First-order Phase Transitions In Two-Dimensional Systems (Adsorbed Layers)

by

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FIRST-ORDER PHASE TRANSITIONS IN. TWO-DIMENSIONAL SYSTEMS

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Abstract

Interest in thin films arises both from a theoretical point of view and from the wide range of applications they can offer. All the advantages and applications of thin films are too many to mention. But some of them are, their use, as compact technological devices, corrosion protections, optical instruments and sensors of scientific research.

The aim of the present paper consists in the theoretical investigation of first-order phase transitions in physisorbed monolayers. Hereby, mainly thermodynamic methods are applied. Therefore, first a thermodynamic theory of homogeneous and heterogeneous monolayers is developed. In particular, general equations for the curvature dependence of the line tension are obtained. It is shown that curvature dependence of line tension is of importance only for very small 2-d clusters. A general thermodynamic analysis of first-order phase transitions, starting from metastable initial states, is given. It is shown that in real situations, when depletion effects are taken into account, the transition proceeds via three main stages: a stage of nucleation and possible simultaneous growth, a stage of independent growth of the clusters, their number being nearly constant and a third stage of competitive growth of Ostwald ripening. The results are analogous to phase transitions in 3-d systems, as was discussed by Schmelzer [19, 20], Ulbrich et.al [1]. Based on the thermodynamic investigation, a kinetic description of the growth of single and ensemble of 2-d clusters is developed. It is shown that in the stage of independent growth, the mean radius of the ensemble of clusters grows as, $R \sim t$ for kinetic limited growth and as $R^2 \sim t$ for diffusion limited growth. Moreover, a kinetic theory of Ostwald ripening in

monolayers is developed which allows a description of the whole course of the process. In the asymptotic region, the results coincide with the predictions obtained first by Lifshitz and Slyozov [23].

The results are used for a theoretical explanation of the computer simulation of a first-order phase transition in a physisorbed monolayer carried out by Kock et.al. [4]. That is, first the asymptotic result of $R^2 \sim t$ for the case of Ostwald ripening in kinetic-limited growth is reconfirmed. In addition, the developed theory allows the interpretation for the initial slow increase of the mean cluster size, R, in the first stage of Ostwald ripening.

The analysis, carried out here, is for isothermal conditions and one component systems. A generalization to other types of constraints, e.g., adiabatic conditions and multicomponent systems is possible.

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Chapter One

Introduction

1.1 Surface Thermodynamics

Classical thermodynamics has been developed orginially for the description of large macroscopic systems where surface effects may be neglected. However, if the surface area to volume ratio is not negligible, surface contributions may determine the thermodynamic properties of the system of interest. In particular this may be the case for systems consisting of different nearly homogeneous phases, divided by inhomogeneous interfacial regions.

The basic concepts for a description of thermodynamic properties of surfaces were developed in the works of Josiah Williard Gibbs, Van der Waals and Guggenheim. Gibbs and van der Waals developed theories for heterogeneous systems, in that Gibbs considered the interface of zero thickness while van der Waals considered a continuous variation of the thermodynamic parameters of the inhomogeneous surfaces and Guggenheim treated the interface as a three dimensional thermodynamic phase with a certain volume.

1.2 Surface Effects and Phase Transitions

Surface effects are important in the course of first-order phase transitions in three dimensional systems* because the new

*From now on wards three-dimensional is to be shortened by (3-D) and two-dimensional by (2-D).

phase can develop first in small amounts with a large interface and evolves to a bulk phase in the course of the transition. The kinetics of both formation and growth of physically new phases can be understood only if surface effects are properly considered for metastable states, i.e. states which are stable against small fluctuations and unstable for large fluctuations; because existence of metastable states are direct consequences of surface effects. Moreover surface effects determine the whole course of first-order phase transitions.

The main topic of our investigations is the theoretical description of first-order phase transition in adsorbed layers. Hereby we understand phase transition as qualitative changes in structure or response of a physical system to a variation of external parameters, as temperature pressure, electric and magnetic fields.

1.3 Adsorbed Layers

Mechanism of their Formation

Adsorption is the mechanism of attachment of foreign particles onto a surface called the substrate or adsorbent. The adsorbed substance is called an adsorbate. There are two fundamental adsorption processes: physisorption and chemisorption. These adsorption types differ mainly in the magnitude

of their interaction with the substrate. In physisorption, the coupling strength between adsorbate-adsorbent is weaker than in chemisorption which can result in the formation of a new surface chemical compound.

Some methods of adsorption are electrodeposition and vacuum deposition. In the former certain ionic solutions can release chemicals to be adsorbed at the substrate electrode. In physisorption, particles may be removed from a bulk part by evaporation and sputtering and forced to stick onto a substrate in a vacuum.

1.4 Adsorbed Layers as 2-d Systems

Adsorbed layers may be divided with respect to the solubility of the adsorbed particles in the adjacent bulk phases. For instance, if a solute is added to some liquid solvent, often a lowering of the surface tension occurs connected with a relative enrichment of the surface with solute particles. The region that is enriched with such particles usually being of a molecular size can be considered as a monolayer or Gibbs' layer. On the other hand, different substances which are insoluble in the adjacent bulk phase may form monolayers which can be called insoluble films or insoluble layers.

Both types of monlayers can be treated theoretically in the same way. Moreover, in the variation of the physical state, the thickness of the layers can be considered as constant and we may denote them as 2-d systems.

1.5 Theoretical Description of Phase Transitions in Monolayers, Achievements and Our Aim

Monolayer systems have been theoretically predicted and experimentally verified to show most, if not all, of the thermodynamic properties of the bulk phases. In particular, it was found that as in 3-d systems, first-order phase transition may occur in 2-d systems. [2,...,9]. However, the intensities and the quantitative values of thermodynamic parameters describing the transition process in 2-d systems may not be the same to that of the 3-d systems, i.e. types of transitions are possible, which have no analogue in 3-d systems (e.g. commensurate-incommensurate transitions)[5, 7]. Phase transition in monolayer systems have been studied intensively by methods of computer simulations and experimental investigations, which a short account of such investigations is to be presented in Chapter Two, and the results obtained were rewarding. [2,4,5,6,7].

The objective of the paper is a theoretical investigation of first-order phase transitions in 2-d systems, specifically it emphasizes on the investigation of the transition process starting from metastable initial states via. the formation and growth of monolayer clusters with a higher surface density compared with the initial homogeneous initial state.

The study will test if the general scenario of the phase transition and the methods of theoretical description applied

for the investigations of phase transitions in 3-d systems [1] are equally valid also for 2-d systems.

Here we will widely use thermodynamic methods. Consequently, we have to formulate first a thermodynamic theory of homogeneous and heterogeneous monolayers, that is discussed in Chapter three to quicken our arguments in the subsequent chapters. This theory is developed based on Gibbs approach because this seems the most natural and consequent extension of classical thermodynamics to heterogeneous systems.

Based on the thermodynamic descriptions developed in Ch. (3), a static description of the main stages of the transition for different thermodynamic constraints is studied in Chapter four.

Under a thermodynamic approach the kinetics of growth of ensembles of clusters and Ostwald ripening in 2-d systems is discussed in Chapter five.

1.6 Application of Thin Films

The rapid development of research on thin films is stimulated by their wide applications. Thin films are used as compact technological devices as in: computer memories, in the manufacture of optical instruments, in surface protections, in the reduction of water evaporations from reservoirs and because of their thinness and good sensitivity they are manufactured for medical uses, and biological research as in

intravascular pressure measurements, in the continuous monitoring of organ functionings, as sensors of concentration of gaseous components and ions in the blood stream and tissue cells [10,11,12]. Thus the investigation of the properties of thin films is not only of theoretical interest but has a great technological relevance.

Chapter Two

Recent Theoretical Predictions and Experimental Findings on Phase Transition in Monolayers

Investigations of thin films in general and monolayers in particular have a long history connected first mainly with the works of Rayleigh, Pockels, Devaux, Marcelin, Langmuir and Adam. However, it was only in the last decades, when the considerable lapse in time between theory and experiment started to be narrowed by ingeneous experimentalists that the study has come to be lively, promising and inviting field of research in physical chemistry with a large number of applications.

Modern surface analysis techniques such as the low-energy-electron-diffraction (LEED) are becoming informative on the structure and thermodynamic properties of adsorbed monolayer films. In particular it is shown that physisorbed monolayers may exist in different phases and as a result of the variation of some external parameters, phase transition may occur [2,5,6,7]. On one hand such 2-d phase transitions show similarities to the corresponding transitions in 3-d system, and on the other hand phases and phase transitions may exist which have no analogue in 3-d systems.[5,6,10]. These differences are believed to occur due to differences in dimensionality and the adsorbate-adsorbent interactions.

To have some impression on the current state of experimental and theoretical investigations on phase transitions in

adsorbed layers, some research studies by different authors are summarized below.

J.G. Dash

Between two and three Dimensions [7]

Astriking qualitative similarity between phases of adsorbed monolayers and a typical 3-d gas-liquid-solid phase diagram for Xenon (see fig, 2.1) indicates the existence of a 2-d triple point and the 2-d gas-liquid critical point shown in the fig. The corresponding critical and triple point temperatures are approximately: $T_c(2\text{-d}) \approx 118^{\circ}k$ $T_c(3\text{-d}) \approx 290^{\circ}k$; $T_t(2\text{-d}) \approx 100^{\circ}k$, $T_t(3\text{-d}) \approx 165^{\circ}k$. Dash further discussed the behavior of solid monolayers at low temperatures. In this, the quadratic temperature dependence of the heat capacity of incommensurate adsorbed solid monolayers ($C \sim T^2$) contrasted with the Debye cube law for 3-d solids ($C \sim T^3$) is stressed to be a difference attributed to systems of reduced dimension.

F.F. Abraham

"Melting in 2-d is first order: An Isothermal Isobaric Monte-Carlo Study" [2]

An isothermal-isobaric Monte-Carlo computer study of a monolayer Lennard-Jones system carried out by F. Abraham gives the information that melting in 2-d is first order; disproving the theoretical suggestions forwarded by Halperin and Nelson

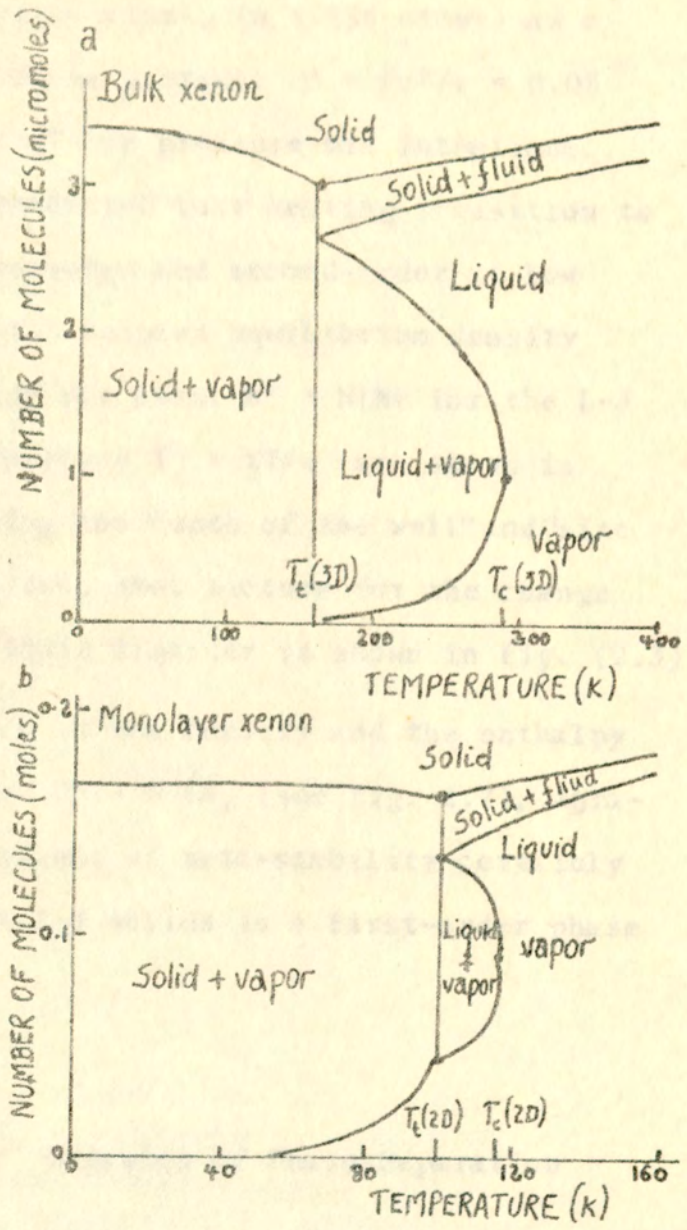


Fig. 2.1: Phase digs.,

a) for 3-d Xenon and

b) 2-d Xenon (after J.G. Dash) [7]

In this study, a number of atoms, (N = 256 atoms) as a sample system at a fixed reduced pressure $P^* = P\sigma^2/\varepsilon = 0.05$ was considered. The choice of low pressure was intentional, since Nelson and Halperin predicted that melting transition to be a first-order at high pressures and second-order at low pressures. The diagram of the reduced equilibrium density $^*\rho = \rho\sigma^2$ and reduced enthalpy per atom, $h^* = H/N\varepsilon$ for the L-J system against reduced temperature $T^* = KT/\varepsilon$ are shown in fig. (2.2), with ε and σ being the "depth of the well" and "size parameters" respectively. A snap shot picture for the change from crystalline order to liquid disorder is shown in fig. (2.3)

From the discontinuities in the density and the enthalpy at the transition temperature $T^* = 0.48$, (see fig. 2.2), Abraham concluded that "the existence of meta-stability certainly demonstrates that melting in 2-d solids is a first-order phase transition."

Koch, et.al.

Computer simulation study of "Dynamics of Phase Separation in 2-d fluids" [4]

In this research a molecular dynamics computer simulation study of the evolution of a 2-d fluid system of many atoms (5041) interacting by the L-J potential was carried out jointly by S.W. Koch, R.C. Desai and F.F. Abraham [4]. The computer simulation result for a kinetic limited growth of clusters

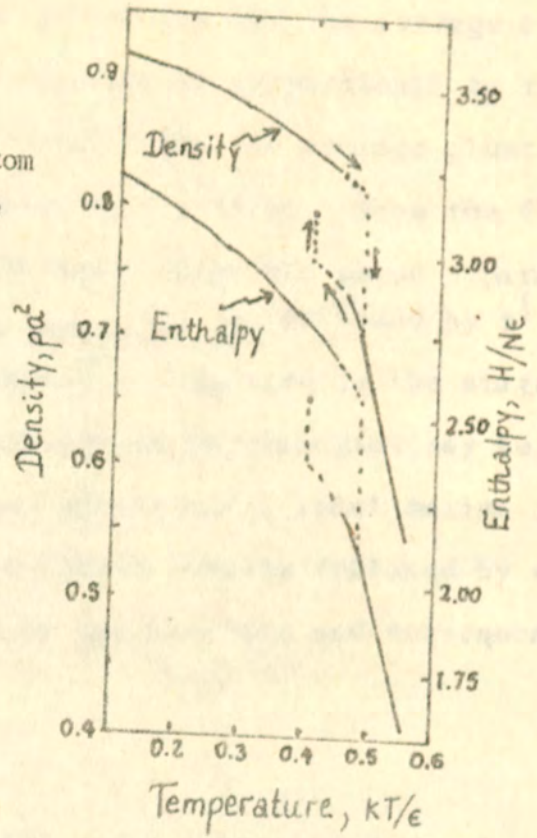


Fig. 2.2: Equilibrium density and enthalpy per atom against temperature for the Lennard-Jones system at a constant pressure. (After F.F. Abraham) [2]

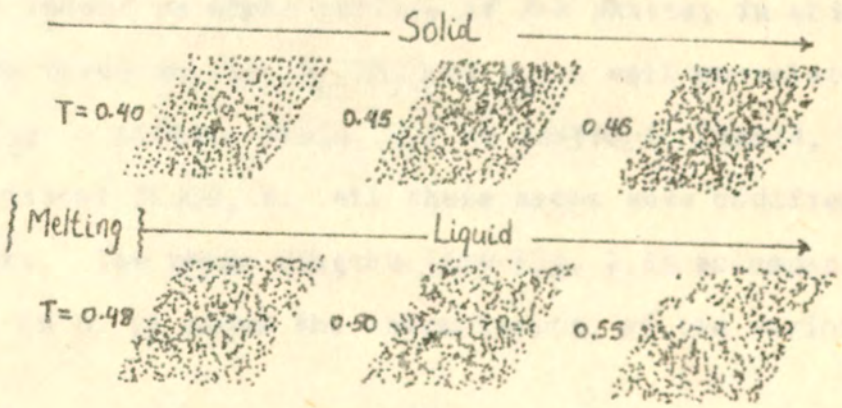


Fig. 2.3: Snapshot pictures of a L-J system simulated by an isothermal - isobaric Monte Carlo study for the given temperatures

show that the late time growth law for the average cluster size in an isothermal condition is proportional to $t^{\frac{1}{2}}$. A sketch of the computer results for the average cluster size, R(t) against time is shown by fig (2.4). From the figure it is an evident that at an early stage the phase separation process depends on time nearly as $t^{1/5}$ followed by $t^{\frac{1}{2}}$ for the late stage. The difference is suggested by the statement, "The time developing interatomic morphologies may be characterised as wave creation and growth until local maxima in density approaches the condensed liquid density followed by wave necking or break up leading to the creation and subsequent growth of macroscopic clusters."

J.M. Gay, et.al.

"Low-Energy-Electron-Diffraction (LEED) Studies of Ethane Films on Graphite." [6]

Properties of ethane monolayers have been investigated by the LEED method in the temperature range of 63.9-100K. The study showed an ample variety of 2-d phases; in which there were three solids, S_1, S_2 and S_3; a well correlated liquid, I_2; a lattice fluid, I_1; an isotropic liquid, L and a hypercritical fluid, F. All these names were codified by the authors. The phase diagram (see fig. 2.5) accompanied by the table on p. 14 shows the characterstic of the various 2-d phases.

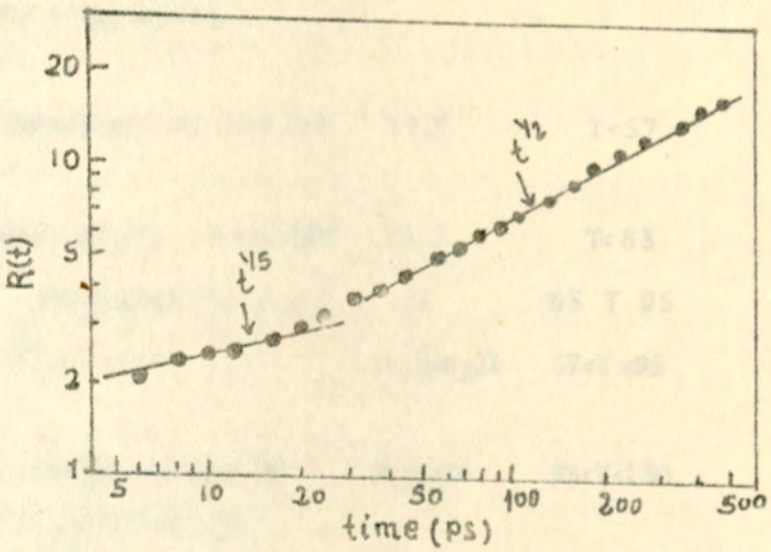


Fig. 2.4: Cluster size R(t) against time in the dynamics of phase separation in 2-d fluids. (After S.W. Koch. et.al.) [4]

Phases	Structure	Area per Molecules a/A^{o2}	Temperature Range (K)
S_1	Rectangular commensurate $4\sqrt{3}$ herringbone packing lying down molecules	21	T<65
S_2	rectangular commensurate $10 \times 2\sqrt{3}$ packing unknown	17.5	T<57
S_3	hexagonal commensurate $3 \times \sqrt{3}/\sqrt{s0^o}$	15.7	T<85
I_1	Lattice fluid commensurate 2 x 2	21	65 T 95
I_2	Well correlated liquid incommensurate	$16.5 \leq a \leq 21$	57<T<95
L	Isotropic liquid continious loss of positional and bond orientational order. (high-temp. I_1)	$21 \leq a \leq 24$	95<T<130
F	Hypercritical fluid, T_c (2-d)=130	$15.7 \leq a < \infty$	T>130

Some isothermal gas-I_1 transition curves which all have a structure of a sharp vertical step giving an impression of a first-order phase transition are shown in fig. (2.6a). The plot of the position of the step on a log (P) against 1/T diagram is shown by I_1 in fig. (2.7). The slope of this clapeyron line gives a value of the latent heat of condensation of phase I_1. Its value was found to be $Q(I_1) = 5.9 \pm 0.2$ K cal/mole.

In addition some selected isotherms of the 2-d I_2-S_3 transition are shown in fig (2.6b) all with a structure of vertical step being a sign of the first-order phase transition. This transition is clearly assured by the coexistence of the I_2 and S_3 LEED patterns along the vertical part of the isotherm. A plot of the transition temperature and pressure as in the case of 2-d gas-I_1, transition is given by line S_3 (see fig. 2.7). The isosteric heat transition is given by $Q(I_2\text{-}S_3) = 7.4 \pm 0.2$ Kcal/mole.

The LEED study carried out by the authors has shown the well correlated liquid phase structure of I_2 and the existence of an isotropic 2-d liquid L upto the critical temperature, T_c = 130K. Recalling the 3-d critical temperature, T_c (3-d)=305.5K for ethane, a ratio of T_c (2-d)/T_c (3-d) = 0.42 is obtained. This is one example of the special properties of matter of reduced dimensionality that has been confirmed by others [7].

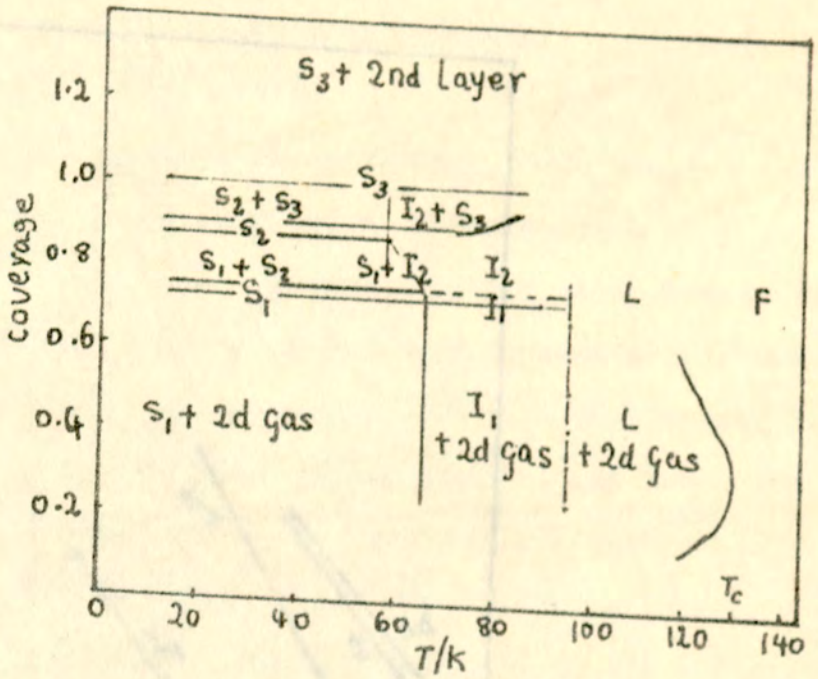


Fig. 2.5:
Phase dig. of monolayer ethane adsorbed on graphite (after J.M. Gay et.al.) [6]

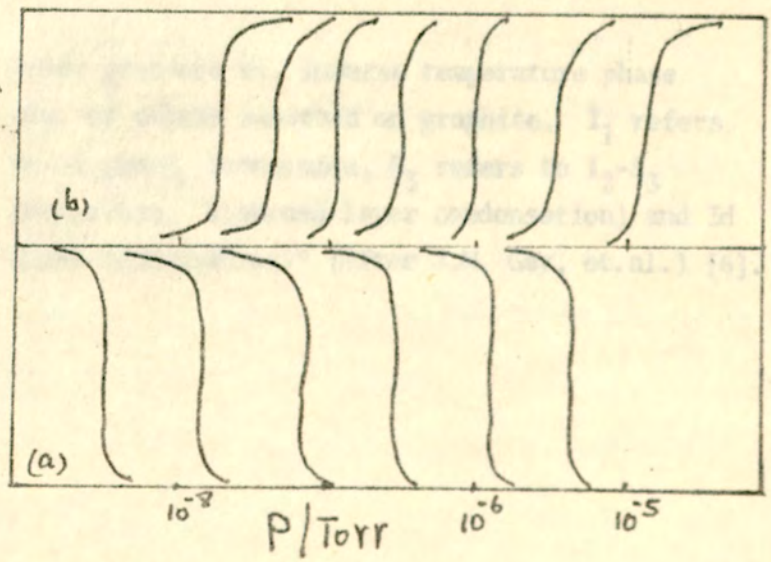


Fig. 2.6
Equilibrium isotherms of monolayers: (LEED study)
a) in the nbhd. of 2-d gas-I_1 transition and
b) in the nbhd. of I_2-S_3 transition. (after J.M. Gay ettal.) [6]

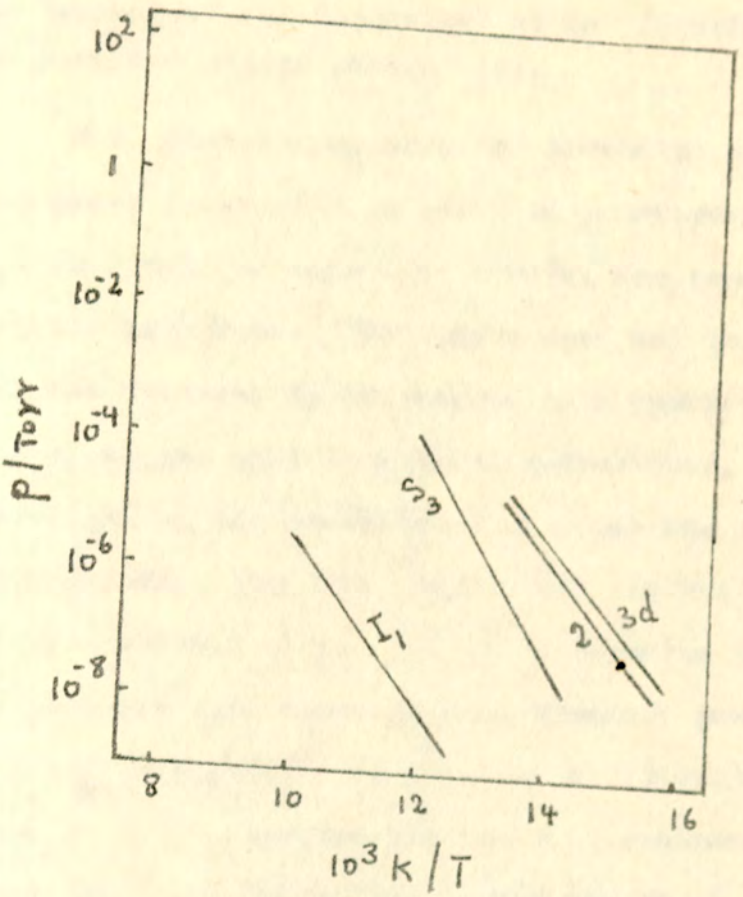


Fig. 2.7: Vapor pressure Vs. inverse temperature phase dig. of ethane adsorbed on graphite. I_1 refers to 2d gas-I_1 transition, S_3 refers to I_2-S_3 transition, "2(second-layer condensation) and 3d (bulk condensation)" (After J.M. Gay, et.al.) [6].

M.E.Fisher

An "apologia" and "overview" of an "interface wandering in pure and impure phases" [5].

M.E. Fisher considers the schematic phase diagram for a 2-d phase transition in adsorbed monolayers given in fig. (2.8) for an atomic or molecular species adsorbed on a planar crystalline adsorbent. The figure does not necessarily illustrate all the features to correspond to a specific real system. Fisher argues that at a given temperature, T and monolayer coverage, n, the coexistence of a gas and a liquid phase may be observed. When the temperature reaches the neighbourhood of the critical value, T_c, it is expected that the difference in coverage diminishes as an asymptotic power law given by $n_{Liq}-n_{gas} \approx B(\frac{T}{T_c}-1)^{\beta}$ as $\frac{T}{T_c}-1 \longrightarrow 0$. B is the critical amplitude, β is an experimental critical exponent which Onsager predicted to be $\frac{1}{8}$ for 2-d system and which has experimentally been verified by Kim and Chan [9] in a model of lattice gas system of methane adsorbed on graphite at $T_c \approx 68.67$ K. β was found in their specific-heat analysis data to be $\beta = 0.127 \pm 0.20$.

Moreover, the phase diagram of fig. (2.8) shows the possibility of occurence of phases and phase transitions which have no analogue in a 3-d system.

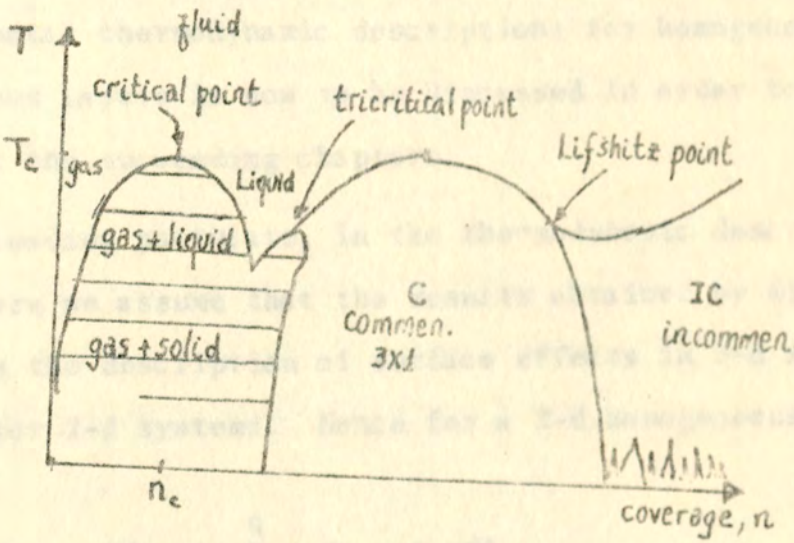


fig. 2.8: Schematic phase dig. of simple adsorbate on crystalline adsorbent. [illegible] not correspond to a specific real system. (After M.E. Fisher) [5].

Chapter Three

Thermodynamic Investigations of First-order Phase Transition in 2-D Systems

3.1 Basic Equations for Homogeneous Layers

As mentioned in the introduction, a general overview of the fundamental thermodynamic descriptions for homogeneous and heterogeneous layers is now to be discussed in order to develop a basis for the succeeding chapters.

As a leading postulate, in the thermodynamic description of 2-d layers we assume that the results obtained by Gibbs approach in the description of surface effects in 3-d systems are valid for 2-d systems. Hence for a 2-d homogeneous layer we have

$$du_f = Tds_f + \sum_{i=1}^{q} \mu_i dn_{if} + \sigma dA \qquad 3.1$$

$$u_f = Ts_f + \sum_{i=1}^{q} \mu_i dn_{if} + \sigma A \qquad 3.2$$

$$s_f dT + \sum_{i=1}^{q} n_{if} d\mu_i + Ad\sigma = 0 \qquad 3.3$$

u_f is the internal energy, T, the temperature, s_f the entropy, μ_i the chemical potential, n_{if} the number of particles or moles of the i^{th} component, σ the surface tension, A the surface area of the considered surface region.

A weak,layer-substrate interaction (physisorption) and thus the possibility of an independent time evolution of the layer is assumed. Consequently, in a state of thermal equi-

librium, the chemical potential, surface tension and temperature are the same throughout the layer. This assumption can be derived from the necessary equilibrium condition, which for the case of constant entropy, s_f, constant surface area, A, and constant number of moles, n_{if}, on the surface we obtain

$$(\delta u_f)_{s_f,A,n_{if}} = 0 \tag{3.4}$$

Since eq. (3.1) is of the same structure as the corresponding equation describing 3-d homogeneous systems, the condition for stable equilibrium are given by

$$\delta s_f \delta T + \delta\sigma\delta A + \sum_{i=1}^{q} \delta u_{if}\delta n_{if} > 0 \tag{3.5}$$

where δ denotes infinitesimal deviation from the considered state. From eq. (3.5) a number of relations valid for stable equilibrium states can be deduced. If we assume, e.g. isotermal conditions and take n_{if} and A as independent variables, we get

$$\sum_{i=1}^{q}\sum_{j=1}^{q} \frac{\partial u_{if}}{\partial n_{jf}} \delta n_{if}\delta n_{jf} + \sum_{i=1}^{q} \frac{\partial \mu_{if}}{\partial A} \delta n_{if}\delta A + \sum_{j=1}^{q} \frac{\partial\sigma}{n_{jf}} \delta n_{jf}\delta A + \frac{\partial\sigma}{\partial A}(\delta A)^2 > 0 \tag{3.6}$$

q, being the number of the different components. This condition is always fulfilled if all major subdeterminants and the determinant of matrix, J in (3.7) are positive

$$J = \begin{bmatrix} \frac{\partial \mu_{1f}}{\partial n_{1f}} & \frac{\partial \mu_{1f}}{\partial n_{2f}} & \cdots\cdots & \frac{\partial \mu_{1f}}{\partial n_{qf}} & \frac{\partial \mu_{1f}}{\partial A} \\ \frac{\partial \mu_{2f}}{\partial n_{1f}} & \frac{\partial \mu_{2f}}{\partial n_{2f}} & \cdots\cdots & \frac{\partial \mu_{2f}}{\partial n_{qf}} & \frac{\partial \mu_{2f}}{\partial A} \\ & & & & \\ \frac{\partial \mu_{qf}}{\partial n_{1f}} & \frac{\partial \mu_{qf}}{\partial n_{2f}} & \cdots\cdots & \frac{\partial \mu_{qf}}{\partial n_{qf}} & \frac{\partial \mu_{qf}}{\partial A} \\ \frac{\partial \sigma}{\partial n_{1f}} & \frac{\partial \sigma}{\partial n_{2f}} & \cdots\cdots & \frac{\partial \sigma}{\partial n_{qf}} & \frac{\partial \sigma}{\partial A} \end{bmatrix} \tag{3.7}$$

In particular it follows that ineq. (3.8) have to be fulfilled.

$$\left(\frac{\partial \sigma}{\partial A}\right)_{T,n_{jf}} > 0 \quad ; \quad \left(\frac{\partial \mu_{jf}}{\partial n_{jf}}\right)_{T,A,n_{if}} > 0 \tag{3.8}$$

For non-equilibrium processes in the layer, eq. (3.1) has to be replaced by

$$du_f \leq Tds_f + \sum_{i=1}^{q} \mu_i dn_{if} + \sigma dA \tag{3.9}$$

for a constant temperature eq. (3.9) can be expressed as

$$d(u_f - Ts_f) \leq \sum_{i=1}^{q} \mu_i dn_{if} + \sigma dA \tag{3.10}$$

and for an isothermal closed system of constant surface area it is given by

$$dF_f \leq 0 \tag{3.11}$$

where here the 2-d Helmholtz free energy, F_f of the surface is defined in the usual way by

$$F_f = u_f - Ts_f \tag{3.12}$$

If the surface area is variable but the surface tension of the considered layer is constant, we may have eq. (3.13) instead of eq. (3.10)

$$d(u_f - Ts_f - \sigma A)_{T,\sigma} \leq 0 \tag{3.13}$$

and the 2-d Gibbs function is defined by

$$G_f = u_f - Ts_f - \sigma A = F_f - \sigma A \tag{3.14}$$

The above definitions are introduced to make the properties of 2-d potentials similar to the corresponding potentials in the 3-d case.

3.2 Thermodynamics of Adsorbed Heterogeneous Layers in Equilibrium States

For the development of the theory, the coexistence of two different and nearly homogeneous layers in thermodynamic equilibrium is considered. The coexistence of such two phases implies the presence of an inhomogeneous interfacial region (see fig. 3.1). In addition it is assumed that our system is not disturbed by external fields like magnetic and electric fields. Moreover all particles that hit the substrate are assumed to stick to it and as monolayer coverage is approached, late arriving and impinging particles will hit occupied areas and rebound without influencing the layer.

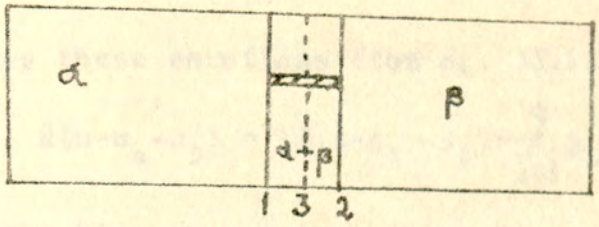


Fig (3.1) a monolayer model fig. of two different homogeneous regions α and β with an inhomogeneous interface region, α - β. 1 and 2 specify lines separating the homogeneous regions from the inhomogeneous one. 3 is an ideal dividing line.

Considering an infinitesimal part of the interfacial region of fig. (3.1), we postulate (2) that for fixed positions of lines 1, 2, and 3 the internal energy of the infinitesimal section can be expressed by

$$du = Tds + \sum_{i=1}^{q} \mu_i dn_i \qquad (3.15)$$

where at equilibrium, the values T, and μ_i are equal to the corresponding values of the surrounding phases. The subscript "f" is omitted for convenience.

Going over from the actual interface region to an idealized dividing model, (line 3), in the α - β region where this line divides the region into two parts with the same properties as in the homogeneous regions, α and β respectively the internal energy of each homogeneous phase for a fixed position of line 3 is given by

$$du_\alpha = Tds_\alpha + \sum_{i=1}^{q} \mu_i dn_{i\alpha} \qquad (a)$$

$$du_\beta \quad Tds_\beta + \sum_{i=1}^{q} \mu_i dn_{i\beta} \qquad (b) \qquad (3.16)$$

subtracting these equations from eq. (3.15) it gives

$$d(u-u_\alpha-u_\beta) = Td(s-s_\alpha-s_\beta)+\sum_{i=1}^{q}\mu_i(n_i-n_{i\alpha}-n_{i\beta}) \quad (3.17)$$

Defining the line excess quantities by

$$u_L = u-u_\alpha-u_\beta\ ,\ s_L=s-s_\alpha-s_\beta\ ,\ n_{iL}= n_i-n_{i\alpha}-n_{i\beta} \quad (3.18)$$

eq. (3.17) may be expressed as

$$du_L = Tds_L + \sum_{i=1}^{q}\mu_i dn_{iL} \quad (3.19)$$

The line excess quantities introduced here are excess quantities over the values which would describe the film system consisting of two uniform parts [14]. The above relations are valid for any arbitrary position of lines 1 and 2 and can be identifies with the boundaries of the system as a whole.

Taking the length, l, and curvature, c, of the ideal dividing line as an additional thermodynamic variables, the correction term, du_L is expressed in the following way (Postulate 3).

$$du_L = Tds_L + \sum_{i=1}^{q}\mu_i dn_{iL} + \kappa dl + Cdc \quad (3.20)$$

κ and C are parameters that can be functions of T, μ_i, l and c. Depending on the position of the dividing line, κ and the parameter, C, can have different values. It is possible to define the position of the dividing line in such a way that $C = 0$ (to be shown later). This special position of the dividing line is named as line of tension and κ as the line tension [15].

From the extensive characterstics of s_L, n_{iL}, 1 and the intensive characterstic of c and by Euler's theorem we can have eq. (3.21).

$$u_L = Ts_L + \sum_{i=1}^{q} \mu_i n_{iL} + \kappa l \tag{3.21}$$

out of which we have eq. (3.22) in regard to eq. (3.20).

$$s_L dT + \sum_{i=1}^{q} n_{iL} d\mu_i + l d\kappa = C dc \tag{3.22}$$

With the imposition of C = 0, we obtain

$$s_L dT + \sum_{i=1}^{q} n_{iL} d\mu_i + l d\kappa = 0 \tag{3.23}$$

eq. (3.23) is analogous to the Gibbs adsorption equation. For the isothermal case it gives

$$\sum_{i=1}^{q} n_{iL} d\mu_{iL} + l d\kappa = 0 \tag{3.24}$$

If the position of the boundaries of the system as a whole and of the dividing line varies, eqs. (3.16) have to read as

$$\begin{aligned} du_\alpha &= Tds_\alpha + \sum_{i=1}^{q} \mu_i dn_{i\alpha} + \sigma_\alpha dA_\alpha \quad (a) \\ du_\beta &= Tds_\beta + \sum_{i=1}^{q} \mu_i dn_{i\beta} + \sigma_\beta dA_\beta \quad (b) \end{aligned} \tag{3.25}$$

and the total change of the inernal energy of our considered system is

$$du = Tds + \sum_{i=1}^{q} \mu_i dn_i + \sigma_\alpha dA_\alpha + \sigma_\beta dA_\beta + \kappa dl + C dc \tag{3.26}$$

where, $u = u_\alpha + u_\beta + u_L$, $s = s_\alpha + s_\beta + s_L$, $n_i = n_{i\alpha} + n_{i\beta} + n_{iL}$ (3.27)

Applying eq. (3.4) and taking the constraint, $A = A_\alpha + A_\beta =$ constant, into account, the mechanical equilibrium condition reads as

$$\sigma_\alpha - \sigma_\beta + \kappa \frac{dl}{dA_\alpha} + C \frac{dc}{dA_\alpha} = 0 \tag{3.28}$$

For a minimum value of u_L, a minimum length of a closed curve, l, of the ideal dividing line is required. This minimum is reached for a circle and eq. (3.28) is reduced to eq. (3.29).

$$\sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha} - \frac{C}{2\Pi r_\alpha^3} = 0 \tag{3.29}$$

r_α is the radius of the circular region of the α-phase. If we rearrange eq. (3.29) we obtain

$$\sigma_\beta - \sigma_\alpha = \frac{\kappa}{r_\alpha} - \frac{C}{2\Pi r_\alpha^3} \tag{3.30}$$

This is analogous to the Young-Laplace relation given for 3-d case [16].

Redefining the position of the dividing line in a way that the physical state of the system is not affected, i.e., u, T, s, μ_i, n_i, σ_α, σ_β being constants, eq. (3.26) yields

$$\sigma_\alpha - \sigma_\beta + \kappa \left[\frac{dl}{dA_\alpha}\right] + C \left[\frac{dc}{dA_\alpha}\right] = 0 \tag{3.31}$$

where the square brackets denote the special variation considered. Moreover, for such type of variation, eq. (3.22) leads to eq. (3.32).

$$l\,[d\kappa] = C\,[dc] \tag{3.32}$$

Eqs. (3.31) and (3.32) give

$$\sigma_\alpha - \sigma_\beta + \kappa \left[\frac{dl}{dA}\right]_\alpha + 1\left[\frac{d\kappa}{dA}_\alpha\right] = 0 \qquad \text{(a)}$$

$$\sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha} + \left[\frac{d\,\kappa}{dr_\alpha}\right] = 0 \qquad \text{(b)} \tag{3.33}$$

This is the 2-d analogue of the generalized 3-d Young-Laplace equation [16]. Eq. (3.33b) describes the variation of κ with a change of the position of the dividing curve and the physical state being unvaried. There may exist a specific position of this line, in which κ has an extremum value defined by

$$\left[\frac{d\,\kappa}{dr_\alpha}\right] = \sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha} = 0 \tag{3.34}$$

Comparing eqs. (3.29) and (3.33b), we obtain

$$\left[\frac{d\kappa}{dr}\right]_\alpha = \frac{C}{2\Pi r_\alpha^3} = 0 \tag{3.35}$$

Thus we come to the conclusion, that for the line of tension, ($C = 0$), κ has an extremum value compared with all other possible definitions of the dividing line. This extremum is aminimum since

$$\frac{d^2\kappa}{dr_\alpha^2} = \frac{\kappa}{r_\alpha^2} > 0 \tag{3.36}$$

For the line of tension being the dividing line, the mechanical equilibrium condition can be expressed by the modified 2-d Young-Laplace eq. (3.37).

$$\sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha} = 0 \tag{3.37}$$

3.3 Non-Equilibrium States of Heterogeneous Layers and the Thermodynamic Potentials

To generalize the thermodynamic descriptions of heterogeneous layers we postulate (4) that in non-equilibrium states, each of the 2-d bulk phases and the boundary-phase are in a state of intrinsic thermodynamic equilibrium described by

$$\begin{aligned} u_\alpha &= T_\alpha s_\alpha + \sigma_\alpha A_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} n_{i\alpha} \\ du_\alpha &= T_\alpha ds_\alpha + \sigma_\alpha dA_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} dn_{i\alpha} \end{aligned} \qquad \text{(a)}$$

$$\begin{aligned} u_\beta &= T_\beta s_\beta + \sigma_\beta A_\beta + \sum_{i=1}^{q} \mu_{i\beta} n_{i\beta} \\ du_\beta &= T_\beta ds_\beta + \sigma_\beta dA_\beta + \sum_{i=1}^{q} \mu_{i\beta} dn_{i\beta} \end{aligned} \qquad \text{(b)} \qquad (3.38)$$

$$\begin{aligned} u_L &= T_L s_L + \kappa l + \sum_{i=1}^{q} \mu_{iL} n_{iL} \\ du_L &= T_L ds_L + \kappa dl + \sum_{i=1}^{q} \mu_{iL} dn_{iL} \end{aligned} \qquad \text{(c)}$$

Moreover the 2-d analogue of the Gibbs adsorption and the Gibbs adsorption equations themselves have to be fulfilled as (3.39).

$$s_\alpha dT_\alpha + A_\alpha d\sigma_\alpha + \sum_{i=1}^{q} n_{i\alpha} d\mu_{i\alpha} = 0 \qquad \text{(a)}$$

$$s_\beta dT_\beta + A_\beta d\sigma_\beta + \sum_{i=1}^{q} n_{i\beta} d_{\mu i\beta} = 0 \qquad \text{(b)} \qquad (3.39)$$

$$s_L dT_L + l d\kappa + \sum_{i=1}^{q} n_{iL} d\mu_{iL} = 0 \qquad \text{(c)}$$

In principle, T_α, T_β, $\mu_{i\alpha}$, $\mu_{i\beta}$, σ_α and σ_β and κ may be measured directly from their respective phases. But T_L and μ_{iL} cannot be determined directly from the adjacent homogeneous phases and thus we postulate (5) that these parameters are equal to the respective variables of the phase with a higher surface density - α-phase in our case [11,15]. This will lead to the physically satisfactory conclusion that κ is determined by the properties of the surface with higher surface density.

Considering an evolution of a 2-d cluster (α-phase) of higher density compared with the medium (β-phase), we may thus write eq. (3.40) for the internal energy of the considered system (cluster in the otherwise homogeneous medium).

$$u = T_\alpha \tilde{s} + \sigma_\alpha A_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} \tilde{n}_{i\alpha} + T_\beta s_\beta + \sigma_\beta A_\beta + \sum_{i=1}^{q} \mu_{i\beta} n_{i\beta} + \kappa l \qquad (3.40)$$

In which we have introduced the notations:

$$\tilde{s}_\alpha = s_\alpha + s_L \,, \quad \tilde{n}_{i\alpha} = n_{i\alpha} + n_{iL}$$

The change in internal energy, du, is:

$$\begin{aligned} du = {} & T_\alpha d\tilde{s}_\alpha + \sigma_\alpha dA_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} d\tilde{n}_{i\alpha} \\ & + T_\beta ds_\beta + \sigma_\beta dA_\beta + \sum_{i=1}^{q} \mu_{i\beta} dn_{i\beta} + \kappa dl \end{aligned} \qquad (3.41)$$

Considering the constraints

$$\begin{aligned} s &= \tilde{s}_\alpha + s_\beta = \text{const.} \\ A &= A_\alpha + A_\beta = \text{const.} \\ n_i &= \tilde{n}_{i\alpha} + n_{i\beta} = \text{const.} \,, \end{aligned} \qquad (3.42)$$

for equilibrium process the internal energy is expressed by eq. (3.43)

$$du = (T_\alpha - T_\beta)d\tilde{s}_\alpha + (\sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha})dA_\alpha + \sum_{i=1}^{q} (\mu_{i\alpha} - \mu_{i\beta})d\tilde{n}_{i\alpha} \tag{3.43}$$

and the equilibrium conditions are obtained as

$$T_\alpha = T_\beta \ , \ \mu_{i\alpha} = \mu_{i\beta} \ , \ \sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha} = 0 \tag{3.44}$$

Once we have the internal energy expression, the other thermodynamic potentials may be introduced easily. If the temperature is constant, the Helmholtz free energy is defined by eq. (3.45) below.

$$F = u - Ts \tag{3.45}$$

From eq. (3.40) and the above considered equations, we can have eqs. (3.46)

$$F = \sigma_\alpha A_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} \tilde{n}_{i\alpha} + \sigma_\beta A_\beta + \sum_{i=1}^{q} \mu_{i\beta} n_{i\beta} + \kappa l$$

$$dF = \sigma_\alpha dA_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} d\tilde{n}_{i\alpha} + \sigma_\beta dA_\beta + \sum_{i=1}^{q} \mu_{i\beta} dn_{i\beta} + \kappa dl \tag{3.46}$$

It is evident from eq. (3.46), that κ is in some approximation the Helmholtz free energy per unit length of the dividing line. It follows, that $\kappa > 0$ otherwise the cluster would dissolve and a two-phase system would not evolve.

The Gibbs function is similarly defined by

$$G = u - Ts - \sigma A \; ; \quad A = A_\alpha + A_\beta = \text{const.} \tag{3.47}$$

For $\sigma_\beta = \sigma = \text{constant}$, eq. (3.47) gives eq. (3.48)

$$G = (\sigma_\alpha - \sigma_\beta)A_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} \tilde{n}_{i\alpha} + \sum_{i=1}^{q} \mu_{i\beta} n_{i\beta} + \kappa l$$

$$dG = (\sigma_\alpha - \sigma_\beta)dA_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} d\tilde{n}_{i\alpha} + \sum_{i=1}^{q} \mu_{i\beta} dn_{i\beta} + \kappa dl \tag{3.48}$$

These are the fundamental thermodynamic potentials we will need in our work, because they contain all the thermodynamic information about the monolayer systems for the constraints we will discuss in detail in the next chapters.

3.4 Stability Investigation

The stability analysis we go over in this section is developed for the case of a circular 2-d single cluster (α) in the homogeneous medium (β) and can be generated easily to many clusters. As an approximation we assume a zero value of the correction terms n_{iL}. In addition constancy of the temperature is supposed. The equilibrium states are then determined by

$$\delta G = (\sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha})\delta A_\alpha + \sum_{i=1}^{q} (\mu_{i\alpha} - \mu_{i\beta})\delta n_{i\alpha} = 0 \tag{3.49a}$$

or

$$\delta F = (\sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha})\delta A_\alpha + \sum_{i=1}^{q} (\mu_{i\alpha} - \mu_{i\beta})\delta n_{i\alpha} = 0 \tag{3.49b}$$

For both of the cases we considered, these states are stable states if they fulfill the inequality requirements of (3.50).

$$\delta^2 F > 0 \quad \text{or} \quad \delta^2 G > 0 \tag{3.50}$$

If $n_{i\alpha}$ and A_α are taken as the independent variables, then the inequality expressions of (3.50) yield

$$\sum_{\substack{i=1\\j=1}}^{q} \left(\frac{\partial \mu_{i\alpha}}{\partial n_{j\alpha}} - \frac{\partial \mu_{i\beta}}{\partial n_{j\alpha}}\right) n_j \delta n_{j\alpha} \delta n_{i\alpha} + \sum_{i=1}^{q} \left(\frac{\partial \mu_{i\alpha}}{\partial A_\alpha} - \frac{\partial \mu_{i\beta}}{\partial A_\alpha}\right) A \delta n_{i\alpha} \delta A_\alpha > 0 \tag{3.50a}$$

$$+ \sum_{j=1}^{q} \left(\frac{\partial \sigma_\alpha}{\partial n_{j\alpha}} - \frac{\partial \sigma_\beta}{\partial n_{j\alpha}}\right) n_j, r_\alpha \delta A_\alpha \delta n_{j\alpha} + \left(\frac{\partial \sigma_\alpha}{\partial A_\alpha} - \frac{\partial \sigma_\beta}{\partial A_\alpha} - \frac{\kappa}{2\pi r_\alpha^3}\right) A (\delta A_\alpha)^2$$

This can be written in the form of

$$\sum_{\substack{i=1\\j=1}}^{q} \left(\frac{\partial \mu_{i\alpha}}{\partial n_{j\alpha}} - \frac{\partial \mu_{i\beta}}{\partial n_{j\beta}}\right) n_j \delta n_{j\alpha} \delta n_{i\alpha} + \sum_{i=1}^{q} \left(\frac{\partial \mu_{i\alpha}}{\partial A_\alpha} + \frac{\partial \mu_{i\beta}}{\partial A_\beta}\right) A \delta n_{i\alpha} \delta A_\alpha > 0 \tag{3.50b}$$

$$+ \sum_{j=1}^{q} \left(\frac{\partial \sigma_\alpha}{\partial n_{j\alpha}} + \frac{\partial \sigma_\beta}{\partial n_{j\beta}}\right) n_j, r_\alpha \delta A_\alpha \delta n_{j\alpha} + \left(\frac{\partial \sigma_\alpha}{\partial A_\alpha} + \frac{\partial \sigma_\beta}{\partial A_\beta} - \frac{\kappa}{2\pi r_\alpha^3}\right) (\delta A_\alpha)^2$$

This inequality holds always if the principal subdeterminants and the determinant J of matrix (3.51) are positive

$$J = \begin{vmatrix} \frac{\partial \mu_{1\alpha}}{\partial n_{1\alpha}} + \frac{\partial \mu_{1\beta}}{\partial n_{1\beta}} & \frac{\partial \mu_{1\alpha}}{\partial n_{2\alpha}} + \frac{\partial \mu_{1\beta}}{\partial n_{2\beta}} & \cdots & \frac{\partial \mu_{1\alpha}}{\partial A_{\alpha}} + \frac{\partial \mu_{1\beta}}{\partial A_{\beta}} \\ \frac{\partial \mu_{2\alpha}}{\partial n_{1\alpha}} + \frac{\partial \mu_{2\beta}}{\partial n_{1\beta}} & \frac{\partial \mu_{2\alpha}}{\partial n_{2\alpha}} + \frac{\partial \mu_{2\beta}}{\partial n_{2\beta}} & \cdots & \frac{\partial \mu_{2\alpha}}{\partial A_{\alpha}} + \frac{\partial \mu_{2\beta}}{\partial A_{\beta}} \\ \vdots & \vdots & & \vdots \\ \frac{\partial \mu_{q\alpha}}{\partial n_{1\alpha}} + \frac{\partial \mu_{q\beta}}{\partial n_{1\beta}} & \frac{\partial \mu_{q\alpha}}{\partial n_{2\alpha}} + \frac{\partial \mu_{q\beta}}{\partial n_{2\beta}} & \cdots & \frac{\partial \mu_{q\alpha}}{\partial A_{\alpha}} + \frac{\partial \mu_{q\beta}}{\partial A_{\beta}} \\ \frac{\partial \sigma_{\alpha}}{\partial n_{1\alpha}} + \frac{\partial \sigma_{\beta}}{\partial n_{1\beta}} & \frac{\partial \sigma_{\alpha}}{\partial n_{2\alpha}} + \frac{\partial \sigma_{\beta}}{\partial n_{2\beta}} & \cdots & \frac{\partial \sigma_{\alpha}}{\partial A_{\alpha}} + \frac{\partial \sigma_{\beta}}{\partial A_{\beta}} - \frac{\kappa}{2\Pi r_{\alpha}^{3}} \end{vmatrix} \qquad (3.51)$$

Due to the intrinsic stability condition of each homogeneous phases (cf. section 3.1), all subdeterminants are positive and the condition for stability is only when $J > 0$.

For our special case of a one component system, the stability condition is reduced to inequality form of 3.52) below.

$$\begin{vmatrix} \frac{\partial \mu_{\alpha}}{\partial n_{\alpha}} + \frac{\partial \mu_{\beta}}{\partial n_{\beta}} & \frac{\partial \mu_{\alpha}}{\partial A_{\alpha}} + \frac{\partial \mu_{\beta}}{\partial A_{\beta}} \\ \frac{\partial \sigma_{\alpha}}{\partial n_{\alpha}} + \frac{\partial \sigma_{\beta}}{\partial n_{\beta}} & \frac{\partial \sigma_{\alpha}}{\partial A_{\alpha}} + \frac{\partial \sigma_{\beta}}{\partial A_{\beta}} - \frac{\kappa}{2\Pi r_{\alpha}^{3}} \end{vmatrix} > 0 \qquad (3.52)$$

μ_{α}, σ_{α} and μ_{β}, σ_{β} can be considered as functions of the surface densities Γ_{α} and Γ_{β} respectively as it can be shown below.

For isothermal conditions we can write the variation of the Helmholtz free energy for the bulk α-phase as

$$dF_\alpha = \sigma_\alpha dA_\alpha + \sum_{i=1}^{q} \mu_{i\alpha} dn_{i\alpha}$$

out of which σ_α and $\mu_{i\alpha}$ are to be

$$\sigma_\alpha = \left(\frac{\partial F_\alpha}{\partial A_\alpha}\right)_{T,n_{i\alpha}}, \quad \mu_{i\alpha} = \left(\frac{\partial F_\alpha}{\partial n_{i\alpha}}\right)_{T,A_\alpha,n_{j\alpha}} \tag{3.53}$$

Since F_α is a function of the independent variables A_α and $n_{i\alpha}$, it is obvious, that for the one component case,

$$\begin{aligned} \sigma_\alpha &= \sigma_\alpha(n_\alpha, A_\alpha) \\ \mu_\alpha &= \mu_\alpha(n_\alpha, A_\alpha) \end{aligned} \tag{3.54}$$

or

$$\begin{aligned} \sigma_\alpha &= \sigma_\alpha(\Gamma_\alpha) \\ \mu_\alpha &= \mu_\alpha(\Gamma_\alpha) \end{aligned} \quad ; \quad \Gamma_\alpha = \frac{n\alpha}{A_\alpha}$$

The same argument can lead to $\mu_\beta(\Gamma_\beta)$ and $\sigma_\beta(\Gamma_\beta)$.

Moreover, for isothermal conditions and one component system we obtain, from eq. (3.39a):

$$A_\alpha d\sigma_\alpha + n_\alpha d\mu_\alpha = 0$$

and the partial derivatives of the surface tension can be expressed in terms of the chemical potentials as below.

$$\frac{\partial \sigma_\alpha}{\partial n_\alpha} = -\Gamma_\alpha \frac{\partial \mu_\alpha}{\partial n_\alpha} = -\Gamma_\alpha \frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} \frac{\partial \Gamma_\alpha}{\partial n_\alpha} = -\frac{\Gamma_\alpha}{A_\alpha} \frac{\partial \mu_\alpha}{\partial \Gamma_\alpha}$$

$$\frac{\partial \sigma_\beta}{\partial n_\beta} = -\frac{\Gamma_\beta}{A_\beta} \frac{\partial \mu_\beta}{\partial \Gamma_\beta}$$

$$\frac{\partial \sigma_\alpha}{\partial A_\alpha} = -\Gamma_\alpha \frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} \frac{\partial \Gamma_\alpha}{\partial A_\alpha} = \frac{\Gamma_\alpha^2}{A_\alpha} \frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} \qquad (3.55)$$

$$\frac{\partial \sigma_\beta}{\partial A_\beta} = \frac{\Gamma_\beta^2}{A_\beta} \frac{\partial \mu_\beta}{\partial \Gamma_\beta}$$

The partial derivative of the chemical potentials with respect to A_α can be transformed to a derivative with respect to Γ_α as

$$\frac{\partial \mu_\alpha}{\partial A_\alpha} = -\frac{\Gamma_\alpha}{A_\alpha} \frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} \qquad (3.56)$$

Thus instead of inequality (3.52) we may have (3.57).

$$\begin{vmatrix} \frac{1}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} + \frac{1}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} & -\frac{\Gamma_\alpha}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} - \frac{\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} \\ -\frac{\Gamma_\alpha}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} - \frac{\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} & \frac{\Gamma_\alpha^2}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} + \frac{\Gamma_\beta^2}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} - \frac{\kappa}{2\Pi r_\alpha^3} \end{vmatrix} > 0 \qquad (3.57)$$

when (3.57) is evaluated we get

$$-\frac{\kappa}{2\Pi r_\alpha^3}\left(\frac{1}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} + \frac{1}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta}\right) + \frac{(\Gamma_\alpha - \Gamma_\beta)^2}{A_\alpha A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta}\frac{\partial \mu_\alpha}{\partial \Gamma_\beta} > 0 \qquad (3.58)$$

From the stability condition of (3.58) the following conclusions can be developed.

When the characterstic potential is F, it means, if the constraints are given by

$$A = A_\alpha + A_\beta = \text{const.} \, , \; T = \text{const.} \, ,$$
$$n = n_\alpha + n_\beta = \text{const.}$$

the variation of the size of the cluster leads to a depletion which is a variation of the state of the medium. As a result, a stable equilibrium state - evolution of a cluster of finite size in the otherwise homogeneous medium (β-phase), is possible.

In contrast, if depletion effect does not occur, $\mu_\beta = \mu_\beta(\Gamma_\beta)$ is constant and a finite sized state cluster cannot evolve and only unstable equilibrium states are possible.

All the arguments and the results obtained are qualitatively similar to 3-d case [17,18]. Under the same footing, the stability analysis can be carried out for any other constraints and also for the case where many clusters exist in the system.

3.5 Curvature Dependence of Line Tension

The parameters of a 2-d cluster in equilibrium with the medium in which both belong to a one-component system under isothermal conditions, are (cf. eq. (3.44) given by:

$$\mu_\alpha = \mu_\beta = \mu$$
$$\sigma_\alpha - \sigma_\beta + \frac{\kappa}{r_\alpha} = 0 \qquad (3.59)$$

The line of tension is chosen as the dividing line and for a given size of the clusters, the line tension, κ has a properly defined value. It is of interest to investigate how this line tension depends on the size of the cluster. Such an analysis is carried out now to check, under which conditions such a dependence has to be taken into account.

From eqs. (3.59) we can have

$$d\mu_\alpha = d\mu_\beta = d\mu \quad (a)$$
$$d\sigma_\alpha - d\sigma_\beta = - d\left(\frac{\kappa}{r_\alpha}\right) \quad (b) \qquad (3.60)$$

and from the Gibbs adsorption isotherms of eqs. (3.61),

$$A_\alpha d\sigma_\alpha + n_\alpha d\mu_\alpha = 0$$
$$A_\beta d\sigma_\beta + n_\beta d\mu_\beta = 0 \qquad (3.61)$$

eq. (3.60b) is reduced to

$$(\Gamma_\beta - \Gamma_\alpha)\, d\mu = - d\left(\frac{\kappa}{r_\alpha}\right), \quad (a)$$
$$(\Gamma_\beta - \Gamma_\alpha)\, d\mu = - \frac{d\kappa}{dr_\alpha} - \kappa d\left(\frac{1}{r_\alpha}\right), \quad (b) \qquad (3.62)$$

Again for isothermal conditions and a one component system eq. (3.23) reads:

$$d\kappa = - \frac{n_L}{\ell} d\mu = - \Lambda_L d\mu \; ; \quad \Lambda_L = \frac{n_L}{\ell} \qquad (3.63)$$

and thus from eqs. (3.62b) and 3.63) we have

$$-\left[\frac{\Gamma_\beta - \Gamma_\alpha}{\Lambda_L} - \frac{1}{r_\alpha}\right] d\kappa = -\kappa d\left(\frac{1}{r_\alpha}\right)$$

$$\left[\frac{1}{\Psi} + \frac{1}{r_\alpha}\right] d\kappa = -\kappa d\left(\frac{1}{r_\alpha}\right) \qquad (3.64)$$

where, $\Psi = \dfrac{\Lambda_L}{\Gamma_\alpha - \Gamma_\beta}$ is a 2-d Tolman coefficient.

Rearranging eq. (3.64) we have

$$d\ln(\kappa) = -d\ln\left[1 + \frac{\Psi}{r_\alpha}\right] + \frac{\frac{1}{r_\alpha} d\Psi}{1+(\Psi/r_\alpha)}$$

The general solution of this differential equation is given by

$$\kappa(r_\alpha) = \frac{\kappa_\infty}{1+(\Psi/r_\alpha)} \mathrm{EXP} \int_\infty^{r_\alpha} \frac{\frac{1}{r}\frac{\partial \Psi}{\partial r}}{1+(\Psi/r)} dr \qquad (3.65)$$

Eq. (3.65) is one form of the most general thermodynamic relation that describe the curvature dependence of the line tension. It is qualitatively analogous to the expression for the curvature dependence of surface tension [16].

When Ψ is constant eq. (3.65) is reduced to eq. (3.66)

$$\kappa(r_\alpha) = \frac{\kappa_\infty}{1+(\Psi/r_\alpha)} \qquad (3.66)$$

and it is the 3-d analogue of 2-d Tolman equation for the curvature dependence of line tension [16].

From eq. (3.66) and also from the general expression of eq. (3.65), it is evident that the region where a curvature dependence of line tension becomes important is determined by the value of Ψ. To determine Ψ let us discuss in addition to Gibbs' dividing line of tension also another dividing line (see fig. 3.2), called as the equimolecular dividing line, defined by $n_L = 0$.

For the Gibbs' dividing line ($C = 0$), the total number of particles, n, are expressed by: (cf. eq. 3.27).

$$n = n_\alpha + n_\beta + n_L = \Gamma_\alpha A_\alpha + \Gamma_\beta A_\beta + n_L \qquad (3.67a)$$

For the equimolecular dividing line we have for n as

$$n = n_\alpha^{(e)} + n_\beta^{(e)} = \Gamma_\alpha A_\alpha^{(e)} + \Gamma_\beta A_\beta^{(e)} \qquad (3.67b)$$

The superscript, e, indicates the equimolecular dividing line.

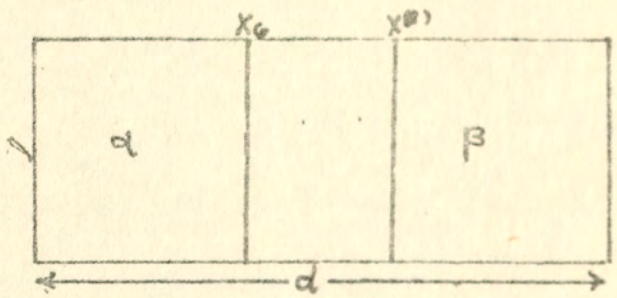


Fig. 3.2: Model fig. for the two arbitrary interfaces, $X_G, X^{(e)}$ of a finite 2-d system.

X_G and $X^{(e)}$ in fig. 3.2, are the position of Gibbs' dividing line, ($C = 0$), and the position of the equimolecular dividing line respectively.

By the conservation of particles,

$$\Gamma_\alpha A_\alpha + \Gamma_\beta A_\beta + n_L = \Gamma_\alpha A_\alpha^{(e)} + \Gamma_\beta A_\beta^{(e)}$$

$$\Gamma_\alpha 1 X_G + \Gamma_\beta (d - X_G) 1 + n_L = \Gamma_\alpha 1 X^{(e)} + \Gamma_\beta 1 (d - X^{(e)}) \qquad (3.68)$$

Rearranging eq. (3.68) we obtain eq. (3.69).

$$X^{(e)} - X_G = \frac{\Lambda_L}{\Gamma_\alpha - \Gamma_\beta} = \Psi \qquad (3.69)$$

Since the distance between both dividing lines is, in general, very small - less than the width of the interfacial region, Ψ is also much less than this width and in a good approximation, κ can be taken as a constant.

Chapter Four

Formation of 2-D Clusters Under Different Constraints

4.1 Thermodynamic Analysis of the Formation of one 2-D Cluster

Till now a discussion of the general thermodynamic theory of heterogeneous 2-d systems without any regard to the process of formation of clusters is given.

Here as special cases, two thermodynamic potentials, the Gibbs function and the Helmholtz free energy are analyzed under the constraints $\sigma_\beta = \sigma = \text{const.}$, $T = \text{const.}$, $n = \text{const.}$ and $A = \text{const.}$, $T = \text{const.}$, $n = \text{const.}$, respectively which give adequate description for the analysis of cluster formation (see also Ch.3).

As a model system an adsorbed thin film developed on and supported by a firm base or substrate is assumed as in fig. (4.1) below.

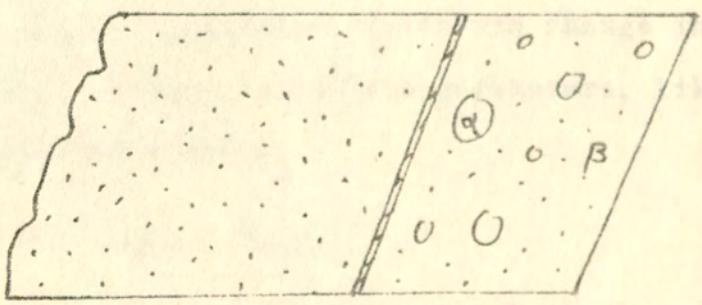


Fig. 4.1: Model system for the study of 2-d phase transitions.

In the transition that leads to the formation of one α-phase cluster, the two potentials are described by (cf. eqs. 3.46 and 3.48).

$$G_{Het} = A_\alpha(\sigma_\alpha - \sigma_\beta) + n_\alpha(\mu_\alpha - \mu_\beta) + n\mu_\beta + \kappa l \quad (a)$$

$$F_{Het.} = \sigma_\alpha A_\alpha + n_\alpha \mu_\alpha + \sigma_\beta A_\beta + n_\beta \mu_\beta + \kappa l \quad (b) \qquad (4.1)$$

As usual, A is the surface area, n, the number of moles, σ, the surface tension, μ, the chemical potential, l the length of the boundary line between the two phases and κ, the line tension. The thermodynamic parameters with a subscript α correspond to the cluster (α-phase) and with a subscript β correspond to the medium (β-phase). Eqs. (4.1) are equations of heterogeneous systems. For a homogeneous phase, particularly for the initial metastable state, these potentials are described by

$$G_{Hom.} = \mu n \quad (a)$$

$$F_{Hom.} = \mu n + \sigma A \quad (b) \qquad (4.2)$$

Since the change in potentials rather than the mere potentials themselves are of importance, first the change in Gibbs' functions with respect to certain parameters, like the size of the cluster is given by

$$\Delta G = G_{Het} - G_{Hom.}$$

$$\Delta G = n_\alpha(\mu_\alpha - \mu_\beta) + A_\alpha(\sigma_\alpha - \sigma_\beta) + \kappa l \qquad (4.3)$$

As μ and σ are functions of the surface concentration, Γ, both values are constant in the Gibbs potential case and is equal

to the values for the homogeneous metastable state, ($\sigma_\beta = \sigma$, $\mu_\beta = \mu$). Moreover from the Gibbs adsorption relation of the form:

$$d\sigma_\alpha = -\Gamma_\alpha d\mu_\alpha \tag{4.4}$$

and a reasonable assumption of the incompressibility of the 2-d liquid (α-phase) we get:

$$\sigma_\alpha - \sigma = -\Gamma_\alpha [\mu_\alpha(\sigma) - \mu_\beta(\sigma)] \; ; \tag{4.5}$$

where $\mu_\alpha(\sigma)$ is the chemical potential of the particles in the cluster for a value of the surface tension being equal to the external tension σ. Thus substituting eq. (4.5) into eq. (4.3) we obtain eq. (4.6) as follows.

$$\Delta G = n_\alpha [\mu_\alpha(\sigma) - \mu_\beta(\sigma)] + \kappa l \tag{4.6}$$

The change of the Gibbs function with the size of the cluster is then given by

$$\frac{d\Delta G}{dr_\alpha} = 2\Pi r_\alpha \Gamma_\alpha (\mu_\alpha - \mu_\beta) + 2\Pi\kappa \tag{4.7}$$

and the critical cluster size is determined to be

$$r_c = \frac{k}{\Gamma_\alpha(\mu_\beta - \mu_\alpha)} \tag{4.8}$$

It can then be said, from eq. (4.8), that a phase transition may proceed only if the chemical potential of the medium, (β-phase) is greater than the chemical potential of the particles

in the cluster (α-phase). Otherwise, ΔG as a function of r_α would be a monotonically increasing function and the homogeneous initial state is globally stable. In the test for the stability of the equilibrium state of eq. (4.8) we obtain:

$$\frac{d^2\Delta G}{dr_\alpha^2}\Big|_{r_\alpha=r_c} = 2\Pi\Gamma_\alpha(\mu_\alpha-\mu_\beta) = -\frac{2\Pi\kappa}{r_\alpha} \qquad (4.9)$$

Hence, the potential, ΔG being the potential for the case of constant surface tension as a constraint has only one extremum, a maximum. The above analytic arguments are verified by fig. (4.2).

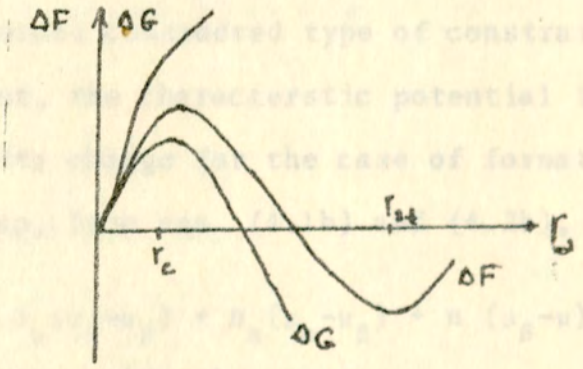


Fig. 4.2: Description of the thermodynamic potential changes as a function of the size of cluster (cf. 3-d case) [1]

The figure shows that for a cluster of size $r_\alpha < r_c$, the cluster shrinks. In contrast, for a cluster of size $r_\alpha > r_c$, ΔG has to decrease, fulfilling the criterion of evolution to equilibrium which results in a further growth of the cluster. A cluster of size $r_\alpha = r_c$ has an equal chance for shrinking as it has for growing and it is unstable.

An equivalent argument for the above description is as follows:

$$\Delta G(r_c) = [\Gamma_\alpha \Pi r_\alpha^2 (\mu_\alpha - \mu_\beta) + \kappa l]_{r_\alpha = r_c}$$
$$\Delta G(r_c) = \frac{\kappa l_c}{2} \tag{4.10}$$

From eqs. (4.6) and (4.10), eq. (4.11) is formulated.

$$\frac{\Delta G}{\Delta G_c} = - \left(\frac{r_\alpha}{r_c}\right)^2 + 2\left(\frac{r_\alpha}{r_c}\right) \tag{4.11}$$

Eq. (4.11) has the same structure given for ΔG in fig. (4.2) but in a dimensionless form.

For the second considered type of constraints, A, n and T being constant, the characterstic potential is the Helmholtf free energy. Its change for the case of formation of one cluster is given, from eqs. (4.1b) and (4.2b), as

$$\Delta F = A_\alpha(\sigma_\alpha - \sigma_\beta) + n_\alpha(\mu_\alpha - \mu_\beta) + n\,(\mu_\beta - \mu) + A(\sigma_\beta - \sigma) + \kappa l \tag{4.12}$$

From the incompressibility of the cluster, we can have

$$\mu_\alpha(\sigma_\alpha) = \mu_\alpha(\sigma') - \frac{1}{\Gamma_\alpha}(\sigma_\alpha - \sigma') \tag{4.13}$$

and,

$$\Delta F = A_\alpha(\sigma' - \sigma_\beta) + [\mu_\alpha(\sigma') - \mu_\beta(\sigma_\beta)]\, n_\alpha + A(\sigma_\beta - \sigma) + n\,(\mu_\beta - \mu) + \kappa l \tag{4.14}$$

where σ and μ refer to the homogeneous phase and are constant. σ' is the value of σ for the 2-d liquid-vapor saturation state and n is the total number of monomers in the considered system. The

$$\frac{\partial \Delta F}{\partial r_\alpha} = 2\Pi r_\alpha(\sigma' - \sigma_\beta) + 2\Pi r_\alpha \Gamma_\alpha [\mu_\alpha(\sigma') - \mu_\beta(\sigma_\beta)]$$

$$- n_\alpha \frac{\partial \mu_\beta}{\partial r_\alpha} + n \frac{\partial \mu_\beta}{\partial r_\alpha} + A \frac{\partial \sigma_\beta}{\partial r_\alpha} - A_\alpha \frac{\partial \sigma_\beta}{\partial r_\alpha} + 2\Pi\kappa \qquad (4.15)$$

$$\frac{\partial \Delta F}{\partial r_\alpha} = 2\Pi r_\alpha(\sigma' - \sigma_\beta) + 2\Pi r_\alpha \Gamma_\alpha(\mu' - \mu_\beta) + 2\Pi\kappa$$

where $\mu_\alpha(\sigma') = \mu'$

Applying the isothermal Gibbs adsorption relation for the β-phase

$$d\sigma_\beta = - \Gamma_\beta \, d\mu_\beta \, ,$$

and introducing a mean value, $\langle \Gamma_\beta \rangle$ in the interval (Γ', Γ) we have

$$\sigma' - \sigma_\beta = - \langle \Gamma_\beta \rangle (\mu' - \mu_\beta) \qquad (4.16)$$

where at the saturation state, $\mu_\alpha(\sigma') = \mu_\beta(\sigma') = \mu'$. Eq. (4.15) is then rewritten as:

$$\frac{\partial \Delta F}{\partial r_\alpha} = - 2\Pi r_\alpha \langle \Gamma_\beta \rangle (\mu' - \mu_\beta) + 2\Pi r_\alpha \Gamma_\alpha (\mu' - \mu_\beta) + 2\Pi\kappa \qquad (4.17)$$

For a phase transition to occur, μ_β must be greater than μ' (i.e., $\mu_\beta(\sigma_\beta) > \mu_\alpha(\sigma') = \mu_\beta(\sigma')$) and moreover $\partial \Delta F / \partial r_\alpha < 0$. The extrema are evaluated from

$$\sigma' - \sigma_\beta + \Gamma_\alpha(\mu' - \mu_\beta) + \frac{\kappa}{r_\alpha} = 0 \quad \text{(a)}$$

or

$$r_\alpha (\Gamma_\alpha - \langle\Gamma_\beta\rangle)(\mu' - \mu_\beta) + \kappa = 0 \quad \text{(b)} \tag{4.18}$$

to be:

$$r = r_{ext.} = \frac{\kappa}{(\Gamma_\alpha - \langle\Gamma_\beta\rangle)(\mu_\beta - \mu')} \tag{4.19}$$

For stability test, $\partial^2 \Delta F / \partial r_\alpha^2$ is computed at the extrema.

$$\frac{\partial^2 \Delta F}{\partial r_\alpha^2} = -\frac{2\pi\kappa}{r_\alpha}\left[1 - \frac{r_\alpha^2}{\kappa}(\Gamma_\beta - \Gamma_\alpha)\frac{\partial \mu_\beta}{\partial \Gamma_\beta}\frac{\partial \Gamma_\beta}{\partial r_\alpha}\right]$$

$$\frac{\partial^2 \Delta F}{\partial r_\alpha^2} = -\frac{2\pi\kappa}{r_\alpha}\left[1 - \frac{2A_\alpha r_\alpha}{\kappa A}\frac{(\Gamma - \Gamma_\beta)^2}{\frac{(1 - A_\alpha)}{A}3}\frac{\partial \mu_\beta}{\partial \Gamma_\beta}\right] \tag{4.20}$$

Γ is the concentration of particles in the homogeneous initial phase. For very small clusters we obtain

$$\frac{\partial^2 \Delta F}{\partial r_\alpha^2} = -\frac{2\pi\kappa}{r_\alpha} < 0 \tag{4.21}$$

which corresponds to a critical state of the cluster. And for large clusters eq. (4.20) is reduced to

$$\frac{\partial^2 \Delta F}{\partial r_\alpha^2} = \frac{4\pi A_\alpha}{A}\frac{(\Gamma - \Gamma_\alpha)^2}{\frac{(1 - A_\alpha)}{A}^3}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} > 0 \tag{4.22}$$

which corresponds to a stable cluster.

The characterstic potential, ΔF has two extrema, a maximum that corresponds to a thermodynamically unstable cluster and a minimum corresponding to a thermodynamically stable cluster. The behavior of ΔF as a function of cluster size is briefed in fig. (4.2). ΔG and ΔF have different number of extrema. ΔG has only a maximum because the surface tension is kept constant in the system by the translation of the 1-d interface in the course of the transition. (see fig. 4.1) and ΔF has an additional extremum (a minimum) due to depletion effects.

4.2 Depletion Effects and the Work of Formation of Critical Clusters in 2-D System

From the point of view of classical thermodynamics the homogeneous initial state would exist for ever, since, according to thermodynamics, evolution processes are connected with a decrease of the thermodynamic potentials F or G respectively. But in every real system spontaneous deviations from the equilibrium state - fluctuations, occur which are not considered in classical thermodynamics.

Of particular importance for the nucleation process are fluctuations leading to the evolution of clusters with the critical size, r_c. Such clusters can be formed also in a reversible thermodynamic process, if an external work is done on the system. This work of formation of critical

clusters, W is equal to $W = \Delta F_c$ or $W = \Delta G_c$ respectively for both of the considered cases.

According to classical nucleation theory, the nucleation rate, I, i.e. the number of critical clusters formed per unit time is given by

$$I = I_o \exp \{ - \frac{W}{K_B T} \} \qquad (4.23)$$

If depletion effects can be neglected, W is given by

$$W = \Delta G(r_c) = \frac{\kappa l_c}{2} \qquad (4.10)$$

It is evident from both these eqs. that I decreases rapidly with an increasing cluster size. Therefore, phase transitions in layers occur only if the critical cluster contains for about two to ten particles.

Now if the state of the medium is affected by the formation and growth of the clusters, i.e., if depletion effects occur, the critical cluster size is affected by these variations. Let us now analyse the influence of depletion effects on the work of formation of the critical clusters. Here, as an example, the case of constant surface area and constant temperature is considered; where F is the characterstic potential.

From eq. (4.14) we have,

$$\Delta F = A_\alpha (\sigma' - \sigma_\beta) + n_\alpha (u' - \mu_\beta) + \kappa l + \Delta W. \qquad (4.24)$$

where the depletion effect term, ΔW is:

$$\Delta W = A(\sigma_\beta - \sigma) + n(\mu_\beta - \mu)$$

At the extremum, ΔF is given as in the following.

$$\Delta F = -\frac{\kappa}{r_\alpha} A_\alpha + \kappa l + \Delta W$$

$$\Delta F = \kappa \Pi r_\alpha + \Delta W \qquad (4.25)$$

In the absence of depletion effect, $\Delta W = 0$, we have the minimum work for critical cluster formation of eq. (4.26) (cf. eq. 4.10).

$$\Delta F_c = \Delta G_c = \kappa \Pi r_\alpha \Big|_{r_\alpha = r_c} \qquad (4.26)$$

But in general ΔW is not equal to zero. To find out the properties of ΔW, let the parameters σ_β and μ_β be functions of n_β and A_β represented by

$$\sigma_\beta = \sigma(n+\Delta n,\ A+\Delta A) \equiv \sigma(X_1+\Delta X_1,\ X_2+\Delta X_2)$$

$$\mu_\beta = \mu(n+\Delta n,\ A+\Delta A) \equiv \mu(X_1+\Delta X_1,\ X_2+\Delta X_2) \qquad (4.27)$$

and let us denote these independent variables for a while by X_1 and X_2. By a trancated Tayler expansion of σ_β and μ_β we have:

$$\sigma_\beta = \sigma + \sum_{i=1}^{2} \frac{\partial \sigma}{\partial X_i} \Delta X_i + \frac{1}{2} \sum_{i,j}^{2} \frac{\partial^2 \sigma}{\partial X_i \partial X_j} \Delta X_i \Delta X_j \quad \text{(a)}$$

$$\mu_\beta = \mu + \sum_{i=1}^{2} \frac{\partial \mu}{\partial X_i} \Delta X_i + \frac{1}{2} \sum_{i,j=1}^{2} \frac{\partial^2 \mu}{\partial X_i \partial X_j} \Delta X_i \Delta X_j \quad \text{(b)} \qquad (4.28)$$

and the depletion effect term reads

$$\Delta W = A \{ \sum_{i=1}^{2} (\frac{\partial \sigma}{\partial X_i} + \Gamma \frac{\partial \mu_i}{\partial X_i}) \Delta X_i + \frac{1}{2} \sum_{i,j=1}^{2} (\frac{\partial^2 \sigma}{\partial X_i \partial X_j} + \Gamma \frac{\partial^2 \mu}{\partial X_i \partial X_j}) \Delta X_i \Delta X_j \}$$

Using isothermal Gibbs adsorption relation this will reduce to

$$\Delta W = \frac{1}{2} \sum_{i,j=1}^{2} (A \frac{\partial^2 \sigma}{\partial X_i \partial X_j} + n \frac{\partial^2 \mu}{\partial X_i \partial X_j}) \Delta X_i \Delta X_j \qquad (4.29a)$$

From the relation:

$$A \frac{\partial \sigma}{\partial X_i} = - n \frac{\partial \mu}{\partial X_i}$$

we get

$$\Delta W = - \frac{1}{2} \sum_{i,j=1}^{2} (\frac{\partial A}{\partial X_j} \frac{\partial \sigma}{\partial X_i} + \frac{\partial n}{\partial X_j} \frac{\partial \mu}{\partial X_i}) \Delta X_j \Delta X_i \qquad (4.29b)$$

From the intrinsic equilibrium condition (cf. eq. 3.5), we obtain

$$\sum_{i,j=1}^{2} (\frac{\partial A}{X_j} \frac{\partial \sigma}{\partial X_i} + \frac{\partial n}{\partial X_j} \frac{\partial \mu}{\partial X_i}) \Delta X_i \Delta X_j > 0 \qquad (4.30)$$

Hence,

$$\Delta W = - \frac{1}{2} \sum_{i,j=1}^{2} (\frac{\partial A}{\partial X_j} \frac{\partial \sigma}{\partial X_i} + \frac{\partial n}{\partial X_j} \frac{\partial \mu}{\partial X_i}) \Delta X_j \Delta X_i < 0 \qquad (4.31)$$

The depletion effect term, ΔW in the 2-d cluster formation is negative analogous to the 3-d case [1].

Moreover, depletion effects also result in a variation of the radius and the number of particles in the critical cluster. To account for this effect it is realized that r_β can be expressed as:

$$r_\beta = \frac{n-n_\alpha}{A-A_\alpha} \tag{4.32}$$

The parameters of the critical clusters are given by:

$$\begin{aligned} f_1 &= \mu_\alpha(r_\alpha) - \mu_\beta(r_\beta) = 0 \quad (a) \\ f_2 &= \sigma_\alpha(r_\alpha) - \sigma_\beta(r_\beta) + \frac{K}{r_\alpha} = 0 \quad (b) \end{aligned} \tag{4.33}$$

Taking eq. (4.32) in to account it can be concluded that eqs. (4.33) represent two equations of the type

$$f_j(n_\alpha, A_\alpha, n, A) = 0, \; j = 1,2. \tag{4.33c}$$

for the determination of the parameters of the critical clusters.

To obtain expressions for the dependence of the parameters of the critical clusters on depletion effects we start with the argument, that with an increasing size of the total system depletion effects will become less important. Therefore, the analysis may be reduced to the consideration of the dependence of the parameters of the critical clusters on the total size of the system, provided the initial representation is kept constant (see fig. 4.3).

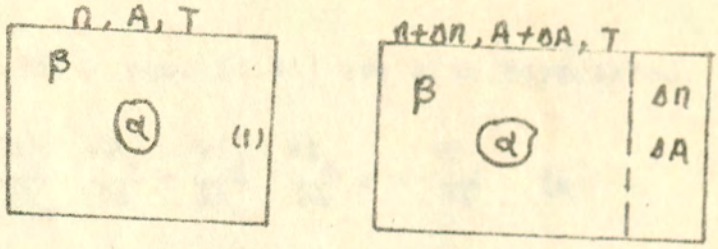


Fig. 4.3: Model used for the investigation of the influence of depletion effects on the parameters of the critical clusters.

The two systems, represented in fig. 4.3, differ by the total number of particles, n and the total surface area, A. According to eq. (4.33), also the parameters of the critical cluster will be different. And for the systems in fig. (4.3) we can formulate eqs. (4.34).

$$n_\alpha^{(1)} = n_\alpha(n,A)\ ;\ n_\alpha^{(2)} = n_\alpha(n+\Delta n,\ A+\Delta A)$$
$$A_\alpha^{(1)} = A_\alpha(n,A)\ ;\ A_\alpha^{(2)} = A_\alpha(n+\Delta n,\ A+\Delta A) \qquad (4.34)$$

Expanding in a Tayler series and neglecting higher order terms, the following eqs. (4.35a) and (4.35b) are obtained for Δn_α and ΔA_α.

$$\Delta n_\alpha = \frac{\partial n_\alpha}{\partial n}\Delta n + \frac{\partial n_\alpha}{\partial A}\Delta A$$
$$\Delta A_\alpha = \frac{\partial A_\alpha}{\partial A}\Delta A + \frac{\partial A_\alpha}{\partial n}\Delta n \qquad (4.35a)$$

or

$$\Delta n_\alpha \simeq (\Gamma\frac{\partial n_\alpha}{\partial n} + \frac{\partial n_\alpha}{\partial A})\Delta A$$
$$\Delta A_\alpha \simeq (\Gamma\frac{\partial A_\alpha}{\partial n} \quad \frac{\partial A_\alpha}{\partial A})\Delta A \qquad (4.35b)$$

From eq. (4.33c), eqs. (4.36) are also formulated.

$$\frac{\partial f_j}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial A} + \frac{\partial f_j}{\partial A_\alpha}\frac{\partial A_\alpha}{\partial A} = -\frac{\partial f_j}{\partial A} \quad \text{(a)}$$

$$\frac{\partial f_j}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial n} + \frac{\partial f_j}{\partial A_\alpha}\frac{\partial A_\alpha}{\partial n} = -\frac{\partial f_j}{\partial n} \quad \text{(b)} \qquad (4.36)$$

The Jacobi determinant, J, of eqs. (4.36) is given by (4.37) below.

$$J = \frac{\partial(f_1, f_2)}{\partial(n_\alpha, A_\alpha)} = \begin{vmatrix} \frac{\partial f_1}{\partial n_\alpha} & \frac{\partial f_1}{\partial A_\alpha} \\ \frac{\partial f_2}{\partial n_\alpha} & \frac{\partial f_2}{\partial A_\alpha} \end{vmatrix} \qquad (4.37a)$$

For the particular case of eqs. (4.33a,b), the Jacobi determinant is

$$J = \begin{vmatrix} \frac{1}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} + \frac{1}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} & -\frac{\Gamma_\alpha}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} - \frac{\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} \\ -\frac{\Gamma_\alpha}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} - \frac{\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} & \frac{\Gamma_\alpha^2}{A_\alpha}\frac{\partial \mu_\alpha}{\partial A_\alpha} + \frac{\Gamma_\beta^2}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} - \frac{\kappa}{2\pi r_\alpha^3} \end{vmatrix} \qquad (4.37b)$$

Using Cramers rule,

$$\frac{\partial n_\alpha}{\partial n}, \frac{\partial n_\alpha}{\partial A}, \frac{\partial A_\alpha}{\partial A}, \frac{\partial A_\alpha}{\partial n}$$

are evaluated by the following eqs. (4.38).

$$\left(\frac{\partial n_\alpha}{\partial A}\right)_{n,A_\alpha} = -\frac{1}{J}\frac{\partial(f_1,f_2)}{\partial(A,A_\alpha)}\;;\quad \left(\frac{\partial A_\alpha}{\partial n}\right)_{A,n_\alpha} = -\frac{1}{J}\frac{\partial(f_1,f_2)}{\partial(n_\alpha,n)}$$

$$\left(\frac{\partial n_\alpha}{\partial n}\right)_{A,A_\alpha} = -\frac{1}{J}\frac{\partial(f_1,f_2)}{\partial(n,A_\alpha)}\;;\quad \left(\frac{\partial A_\alpha}{\partial A}\right)_{n_\alpha,n} = -\frac{1}{J}\frac{\partial(f_1,f_2)}{\partial(n_\alpha,A)} \qquad (4.38)$$

From Eqs. (4.35b) and (4.38), the following can be obtained.

$$\Delta n_\alpha = -\frac{\Delta A}{J}\left[\Gamma\frac{\partial(f_1,f_2)}{\partial(n,A_\alpha)} + \frac{\partial(f_1,f_2)}{\partial(A,A_\alpha)}\right]$$

$$\Delta n_\alpha = -\frac{\Delta A}{J}\begin{vmatrix} \Gamma\dfrac{\partial f_1}{\partial n} + \dfrac{\partial f_1}{\partial A} & \dfrac{\partial f_1}{\partial A_\alpha} \\ \Gamma\dfrac{\partial f_2}{\partial n} + \dfrac{\partial f_2}{\partial A} & \dfrac{\partial f_2}{\partial A_\alpha} \end{vmatrix} \qquad (4.39a)$$

and

$$\Delta A_\alpha = -\frac{\Delta A}{J}\left[\Gamma\frac{\partial(f_1,f_2)}{\partial(n_\alpha,n)} + \frac{\partial(f_1,f_2)}{\partial(n_\alpha,A)}\right]$$

$$\Delta A_\alpha = -\frac{\Delta A}{J}\begin{vmatrix} \dfrac{\partial f_1}{\partial n_\alpha} & \dfrac{\partial f_1}{\partial A} + \Gamma\dfrac{\partial f_1}{\partial n} \\ \dfrac{\partial f_2}{\partial n_\alpha} & \dfrac{\partial f_2}{\partial A} + \Gamma\dfrac{\partial f_2}{\partial n} \end{vmatrix} \qquad (4.39b)$$

Substituting the expressions of f_1 and f_2 of eqs. (4.33) into eqs. (4.39a) and (4.39b) it yields:

$$\Delta n_\alpha = -\frac{\Delta A}{J}\begin{vmatrix} \frac{\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} - \frac{\Gamma}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} & -\frac{\Gamma_\alpha}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} - \frac{\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} \\ -\frac{\Gamma_\beta^2}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} + \frac{\Gamma\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} & \frac{\Gamma_\alpha^2}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} + \frac{\Gamma_\beta^2}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} - \frac{\kappa}{2\pi r_\alpha} \end{vmatrix}$$

and it can be simplified to

$$\Delta n_\alpha = \frac{\Delta A}{J}\left\{\frac{(\Gamma-\Gamma_\beta)}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta}\left[\frac{\Gamma_\alpha}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha}(\Gamma_\alpha-\Gamma_\beta) - \frac{\kappa}{2\pi r_\alpha^3}\right]\right\} \qquad (4.40a)$$

$$\Delta A_\alpha = -\frac{\Delta A}{J}\begin{vmatrix} \frac{1}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} + \frac{1}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} & \frac{\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} - \Gamma\frac{\partial \mu_\beta}{\partial \Gamma_\beta} \\ -\frac{\Gamma_\alpha}{A_\alpha}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha} - \frac{\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} & -\frac{\Gamma_\beta^2}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} + \frac{\Gamma\Gamma_\beta}{A_\beta}\frac{\partial \mu_\beta}{\partial \Gamma_\beta} \end{vmatrix}$$

and this again can be simplified to

$$\Delta A_\alpha = \frac{\Delta A}{J}\left[(\Gamma-\Gamma_\beta)(\Gamma_\alpha-\Gamma_\beta)\frac{1}{A_\alpha A_\beta}\frac{\partial \mu_\alpha}{\partial \Gamma_\alpha}\frac{\partial \mu_\beta}{\partial \Gamma_\beta}\right] \qquad (4.40b)$$

For the variation of density of the cluster we have

$$\Delta \Gamma_\alpha = \frac{n_\alpha + \Delta n_\alpha}{A_\alpha + \Delta A_\alpha} - \frac{n_\alpha}{A_\alpha} = \frac{1}{A_\alpha}(\Delta n_\alpha - \Gamma_\alpha \Delta A_\alpha)$$

substituting the values of Δn_α and ΔA_α we get it to be

$$\Delta\Gamma_\alpha = \frac{\Delta A}{J}\left[-\frac{1}{A_\alpha A_\alpha}(\Gamma-\Gamma_\beta)\frac{\partial\mu_\beta}{\partial\Gamma_\beta}\frac{\kappa}{2\pi r_\alpha^3}\right] \qquad (4.41)$$

To discuss the results, we realize first that the determinant, J, of eq. (4.37b) is identical with the determinant, J, that was discussed in the stability investigations of Chapter 3. Therefore, according to eq. (4.40b), the size of the critical cluster decreases and the size of the stable cluster increases with an increasing surface area, A. This results in an increase of the critical cluster size and an increase of the work of formation of the critical cluster with a decreasing size of the system.

Going back to our initial system - the dependence of the parameters of the critical cluster on depletion effects, we may conclude, that depletion leads to the increase of the size of the critical clusters. Since this increment is a linear function of the variation of the state of the medium, (cf. eq. 4.40b), it is this effect and not the term ΔW that determines the variations of W due to depletion. Therefore, depletion results in an increase of the work of formation of critical clusters and thus in a decrease of the nucleation rate.

4.3 Generalization to Ensembles of 2-D Clusters and the Scenario of Phase Transition

What has been discussed about the change of the thermodynamic potentials due to an evolution of a cluster as a

result of phase transition can be generalized to ensembles of clusters.

For the evolution of N distinct clusters out of the homogeneous metastable initial state, the change in the considered thermodynamic potentials is given by (cf. eqs. 4.6 and 4.14):

$$\Delta G = \sum_{i=1}^{N} [n_\alpha^{(i)} (\mu_\alpha^{(i)}(\sigma) - \mu_\beta(\sigma)) + \kappa^{(i)} l^{(i)}] \quad \text{(a)}$$

$$\Delta F = \sum_{i=1}^{N} [A_\alpha^{(i)} (\sigma' - \sigma_\beta) + n_\alpha^{(i)} (\mu_\alpha^{(i)}(\sigma) - \mu_\beta(\sigma_\beta)) + \kappa^{(i)} l^{(i)}] \quad (4.42)$$

$$+ n(\mu_\beta - \mu) + A(\sigma_\beta - \sigma) \quad \text{(b)}$$

The subscript (i) refers to the different clusters. For N identical clusters, eqs. (4.42) are rewritten as

$$\Delta G = N [n_\alpha (\mu_\alpha(\sigma) - \mu_\beta(\sigma)) + \kappa l] \quad (4.43)$$

$$\Delta F = N [A_\alpha (\sigma' - \sigma_\beta) + n_\alpha (\mu_\alpha(\sigma') - \mu_\beta(\sigma_\beta)) + \kappa l]$$

$$+ n(\mu_\beta - \mu) + A(\sigma_\beta - \sigma)$$

The potentials of eqs. (4.43) depend on the number of clusters, N and their size. For a constant number, N, the extrema of the potentials are computed in the same case as for a single cluster. (cf. eqs. 4.7 and 4.15)

$$\left(\frac{\partial \Delta G}{\partial r_\alpha}\right)_N = 2\pi r_\alpha N \Gamma_\alpha (\mu_\alpha(\sigma) - \mu_\beta(\sigma)) + 2\pi\kappa N = 0$$

$$\left(\frac{\partial \Delta F}{\partial r_\alpha}\right)_N = 2\pi N r_\alpha [(\sigma' - \sigma_\beta) + \Gamma_\alpha (\mu_\alpha(\sigma') - \mu_\beta) + \frac{\kappa}{r_\alpha}] = 0 \qquad (4.44)$$

For the stability test, $\partial^2 \Delta G / \partial r_\alpha^2$ and $\partial^2 \Delta F / \partial r_\alpha^2$ are examined at the extrema. For G we obtain

$$\frac{\partial^2 \Delta G}{\partial r_\alpha^2} = 2\pi N \Gamma_\alpha (\mu_\alpha(\sigma') - \mu_\beta(\sigma))$$

$$\frac{\partial^2 \Delta G}{\partial r_\alpha^2} = -\frac{2\pi N \kappa}{r_\alpha} < 0 \quad \text{(a maximum)} , \qquad (4.45)$$

Moreover ΔG for the N number of clusters can be as eq. (4.46)

$$\Delta G = N \Delta G_c \left[-\left(\frac{r_\alpha}{r_c}\right)^2 + 2\left(\frac{r_\alpha}{r_c}\right)\right] = N \Delta G_1 \qquad (4.46)$$

r_c and ΔG_c being the critical values of the Gibbs free energy for a single cluster and ΔG_1 a value of single cluster.

The extrema (only a maximum) of ΔG is increasing at a fixed critical radius, r_c as N increases and crosses the same point in the r_α-axis irrespective of the number N.

Let us now discuss ΔF at the extrema, it gives

$$\frac{\partial^2 \Delta F}{\partial r_\alpha^2} = 2\pi N r_\alpha \left[(\Gamma_\beta - \Gamma_\alpha) \frac{\partial \mu_\beta}{\partial \Gamma_\beta} \frac{\partial \Gamma_\beta}{\partial r_\alpha} - \frac{\kappa}{r_\alpha^2}\right] \qquad (4.47)$$

By evaluating $\partial \Gamma_\beta / \partial r_\alpha$ as

$$\frac{\partial \Gamma_\beta}{\partial r_\alpha} = \frac{2\pi N r_\alpha}{\Gamma} (\Gamma - \Gamma_\alpha)$$ we get

$$\frac{\partial^2 \Delta F}{\partial r_\alpha^2} = - \frac{2\Pi N \kappa}{r_\alpha} (y + 1) \tag{4.48}$$

where,

$$y = - \frac{2A_\alpha r_\alpha N}{\kappa A} \frac{(\Gamma - \Gamma_\alpha)^2}{(1 - \frac{NA_\alpha}{A})^3} \frac{\partial \mu_\beta}{\partial \Gamma_\beta}$$

From eq. (4.48) two conditions can be predicted.

1) $\frac{\partial^2 \Delta F}{\partial r^2} < 0$ implies $1+y > 0$,

being the condition for the critical state.

2) $\frac{\partial^2 \Delta F}{\partial r^2} > 0$ implies $1+y < 0$,

being the condition for the stable state, (stable, if the number of clusters is fixed).

For an analysis of the qualitative behavior of ΔF as a function of N, the 2-d Gibbs Thomson equation (4.49), obtained from eq. (4.44) is differentiated with respect to N taking into account that r_α is a function of N and evaluated at the extrema.

$$(\sigma' - \sigma_\beta) + \Gamma_\alpha (\mu' - \mu_\beta) + \frac{\kappa}{r_\alpha} = 0 \tag{4.49}$$

$$\frac{\partial}{\partial r_\alpha} [(\sigma' - \sigma_\beta) + \Gamma_\alpha (\mu' - \mu_\beta)] + \frac{\kappa}{r_\alpha}] \frac{dr_\alpha}{dN}$$

$$+ \frac{\partial}{\partial N} [(\sigma' - \sigma_\beta) + \Gamma_\alpha (\mu' - \mu_\beta) + \frac{\kappa}{r_\alpha}] = 0$$

$$\frac{dr_\alpha}{dN} = \frac{-\frac{\partial}{\partial N}\left[(\sigma'-\sigma_\beta) + \Gamma_\alpha(\mu'-\mu_\beta) + \frac{\kappa}{r_\alpha}\right]}{\frac{\partial}{\partial r_\alpha}\left[(\sigma'-\sigma_\beta) + \Gamma_\alpha(\mu'-\mu_\beta) + \frac{\kappa}{r_\alpha}\right]} \tag{4.50}$$

The number of eq. (4.50) can be transformed into:

$$-(\Gamma_\beta-\Gamma_\alpha)\frac{\partial \mu_\beta}{\partial \Gamma_\beta}\frac{\partial \Gamma_\beta}{\partial N} = \frac{\kappa}{2Nr_\alpha}(y) \tag{4.51}$$

and the denominator is:

$$(\Gamma_\beta-\Gamma_\alpha)\frac{\partial \mu_\beta}{\partial \Gamma_\beta}\frac{\partial \Gamma_\beta}{\partial r_\alpha} - \frac{\kappa}{r_\alpha^2} = -\frac{\kappa}{r_\alpha^2}(y+1) \tag{4.52}$$

where y is that determined above. Thus we get

$$\frac{dr_\alpha}{dN} = \frac{-r_\alpha}{2N(1+y^{-1})} \tag{4.53}$$

At the critical state,

$$(1+y^{-1}) < 0 \text{ , consequently, } dr_\alpha/dN > 0$$

and at the stable state,

$$(1+y^{-1}) > 0 \text{ , consequently, } dr_\alpha/dN < 0$$

To finalize the analysis of this section, let us evaluate $d\Delta F/dN$ at the extrema.

$$\frac{d\Delta F}{dN} = \frac{\partial \Delta F}{\partial r_\alpha}\frac{\partial r_\alpha}{\partial N} + \frac{\partial \Delta F}{\partial N} = \frac{\partial \Delta F}{\partial N}$$

$$= A_\alpha\left[(\sigma'-\sigma_\beta) + \Gamma_\alpha(\mu'-\mu_\beta)\right] + \kappa l$$

$$= \kappa \Pi r_\alpha = \frac{\kappa l}{2} > 0 \tag{4.54}$$

From all the arguments for ΔF as a thermodynamic potential for the phase transition in the formation and growth of 2-d clusters, it can be said that the position of $\Delta F(r_\alpha)$ for the critical state increases with the number of clusters and for the stable state it decreases with the number of clusters, N, until both extrema coincide in a common point called the inflexion point characterized by

$$\frac{\partial \Delta F}{\partial r_\alpha} = \frac{\partial^2 \Delta F}{\partial r_\alpha^2} = 0 \qquad (4.55)$$

This point corresponds to the maximum possible number of clusters, N_c of the considered system. The function $\Delta F(r_\alpha)$ for a definite number of clusters is shown in fig. (4.4a).

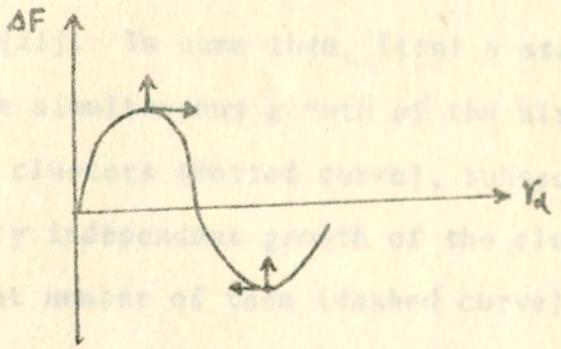


Fig. 4.4a: ΔF as a function of r_α for a given number of identical clusters. The variation of the position of the extrema of F as a function of the number of clusters, N is indicated by arrows.

Fig. 4.4b presents the function $\Delta F = \Delta F(r_\alpha)$ for different

values of the number of clusters. Based on this figure a general scenario of first-order phase transition in 2-d systems, starting from metastable initial states may be developed.

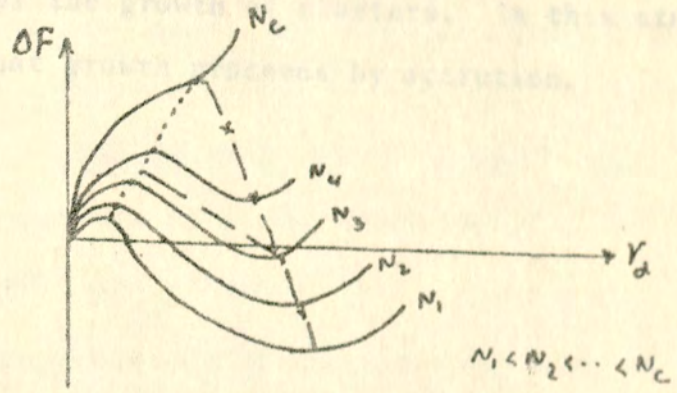


Fig 4.4b: The main stages of a first-order transition in 2-d system: nucleation and possible simultaneous growth (dotted curve), independent growth of the clusters (dashed curve), Ostwald ripening (dashed-stared curve).

The transition stages in fig. (4.4b) are analogous to the 3-d case [21]. To name them, first a stage of nucleation and a possible simultaneous growth of the already formed supercritical clusters (dotted curve), subsequently a second stage of nearly independent growth of the clusters with an almost constant number of them (dashed curve) and a third stage of competitive growth or Ostwald repening where monomers leave the smaller clusters and diffuse over to the large ones because the former have a higher vapor pressure [22] resulting in a decrease of the number of clusters in the system and an increase of their mean radius (dashed-stared curve).

The results of the thermodynamic description developed in the preceding chapters are now to be applied to the kinetic description of the growth of clusters. In this study, it will be assumed that growth proceeds by accretion.

Chapter Five

Kinetics of Phase Transition in Adsorbed Mondayers

So far a static thermodynamic description of the phase transition was discussed. The consideration of the kinetic process when matter or energy or both are transported between parts of the system is to follow in this chapter. The rate of transport process of thermodynamic quantities is the object of study of physical kinetics.

Transport processes of material particles in a finite 2-d system are in general described by the flux, j of a physical quantity, z defined as the amount of the considered quantity crossing a unit length (cf. unit area) in a unit time. Mathematicaly it can be expressed by:

$$j_z = \frac{1}{L}\frac{dz}{dt} \tag{5.1}$$

The flux of matter in diffusion, the flux of heat in thermal conduction and the flux of charges in a conductor are a few examples of kinetic processes. Each of these fluxes is caused by a gradient of a physical quantity like concentration of particles, temperatures, and electric potential. In the case of 2-d kinetics of phase transition the objective of the study is the flux of matter by diffusion.

5.1 Kinetics of Cluster Growth by Diffusion

In the kinetics of phase transition of 2-d systems, the 3-d analogue to the 2-d diffusion equation is expressed by

$$\vec{J} = - \frac{D_i \Gamma_i}{K_B T} \nabla \mu_i \qquad (5.2)$$

D_i, Γ_i μ_i are the partial diffusion coefficient, the surface concentration and the chemical potential of the i-th component in the system respectively. K_B is the Boltzman constant and T the absolute temperature. The negative sign in the equation indicates the direction of duffusion being towards decreasing concentration or what is equivalent is towards decreasing chemical potential. Assuming a perfect mixture, μ_i can be expressed by:

$$\mu_i = \mu_i^{(o)} + K_B T \ln(x_i) \qquad (5.3)$$

where $\mu_i^{(o)}$ is the chemical potential in a standard state, and

$$X_i = \Gamma_i / \Gamma^{(o)} = \frac{(n_i|A)}{(n_t|A)} \qquad (5.4)$$

with A and n_t being the area and total number of moles, respectively. X_i is the mole fraction of the i-th component. The gradient of eq. (5.3) reads for this case

$$\nabla \mu_i = K_B T \nabla \ln(\Gamma_i) = \frac{K_B T}{\Gamma_i} \nabla \Gamma_i \qquad (5.5)$$

Then from eqs. (5.2) and (5.5), eq. (5.6) is obtained for perfect mixtures.

$$\vec{J}_i = -D_i \nabla \Gamma_i \qquad (5.6)$$

For a one component system, eqs. (5.2) and (5.6) are:

$$\vec{J} = -\frac{D\Gamma_\beta}{K_B T}\nabla\mu_\beta \qquad (a)$$

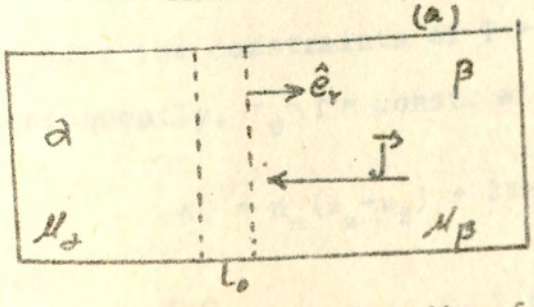
$$\vec{J} = -D\nabla\Gamma_\beta \qquad (b) \qquad (5.7)$$

where μ_β and Γ_β refer to the chemical potential and surface concentration of the β-phase. Based on eq. (5.7a), now a 2-d cluster growth equation is to be developed following the approach introduced by Schmelzer [20] for 3-d clusters. Hereby, is started with the consideration of aregion of the interface between two coexisting phases (see fig. 5.1), consisting of two homogeneous parts of the liquid (α) and vapor (β), divided by an inhomogeneous region with the width l_o. Eq. (5.7a) when refered to such system is written as:

$$\vec{J} = \frac{D\Gamma_\beta}{K_B T}\,\frac{\Delta\mu_{\alpha\beta}}{l_o}\hat{e}_r \qquad (5.8)$$

where,

$\Delta\mu_{\alpha\beta} = \mu_\beta - \mu_\alpha$ and $\hat{e}_r$ is a unit vector perpendicular to the surface of the α-phase.



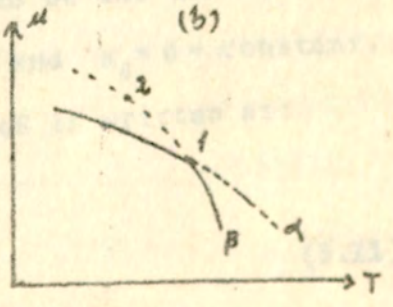


Fig. 5.1: a) Schematic dig. for the transport process between coexisting phases.

b) μ(T) at constant surface tension.

The phase transition process may commence at any point in the metastable state interval (1,2) of the β-phase (see fig. 5.1b). Therefore, for a condensation process to occur, $\Delta\mu_{\alpha\beta}$ must be positive. Equation (5.8) can be generalized now as follows.

From the thermodynamic point of view, a process in a system will take place, if the characterstic thermodynamic potential, Φ, decreases. Therefore, the thermodynamic potential change, $\Delta\phi$, connected with the increment of particles, Δn_α in the α-phase can be taken as the thermodynamic driving force of the transition; and eq. (5.9) is obtained.

$$\vec{J} = \frac{D\Gamma_\beta}{K_B T} \frac{1}{l_o} \frac{\Delta\phi}{\Delta n_\alpha} \hat{e}_r \tag{5.9}$$

Since growth rate may depend on the number of particles in the α-phase we can go over to the limit $\Delta n_\alpha \longrightarrow 0$ and get eq. (5.10).

$$\vec{J} = \frac{D\Gamma_\beta}{K_B T} \frac{1}{l_o} \frac{\partial\phi}{\partial n_\alpha} \hat{e}_r \tag{5.10}$$

As a special case let us take ϕ to be the Gibbs function, G under the constraints of T = const. and $\sigma_\beta = \sigma$ = constant. Consequently, $\Gamma_\beta = \Gamma$ = const. also and ΔG is written as:

$$\Delta G = n_\alpha(\mu_\alpha - \mu_\beta) + 2\Pi\kappa r_\alpha \tag{5.11}$$

and

$$\frac{d\Delta G}{dr_\alpha} = 2\Pi r_\alpha \Gamma_\alpha (\mu_\alpha - \mu_\beta) + 2\Pi\kappa$$

Then the general expression for the density of flux through the interface is to be written as

$$\vec{J} = \frac{D\Gamma}{\Gamma_\alpha K_B T} \frac{\kappa}{l_o} \left[\frac{\Gamma_\alpha}{\kappa} (\mu_\alpha - \mu_\beta) + \frac{1}{r_\alpha} \right] \hat{e}_r \tag{5.12}$$

or

$$\vec{J} = \frac{D\Gamma}{\Gamma_\alpha K_B T} \frac{\kappa}{l_o} \left[-\frac{1}{r_c} + \frac{1}{r_\alpha} \right] \hat{e}_r$$

where r_c is the critical radius (cf. eq. 4.8). Moreover, it can be said of

$$\frac{dn_\alpha}{dt} = - j \, 2\Pi r_\alpha \tag{5.13a}$$

and assuming, again, incompressibility of the cluster phase, we get:

$$\frac{dr_\alpha}{dt} = \frac{j}{\Gamma_\alpha} = \frac{D\Gamma}{r_\alpha^2 K_B T} \frac{\kappa}{l_o} \left[\frac{1}{r_c} - \frac{1}{r_\alpha} \right] \tag{5.13b}$$

Thus from eq. (5.13b) it can be concluded that when

$$r_\alpha < r_c \text{ it implies } \frac{dr_\alpha}{dt} < 0$$

and

$$r_\alpha > r_c \text{ it implies } \frac{dr_\alpha}{dt} > 0 \tag{5.14}$$

The first inequality (5.14a) leads to a shrinkage and consequently to the disappearance of the cluster while inequality (5.14b) leads to a further growth. For a large cluster, $1/r_\alpha << 1/r_c$ and thus we have

$$\frac{dr_\alpha}{dt} = \frac{D\Gamma}{r_\alpha^2 K_B T} \frac{\kappa}{l_o} \left[\frac{1}{r_c}\right] \tag{5.15}$$

To complete the derivation and give a full argument, we have to define the parameter l_o which was introduced as the width of the inhomogeneous region between the coexisting phases. Thus for (interface) or kinetic limited growth, l_o has to be a constant, of the order of a molecular dimension and for diffusion limited growth it has to be equal to the radius of the cluster to a good approximation [8,20]. Therefore, the solution of eq. (5.15) is

$$r_\alpha = \left(\frac{D\Gamma\kappa}{r_\alpha^2 K_B T r_c}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \tag{5.16a}$$

for diffusion limited growth, $(r_\alpha^2 \sim t)$.

$$r_\alpha = \frac{D\Gamma\kappa}{r_\alpha^2 K_B T r_c} \frac{1}{l_o} t \tag{5.16b}$$

for kinetic limited growth, $(r_\alpha \sim t)$.

These results can be obtained also by the diffusion-equation (5.7b) [1]. The method outlined here has the advantage that it has a widder applicability; (see e.g. [1]) and allows in addition the development of a new approach to the kinetic description of Ostwald ripening that we are going to discuss now. This approach was developed first by Schmelzer [20,1] in application to phase transitions in 3-d systems.

5.2 Generalization to the Kinetics of Growth of Ensembles of Clusters: Ostwald Ripening

The growth equation of an arbitrary cluster, (i) out of a number of clusters in a considered system is given by (see eqs. (5.10), (5.13a))

$$\frac{dn_\alpha^{(i)}}{dt} = - \frac{D\Gamma_\beta}{\Gamma_\alpha K_B T} \frac{1}{1_o^{(i)}} \frac{\partial \phi^{(i)}}{\partial r_\alpha^{(i)}} \quad (a)$$

$$\frac{dr_\alpha^{(i)}}{dt} = - \frac{D\Gamma_\beta}{2\Pi r_\alpha^{(i)} \Gamma_\alpha^2 K_B T} \frac{1}{1_o^{(i)}} \frac{\partial \phi^{(i)}}{\partial r_\alpha^{(i)}} \quad (b) \qquad (5.17)$$

The thermodynamic potential, ϕ, can be replaced by ΔG or ΔF given by eqs. (4.42).

In the absence of depletion of the medium by the growth of clusters of a new phase, $\phi = \Delta G$, and clusters develop independently by the growth law equations developed for $\Delta G(r_\alpha)$ in the previous chapter, where r_c is a constant. In contrast, when the growth of each cluster is influenced by the size and total number of all other clusters in a finite system of constant surface area in which the characterstic potential is $\phi = \Delta F$, the growth equation is that given by eq. (5.13) again; but now r_c depends on the number of size of all clusters in the system. However, in the second stage of the phase transition (dashed-curve, see fig. 4.4b) clusters do not affect each other and most of them grow at the expense of free particles

(monomers) of the medium (β-phase) with $r_\alpha \sim t$ for kinetic limited growth and as $r_\alpha^2 \sim t$ for diffusion limited growth.

For the analysis of the kinetic equations of competitive growth or Ostwald ripening of clusters (see the valley points of fig. 4.4b, dash-stared curve) we start with eq. (5.17b) under the additional assumption that all the mass of the new phase is evenly distributed among N identical clusters. For all possible numbers of N identical clusters, and $\phi = \Delta F$, we obtain

$$N \frac{dR}{dt} = - \frac{D\Gamma_\beta}{2\pi R \Gamma_\alpha^2 K_B T} \frac{1}{I_o} \frac{d\Delta F}{dN} \frac{dN}{dR} \qquad (5.18)$$

where the following replacement is made.

$$N \frac{\partial \Delta F^{(i)}}{\partial r_\alpha} \longrightarrow \frac{d\Delta F}{dN} \frac{dN}{dR} \qquad (5.19)$$

ΔF is given now by eq. (4.43). Expression (5.19) is motivated by the argument that in the course of Ostwald ripening, the thermodynamic driving force is the decrease of the thermodynamic potential connected with the decrease of the number of clusters. R is considered as the mean radius of the ensemble of clusters in this stage of the phase transition. From the previous chapter we have:

$$\frac{d\Delta F}{dN} = \kappa \pi R$$

$$\frac{dN}{dR} = - \frac{2N}{R}(1+y^{-1})$$

where

$$y^{-1} = -\frac{\kappa A(1-\frac{NA_\alpha}{A})^3}{2A_\alpha R_\alpha N(\Gamma-\Gamma_\alpha)^2}\frac{\partial\Gamma_\beta}{\partial\mu_\beta}$$

Thus eq. (5.18) yiel[illegible]

$$\frac{dR}{dt} = \frac{D\Gamma_\beta\kappa}{\Gamma_\alpha^2 K_B T R 1_o}(1+y^{-1}) \qquad (5.20)$$

When a numerical correction factor, b is introduced into eq. (5.20) to compensate the above approximations, eq. (5.20) is rewritten as

$$\frac{dR}{dt} = b\frac{D\Gamma_\beta\kappa}{\Gamma_\alpha^2 K_B T R 1_o}(1+y^{-1})$$

b will be determined soon.

To complete the kinetic description of Ostwald ripening, a supplementary equation describing the time-evolution of the number of clusters has to accompany it. To develope this supplimentary equation let us start with the time derivative of Gibbs Thomson equation. It reads:

$$-\frac{d\sigma_\beta}{dt} - \Gamma_\alpha\frac{d\mu_\beta}{dt} - \frac{\kappa}{R^2}\frac{dR}{dt} = 0 \qquad (5.21)$$

$$(\Gamma_\beta - \Gamma_\alpha)\frac{d\mu_\beta}{d\Gamma_\beta}\frac{d\Gamma_\beta}{dt} = \frac{\kappa}{R^2}\frac{dR}{dt}$$

with the value of $\frac{d\Gamma_\beta}{dt}$ being expressed as:

$$\frac{d\Gamma_\beta}{dt} \quad \frac{(\Gamma-\Gamma_\alpha)}{(1-\frac{NA_\alpha}{A})^2} \quad \frac{d}{dt}(\frac{NA_\alpha}{A}) \tag{5.22}$$

equation (5.21) can be rewritten as eq. (5.23)

$$\frac{R(\Gamma-\Gamma_\alpha)^2}{(1-\frac{NA_\alpha}{A})^3} \frac{NA_\alpha}{\kappa A} \frac{d}{dt} \ln(\frac{NA_\alpha}{A}) \frac{d\mu_\beta}{d\Gamma_\beta} = \frac{d}{dt} \ln R \tag{5.23}$$

This is written in a compact form as

$$\frac{d}{dt} [\ln(\frac{NA_\alpha}{A})] = -y^{-1} \frac{d}{dt} [\ln(R^2)] \tag{5.24}$$

Equation (5.24) gives the time-evolution of the number of clusters. The two eqs. (5.20b) and (5.24) can be solved by numerical methods. In the asymptotic region where the system attains its saturation density $\Gamma_\beta = \Gamma'$ and y^{-1} is tending to zero, eq. (5.20b) gets the form of

$$R^3_{(t)} = \frac{3bD\Gamma'\kappa}{\Gamma_\alpha^2 K_B T} t \tag{5.25}$$

for diffusion limited growth, ($l_o = R$); and it will have the form

$$R^2_{(t)} = \frac{2bD\Gamma'\kappa}{\Gamma_\alpha^2 K_B T l_o} t \tag{5.26}$$

for kinetic limited growth.

Asymptotic solutions for the process of Ostwald ripening in the 3-d case were obtained first by Lifshitz and Slyozov

[23]. If their method is applied to the 2-d case considered here, the asymptotic solution for diffusion limited growth is given by eq. (5.27)

$$R^3 = \frac{4}{9} \frac{D\kappa\Gamma'}{r_\alpha^2 K_B T} t \tag{5.27}$$

Since the results of Lifshitz and Slyozov are correct in the asymptotic region we set b of eq. (5.25) equal to

$$b = \frac{4}{27} \tag{5.28}$$

to get an agreement with the results obtained in this limiting case. Let us go over again to eq. (5.24).

$$\frac{d}{dt}\left[\ln\left(\frac{NA_\alpha}{A}\right)\right] = - y^{-1} \frac{d}{dt} \ln(R^2) \tag{5.24}$$

Since $y^{-1} < 0$, it follows that the total surface area or the total mass of the new phase increases with time. In the asymptotic region ($y^{-1} \longrightarrow 0$) the equation is reduced to

$$\frac{d}{dt}\left[\ln\left(\frac{NA_\alpha}{A}\right)\right] = 0 \tag{5.29}$$

and thus

$$\frac{NA_\alpha}{A} = \frac{Nn_\alpha \Gamma}{n\Gamma_\alpha} = \text{constant.} \tag{5.30}$$

Therefore, in this limiting case, any variation in the mass consists only in a redistribution among all the clusters.

To obtain the value of the constant in eq. (5.30) let us analyse the Gibbs Thomson equation in the asymptotic region.

in which the following is obtained.

$$\sigma' - \sigma_\beta + \Gamma_\alpha(\mu' - \mu_\beta) \simeq 0 \tag{5.31}$$

since $\frac{1}{\Gamma_\alpha} \simeq 0$

Moreover,

$$|\sigma' - \sigma_\beta| << |\Gamma_\alpha(\mu' - \mu_\beta)| \tag{5.32}$$

and we have:

$$\mu' - \mu_\beta \simeq 0 \tag{5.33}$$

Again,

$$\mu_\beta(\Gamma_\beta) = \mu_\beta\left(\frac{\Gamma\left(1 - \frac{Nn_\alpha}{n}\right)}{1 - \frac{NA_\alpha}{A}}\right)$$

$$\approx \mu_\beta\left(\Gamma\left(1 - \frac{Nn_\alpha}{n}\right)\right) \tag{5.34}$$

Since the density of the liquid is much more greater than that of the initial gas phase, $NA_\alpha << A$, and we can neglect this term compared with 1. Expanding μ_β about the initial stage, $X = \frac{Nn_\alpha}{n} \approx 0$ and neglecting higher order terms the following is obtained.

$$\mu_\beta = \mu + \frac{\partial \mu_\beta}{\partial \Gamma_\beta} \frac{\partial \Gamma_\beta}{\partial X}(X)$$

$$= \mu \frac{\partial \mu_\beta}{\partial(\Gamma - \Gamma X)} \frac{\partial(\Gamma - \Gamma X)}{\partial X}(X)$$

$$= \mu - \Gamma \frac{\partial \mu}{\partial \Gamma}(X)$$

Then

$$\frac{\partial \mu(X)}{\partial X} \neq 0 \tag{5.35a}$$

or $$\frac{Nn_\alpha}{n}\frac{\Gamma}{\Gamma_\alpha} = \frac{\mu-\mu'}{\Gamma_\alpha}\frac{\partial\Gamma}{\partial\mu} = \text{const.} \qquad (5.35b)$$

This equation is equivalent to eq. (5.30) and gives in addition an estimate of the constant. To find the time evolution of the number of clusters, in the asymptotic region it is possible to write

$$N = \frac{n}{\Pi\Gamma_\alpha R^2}\frac{(\mu-\mu')}{\Gamma}\frac{\partial\Gamma}{\partial\mu} \qquad (5.36)$$

Substituting the value for $R^2(t)$ obtained from eq. (5.25) in eq. (5.36), N(t) for diffusion limited growth is to be

$$N(t) = \left[\left(\frac{K_B T}{3bD\Gamma'\kappa\sqrt{\Gamma_\alpha}}\right)^{2/3}\frac{n}{\Pi}\frac{(\mu-\mu')}{\Gamma}\frac{\partial\Gamma}{\partial\mu}\right] t^{-2/3} \qquad (5.37)$$

and for the kinetic - limited growth, N(t) is given by

$$N(t) = \left[\left(\frac{\Gamma_\alpha K_B T n}{2bD\Gamma'\kappa\Pi}\right)\frac{(\mu-\mu')}{\Gamma}\frac{\partial\Gamma}{\partial\mu}\right] t^{-1} \qquad (5.38)$$

The computer simulation results of first-order phase transitions in 2-d system carried out by Koch and coworkers [4] is theoretically ascertained in the work of this paper. That is, the asymptotic condition for the mean radius of a 2-d cluster in the Ostwald ripening is related with time as $R^2(t) \sim t$ for kinetic - limited growth; while for the slow and early stage predictions of the computer, an approximate value, $y \tilde{\sim} -1$, in the neighbourhood of the inflexion point can be proposed.

The theoretical analysis, carried out here is for isothermal conditions and one component system case. Similar analysis for other constraints, like, adiabatic conditions and multicomponent system case, can be developed.

Discussion

In the present paper a thermodynamic description of physisorbed monolayers was developed. Based on this theory, a thermodynamic analysis of first order phase transition in monolayers and a kinetic description of the process were presented.

The analysis was carried out under a special consideration of isothermal constraints and one component systems. Very often, however, it is more appropriate to assume adiabatic conditions and to consider multi-component systems. Moreover, sometimes the approximation of an incompressible cluster phase may be crude.

It is believed, that similar investigations as for 3-d systems can be considered as a first proof, that the method can also be applied for 2-d systems with qualitatively the same result in these more general situations.

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Declaration

I, the undersigned, declare that this thesis is my original work, done under the supervision and guidance of Dr. Sc. J. Schmelzer, and all sources of material used for the thesis have been duly acknowledged in the body of the thesis and the reference.

Teka G/Medhin

This thesis has been submitted for examination with my approval as University Advisor.

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