2.4), using Eq. (2.3) and denoting by W the work required to form a droplet, we obtain

(2.6)

where $\Delta\mu=\mu-\mu_{eq}$. The last result has been obtained integrating the Gibbs-Duhem relation for the condensed phase assuming it to be incompressible, at constant T, between equilibrium bulk condensed and vapor phase (μ_{eq}), and liquid phase

(2.7)

The critical cluster is the size which is in unstable thermal equilibrium, which means that the work of formation is obtained by maximizing Eq. (2.6) with respect to N_l and N_s.

3. BOWLES et al. METHOD

Bowles et al.[9] derived the NT using conventional thermodynamics. By introducing additional constraints they showed that it is possible to reduce metastable (unstable) states to stable equilibrium states. For a single component system, the fundamental equation of thermodynamics (combined first and second laws) may be written as

(3.1)

The term fdF represents an additional fF work to the pV work. The term f is the intensive parameter while F is the conjugate extensive parameter. Eq. (3.1) may be rewritten as

(3.2)

where it is to be noted that if the term at the right were to equal zero, the second equation in (3.2) would simply be the fundamental thermodynamic equation for a system in a state of stable equilibrium that is capable only of pV work. $D\Phi$ is not a thermodynamic state function. If the system is in a particular state of stable equilibrium it will be set up to perform only pV work, and in this case $D\Phi=0$. The system can be reversibly displaced from its state of equilibrium by the application of a constraint that can exchange work with the system. In Eq. (3.2) fF can represent this work. Of course the system on the path of displacement will have an additional variable corresponding to the constraint, f or F in the above example. Also, by reference of the second law of thermodynamics the work fF performed to displace the system from a state of stable equilibrium is positive, i.e., the work is performed *on* the system. Therefore

(3.3)

If we select a path having S, V, N constant, then from (3.2) and (3.3)

(3.4)

and dU, along this path, does imitate $D\Phi$. U is a thermodynamic potential and increases along the path with S,V,N constant, having a minimum at the initial state of equilibrium.

Alternatively, if we select a path of constant T,V,μ then the grand potential

(3.5)

will be the thermodynamic potential that must be used. Since

(3.6)

and $d\Omega$ imitates $D\Phi$ along this path. The field f displaces an initially homogeneous system, capable of pV work from its state of equilibrium. This field f, performs reversible deformation work given by

(3.7)

The fundamental equation of thermodynamics

(3.8)

becomes

(3.9)

and, equating Eqs.(3.7) and (3.9) yields

(3.10)

and $d\Omega$ imitates $D\Phi$ along this path. Ω increases along this path and has a minimum at the initial state of equilibrium. From these considerations Bowles et. al. [9] derived the equations of the NT (see Appendix).

In this energy representation $(D\Omega)_{T,V,\mu}$ represents the reversible work performed by the field associated with f, required to create an inhomogeneous system. This field may take on a variety of forms as for instance a field that can form a small cluster or drop. The tools so far used belong to macroscopic thermodynamics and the results so far obtained are valid even for molecular sized inhomogeneities as long as they represent the average inhomogeneity under the constraint. This validity for clusters of all sizes becomes explicit when applying SST to an ensemble formed by small systems in a T,V,μ enviroment as will be seen later.

It is important to note that, albeit the specification of the field is not important in the derivation of the NT (see Appendix) it is essential for the derivation of the work to form a critical nucleus, i.e., by maximizing $\Omega=\Omega(T,V,\mu,F)$ with respect to F, i.e.,

(3.11)

yielding the value F^* and the critical work is obtained by integrating Eq. (3.10)

(3.12)

where Ω_0 denotes the value of Ω in the initial equilibrium state in which the system is set up in a manner that allows it to perform only pV work. In that state there are only three independent variables, μ, V and T so that F in that state, denoted by F_0 is itself a function of μ, V and T and is fully determined when these variables are fixed.

4. BOWLES et al. METHOD – ENTROPY REPRESENTATION

The derivation of Eq. (3.10) in the entropy representation [10] will produce further insight into nucleation processes. The fundamental equation of thermodynamics, Eq. (3.1), in the entropy representation

(4.1)

is

(4.2)

In this representation the equivalent to $D\Phi$ in Eq. (3.2) is an entropy like exact differential, $d\overline{\Phi}$, which henceforth will be designated by dS_F [17,18], i.e.,

(4.3)

The grand potential in this representation is

(4.4)

and

(4.5)

From Eq.(4.3)

(4.6)

Therefore

(4.7)

and is the appropriate thermodynamic potential along this path and is equal to the negative of the entropy induced by the field *f* necessary to induce the inhomogeneity in the system. S_F has a maximum at the initial state of equilibrium. For an isothermal process and for a nucleus of macroscopic dimensions (in the thermodynamic limit) TdS_F is the latent heat of formation.

The critical nucleus is obtained by maximizing yielding F^*. The work necessary to form a critical nucleus is

(4.8)

or

(4.9)

where S_{F0} and S_{F^*} refer to the equilibrium state and to the critical nucleus respectively.

5. SMALL SYSTEM THERMODYNAMICS – THE HILL METHOD

Hill [10] considers an ensemble of small systems in a T, V, μ environment. In his treatment the internal energy and entropy are not separated into contributions of each phase. The total energy of a collection of $\mathcal{N}$ small systems with a total internal energy, entropy and number of molecules is labelled by suffix *t.* A change in the system conditions , which includes varying the number $\mathcal{N}$ of subsystems in the ensemble gives a first law of thermodynamics in the form

(5.1)

The term $-p\mathcal{N}dV$ is a conventional work term for the ensemble. Each system has the volume V and any volume change dV is the same for all systems. The presure p is a mean pressure (ensemble average) and can be defined formally by

(5.2)

The term $Wd\mathcal{N}$ is regarded as another pV work term for $d\mathcal{N}$ implies that the volume of the ensemble is changing with S_t and N_t constant by changing the number of available systems of volume V rather then changing V for each of the $\mathcal{N}$ systems. This "integral" pressure is therefore defined by For a macroscopic system ($V \to \infty$) there is no distinction between p and but in general differ for small systems [10].

is the subsystem work of formation since it is the change in internal energy required to create an additional subsystem of volume V at constant entropy, S_t and number of molecules, N_t. For a large ensemble, U_t and S_t are proportional to $\mathcal{N}$, Ω is a constant and Eq. (5.1) intergrates at constant V, T and μ to give

(5.3)

where Ω is therefore the grand potential for a single subsystem written in terms of $\bar{U}$ and $\bar{N}$ which are the ensemble averaged values of the internal energy and molecular number in each droplet plus vapor subsystem. The entropy S is not an average since S_t is a property of the entire ensemnble and each subsystem has the same entropy S. Eq. (5.3) is valid for all states of the subsystem and not just for equilibrium states.

The work of formation of one cluster alone, i.e., without the surrounding vapor, can be found by considering a state of the subsystem which contains just vapor at the same T, V and m and with a grand potential denoted by Ω_0. Ω describes the same subsystem when an additional cluster is included and so the droplet work of formation W is given by

(5.4)

where $\bar{U}_0$, S_0 and $\bar{N}_0$ correspond to pure vapor system and $\bar{U}_c$, S_c and $\bar{N}_c$ are now thermodynamic variables associated with the cluster. They are the mean thermodynamic properties of the cluster minus those of the vapor displaced in forming it.

The driving force is therefore the change in the grand potential of a single small subsystem, expressed by the internal energy and number of particles averaged over the ensemble of subsystems. This averaging implies that the bulk vapor phase contains populations of molecular clusters with a range of sizes. The state of thermodynamic equilibrium of such a system, in contact with a particle and heat reservoir, has a cluster distribution which minimizes the system grand potential. In statistical mechanics this corresponds to choosing a cluster distribution which maximizes the sistem partition function and establishes contact with fluctuation theory [19].

The critical nucleous is obtained by requiring W to be a maximum with respect to N_c , i.e.,

(5.5)

6. ENTROPIC NUCLEATION THEORY

This theory [11,12] was developed in analogy to Cahn and Hilliard's approach [13] and considers the entropy per unit volume to be a function of the enthalpy per unit volume and its spatial derivatives at constant pressure. i.e.,

(6.1)

Expansion of Eq. (6.1) in a Taylor series about the entropy of the system with uniform enthalpy, h, $s(h)$, yields the entropy of a small element with volume V

(6.2)

where κ is a function of second order and third-order derivatives in the Taylor expansion.

The critical nucleus is defined by the functional dependence on position that yields an extremum of Eq. (6.2), subject to the condition that the average enthalpy of the system remains constant, i.e., . Performing the variational calculation one obtains the entropy increase in the volume V due to the formation of the nucleus in an initially homogeneous and isotropic system

(6.3)

where

(6.4)

and the enthalpy h has a spatial variation that satisfies the differential equation

(6.5)

with b.c. given by

(6.6)

The minimum work necessary to form a nucleus of critical size is given by

(6.7)

where $S_0=s(h_0)V$. In this calculation the variational procedure is equivalent to the *fF* work mentioned in paragraph 3 and 4 where the Bowles et al. method was presented. Therefore it is easy to conclude that S_F defined in Eq.(4.3) is related to S given by Eq.(6.1) by

(6.8)

showing that the work necessary to form a nucleus is independent of the nucleation process, i.e., adiabati, isocoric, isothermal, etc.

7. CONCLUSIONS

Homogeneous nucleation is the fundamental first step in the kinetics of phase transitions. The CNT is attractive because it predicts nucleation rates in terms of measurable macroscopic quantities. Early experimental investigations by Volmer et al. [20,21] and later by Katz and co-workers [22] seemed to agree with CNT predictions. When it became possible during the last decade to actually measure the rate of nucleation as a function of supersaturation, several experimental investigations revealed systematic deviations from the predicted by classical theory [23-25]. The observed discrepancies raise doubts concerning the validity of CNT as a whole. CNT involves spatial scales which are large compared to molecular sizes. However critical nuclei can often contain only a few tens of molecules and the use of continuum thermodynamics to describe such systems is of doubtful validity.

An approach often used instead is to apply the methods of statistical mechanics, since the molecular nature of the system can be taken into account in constructing the relevant ensembles and partition functions. However these approaches ususally introduce particular choices of interaction potential, or require definitions of what precisely constitutes a cluster. The generality of thermodynamic predictions can be missing.

Even though the methods of continuum thermodynamics cannot be used to analyse small clusters Bowles et al. [9] and Hill [10] showed that with small modifications the whole apparatus of continuum thermodynamics can be used for these systems. In these methods the grand potential shows to be of central importance when dealing with nucleation processes. It makes contact among Bowles et al. method, SST, ENT and the fluctuation theory. In the entropy representation it shows to be a driving force of entropic nature, S_F.

This entropy, , necessary to form a critical nucleus can be obtained by ENT [11,12] . From it is possible to obtain the grand partition function of a critical nucleus, $\Omega^*=T$, yielding the probability P^* for its formation, i.e. .

A suitable master equation may lead the way to calculate nucleation rates to be comapared with experimental results.

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APPENDIX: DERIVATION OF THE NUCLEATION THEOREM

To obtain the NT it is sufficient to integrate Eq. (3.10) obtaining

(A.1)

and from the Legendre transformation of Ω in Eq. (3.5)

(A.2)

it follows

(A.3)

By differentiation of Eq.(A.1) we obtain the equations of the NT

(A.4)

(A.5)

(A.6)

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