1 Introduction

1.1 Basic Aims and Methods

The problems of the thermodynamic and kinetic description of equilibrium phase transitions of first order are discussed in various original publications and manuals. It may seem that the commonly employed general approach to the different forms of phase transitions based on Gibbs's theory is quite sufficient for most cases of application and further detailed analyses are not required. On the other hand, it is easy to notice that crystal–liquid phase equilibria and phase transitions (the terms phase transition and phase equilibrium are often employed here with a similar meaning except for the cases when the transformation kinetics is studied) are not as thoroughly analyzed as compared to the liquid–vapor phase transition. In the latter case, the existence of a critical point in the coexistence of two fluid phases defines characteristic scales of thermodynamic variables (volume, temperature, pressure, entropy and energy) and allows one to introduce the concepts of corresponding states and thermodynamic similarity of various substances.

For the crystal-liquid phase transitions of simple substances the situation is different. The melting lines were found not to contain with the increase of temperature a fundamental singularity like the liquid-vapor critical point. This feature makes impossible the natural choice of some scaling parameters similar to the liquid-vapor phase transition. But one can implement another approach to the problem, which is based on the low-temperature asymptotic behavior of the melting lines of substances of normal type. Such a procedure requires one to include into the thermodynamic consideration the behavior of the respective phases at metastable conditions. The mere fact of considering systems at such conditions represents one of the distiguishing features of the present book. Here the problem of similarities and differences of crystal-liquid and liquid-vapor phase transitions in single-component systems is the central problem under consideration. In this analysis, much attention is devoted to the revelation of the thermodynamic similarity in the behavior of different substances at the phase transitions. The reason for this is that similarity concepts exhibit the very general deep properties of a class of effects retaining some particular differences in behavior in other particular respects. The more complete is the understanding of the nature of the effects considered the more completely and clearly the similarity in the behavior can be exhibited. In the present work, the mentioned connection is clearly demonstrated in application both to liquid-vapor and crystalliquid phase transitions first in application to the behavior of one-component systems. In the final chapter, the analysis is then extended to crystal-liquid-vapor and liquid-liquid phase equilibria in two-component systems analyzed from the same point of view.

The present work is written employing basically the framework of phenomenological thermodynamics. The application of statistical-mechanical approaches, e.g., by utilizing Gibbs's

Crystal-Liquid-Gas Phase Transitions and Thermodynamic Similarity. Vladimir P. Skripov and Mars Z. Faizullin Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 3-527-40576-3

canonical ensemble method, would have required the introduction of various assumptions and approximations into the analysis, inevitable in order to obtain concrete results. Here we concentrate on the analysis of the general features leaving detailed statistical-mechanical considerations to future investigations or referring to the existing literature.

1.2 States of Aggregation. Phase Diagrams and the Clausius–Clapeyron Equation

First-order phase transitions are characterized by a jump of the first-order derivatives of the Gibbs thermodynamic potential and by the existence of metastable states of each of the phases. An example is given in Fig. 1.1.





Figure 1.1 shows a (p, T)-phase diagram of different states of aggregation of a singlecomponent substance with a crystal phase, where the melting of the latter is characterized by a positive slope of the equilibrium crystal–liquid coexistence curve. The line of coexistence of liquid and vapor is terminated at the critical point denoted in the figure by C. In the critical point, the liquid and vapor phases become identical. The dashed parts of the curves show the

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extensions of phase equilibrium curves into the range of the respective metastable states of the coexisting phases.

The line of phase equilibrium for a homogeneous single-component system is defined by equality of the chemical potentials at the same values of temperature and pressure in both phases. For the liquid–vapor coexistence curve we have

$$\mu_L(T, p) = \mu_V(T, p) . \tag{1.1}$$

Here μ_L and μ_V are the chemical potentials of the liquid and the vapor, respectively, T is the temperature and p is the pressure.

By taking the derivative of Eq. (1.1) along the liquid–vapor equilibrium curve and, taking into account the relations $(\partial \mu / \partial T)_p = -s$, $(\partial \mu / \partial p)_T = v$, we get the Clausius–Clapeyron equation

$$\frac{dp}{dT_{LV}} = \frac{\Delta s_{LV}}{\Delta v_{LV}} , \qquad (1.2)$$

where $\Delta s_{LV} = s_L - s_V$ and $\Delta v_{LV} = v_L - v_V$ are the jumps of specific entropy and volume in the phase transition. Both differences on the right-hand side of Eq. (1.2) are positive and the inequality $(dp/dT_{LV}) > 0$ holds.

Similarly one can write the Clausius–Clapeyron equation for crystal–liquid phase equilibrium. The entropy of the liquid is greater than the entropy of the crystal, $\Delta s_{SL} = s_L - s_S > 0$, so the slope of the melting line is determined by the sign of the difference Δv_{SL} . Substances, obeying the inequalities $\Delta v_{SL} > 0$ and $dp/dT_{SL} > 0$, are called normally melting. Here we will consider only such normally melting substances.

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The curve as determined by Eq. (1.1) can be interpreted as a line of intersection of two surfaces in the (T, p, μ) -space. For both of these surfaces, this line is not a singular one. This property implies the possibility of a smooth extension of both phases into the regions of their metastable states. Figure 1.2 shows the trace of the surfaces for the crystalline $\mu_S(T, p)$ and liquid $\mu_L(T, p)$ phases on the plane p = constant. The point O of the intersection of the lines L'L and SS' corresponds to the phase equilibrium at the given pressure. For the parts OL' and OS' the chemical potential has a higher value than for the competing phase at the same values of T and p.

The relative stability of the phases is determined by the relation between the values of μ_S and μ_L . The more stable phase corresponds to the lower value of the chemical potential. The state of the phase, having at the given temperature and pressure higher values of the chemical potential, is called metastable. The phase in this condition is stable with respect to small (continuous) changes of the thermodynamic parameters and has a finite lifetime. Metastable states are unstable with respect to large-scale disturbances which lead to the formation of viable new phase nuclei. The metastable state is destroyed by nucleation and growth of the nuclei of a new phase which is more stable at the given values of temperature and pressure. In a system which is free of impurities initiating the phase transformation, nucleation takes place due to thermal fluctuations.

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Figure 1.2: Behavior of the chemical potential of the crystalline (SS') and liquid (LL') phases in dependence on temperature on the surface p = constant near the temperature of the phase transition, T_0 .

Metastable states and their quasi-static changes can be described by the equations of equilibrium thermodynamics. In order to allow such a description, the system should obey the following conditions [1]

$$\{t_i\} \ll t_{\exp} < \bar{\tau} , \tag{1.3}$$

where t_i is the characteristic time of relaxation of the system under consideration with respect to the *i*-th state parameter (temperature, pressure, etc.), t_{exp} is the characteristic time of the experiment (the time required to transfer the system into the metastable state and to carry out the subsequent experimental observations), $\bar{\tau}$ is the mean waiting time for the formation of a nucleus of a more stable phase. The left part of the inequality in Eq. (1.3) guarantees the quasi-static character of the thermodynamic properties of the metastable phase. For such kinds of changes, the relations of equilibrium thermodynamics are fulfilled. This statement means that the system can be smoothly transformed into the metastable state without the occurrence of some kind of specific behavior in its properties at the point of the equilibrium phase transformation, if the system remains homogeneous. The latter condition is ensured by the right part of the inequality in Eq. (1.3).

The transfer of the system into metastable states is accompanied by a decrease of the thermodynamic stability of the respective phases. The equilibrium condition of the thermodynamic system (with respect to small (continuous) changes of the state parameters) requires

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the second variation of the specific internal energy u(s, v) to be positive [2], i.e.

$$\delta^2 u = \left(\frac{\partial^2 u}{\partial s^2}\right) (\delta s)^2 + 2\left(\frac{\partial^2 u}{\partial s \partial v}\right) \delta s \delta v + \left(\frac{\partial^2 u}{\partial v^2}\right) (\delta v)^2 > 0.$$
(1.4)

The inequality Eq. (1.4) holds true when the determinant, composed from the coefficients of the real-valued quadratic form Eq. (1.4), and its principal minors are positive

$$D = \begin{vmatrix} \frac{\partial^2 u}{\partial s^2} & \frac{\partial^2 u}{\partial s \partial v} \\ \frac{\partial^2 u}{\partial s \partial v} & \frac{\partial^2 u}{\partial v^2} \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial T}{\partial s}\right)_v & \left(\frac{\partial T}{\partial v}\right)_s \\ \left(\frac{\partial T}{\partial v}\right)_s & -\left(\frac{\partial p}{\partial v}\right)_s \end{vmatrix} > 0, \qquad (1.5)$$

$$\left(\frac{\partial T}{\partial s}\right)_{v} = \frac{T}{c_{v}} > 0 , \qquad -\left(\frac{\partial p}{\partial v}\right)_{s} > 0 , \qquad (1.6)$$

where c_v is the isochoric heat capacity. The derivatives in Eqs. (1.6) are called the adiabatic stability coefficients [3]. Zero values of the determinant D define the boundary of the thermodynamic phase stability with respect to continuous changes of the thermodynamic state parameters: this boundary is denoted as the spinodal.

The connection between the isodynamic partial derivatives and the stability determinant, D, is given by the following expressions [3]

$$\left(\frac{\partial T}{\partial s}\right)_p = -\frac{D}{(\partial p/\partial v)_s},\tag{1.7}$$

$$-\left(\frac{\partial p}{\partial v}\right)_T = \frac{D}{(\partial T/\partial s)_v} \,. \tag{1.8}$$

The stability conditions Eqs. (1.5) and (1.6) are thus reduced to the positivity of the isodynamic partial derivatives

$$\left(\frac{\partial T}{\partial s}\right)_p = \frac{T}{c_p} > 0 , \qquad (1.9)$$

$$-\left(\frac{\partial p}{\partial v}\right)_T = (v\beta_T)^{-1} > 0 , \qquad (1.10)$$

which are also called isodynamic stability coefficients. Here c_p is the isobaric heat capacity and β_T is the isothermal compressibility. Zero values of the derivatives Eqs. (1.9) and (1.10) correspond to the spinodal of the system. Conditions (1.9) and (1.10) allow us to estimate the thermodynamic stability of the system and the distance to the spinodal by properties which may be obtained directly through experiment.

1.4 Phase Transformations in a Metastable Phase. Homogeneous Nucleation

The depth of entering the region of metastable states is naturally connected with the difference of the chemical potentials of the phases at given temperature and pressure. For example, for the supercooled liquid we have (see Fig. 1.2)

$$\Delta \mu_{SL} = \mu_L - \mu_S . \tag{1.11}$$

This value is a measure of the instability of the liquid phase and characterizes the driving force of the phase transformation. The difference of the chemical potentials, $\Delta \mu_{SL}$, can be expressed through the values of thermodynamic parameters which can be measured directly experimentally, i.e., via the corresponding deviation from the point of the equilibrium phase transition with respect to temperature, ΔT , and pressure, Δp [1]. For small deviations from phase equilibrium, the value $\Delta \mu_{SL}$ can be represented as

$$\Delta \mu_{SL} = \left[\left(\frac{\partial \mu_L}{\partial T} \right)_p - \left(\frac{\partial \mu_S}{\partial T} \right)_p \right] \Delta T - \left[\left(\frac{\partial \mu_L}{\partial p} \right)_T - \left(\frac{\partial \mu_S}{\partial p} \right)_T \right] \Delta p$$
$$= (s_L - s_S) \Delta T - (v_L - v_S) \Delta p . \tag{1.12}$$

Here s and v are the specific entropy and volume at the temperature, T, and pressure, p, and the indices S and L refer to the crystal and the liquid, respectively. Expressions like Eq. (1.12) are also valid in cases when the depth of entering the metastable state region cannot be considered as small. In such cases, the values of entropy and volume for the crystal and the liquid are defined as mean values in the interval of supercooling.

The formation of a new phase in a metastable liquid is connected with overcoming the energetic barrier, the work of formation of a nucleus of critical size. If in a metastable system nuclei with sizes above the critical one are formed, then their further growth is governed thermodynamically. The process of formation of the first viable nucleus represents in this way the starting point of the phase transformation in the system. One way of describing processes of formation of clusters of supercritical sizes is homogeneous nucleation theory. Homogeneous nucleation theory presumes that the processes of formation and growth of new phase nuclei are the result of heterophase fluctuations proceeding by thermal fluctuations in the otherwise homogeneous ambient phase. The principal constituent parts of this theory were formulated first by Gibbs [4]. He was also the first to suggest that the thermodynamic stability of a metastable state should be related to the work of critical nucleus formation, W_* . Provided a critical vapor nucleus is formed in a metastable liquid, Gibbs's theory yields the following expression for the work of critical cluster formation

$$W_* = \frac{16\pi}{3} \frac{\sigma_{LV}^3}{(p'' - p')^2} , \qquad (1.13)$$

where

$$p'' - p' = \frac{2\sigma_{LV}}{r_*}$$
(1.14)

is the difference of the pressure inside (p'') and outside (p') a spherical nucleus of critical size (with a radius r_*) and σ_{LV} is the surface tension of the liquid–vapor equilibrium interface. Eq. (1.14) is the condition of mechanical equilibrium in the superheated liquid–vapor system nucleus, denoted commonly as the Young–Laplace equation.

Volmer [5] has formulated the expression for the work of critical nucleus formation in the following widely equivalent way

$$W_* = \frac{16\pi}{3} \frac{\sigma_{LV}^3 v_V^2}{(\Delta \mu_{LV})^2} , \qquad (1.15)$$

where, in application to boiling of liquids, v_V is the specific volume of the vapor phase, $\Delta \mu_{LV}$ is the difference of the chemical potentials of liquid and vapor phases at given pressure and temperature. In application to crystallization of liquids and taking into account Eq. (1.12) one can rewrite the expression for the work of critical crystal nucleus formation in a supercooled melt at given external pressure in the following form [6]

$$W_* = \frac{16\pi}{3} \frac{\sigma_{SL}^3 v_S^2}{(\Delta \mu_{SL})^2} = \frac{16\pi}{3} \frac{\sigma_{SL}^3 v_S^2}{(\Delta s_{SL})^2 (\Delta T)^2} , \qquad (1.16)$$

where σ_{SL} is the surface tension of the crystal-melt interface. In order to describe the state of an equilibrium crystallite in a melt, an effective surface tension is usually introduced by substituting the facetted shape of the crystal by a sphere of a radius *r* having the same volume as the crystal in its equilibrium shape [6]. The values v_S , Δs_{SL} , and σ_{SL} in Eq. (1.16) are supposed to be equal to the respective macroscopic state parameters of the newly evolving phase in equilibrium with the ambient phase. The above considerations are the essence of the thermodynamic approximation for the work of critical cluster formation in homogeneous nucleation theory.

The value W_* in Eq. (1.16) characterizes the height of the Gibbs free energy barrier which the system should overcome due to fluctuations. Increasing the depth of entering the region of metastable states, we decrease this barrier. Therefore, the probability of overcoming the barrier due to thermal fluctuations is increased. Dividing W_* by the mean energy of thermal motion per degree of freedom, k_BT , where k_B is the Boltzmann constant, one gets a natural dimensionless measure for the height of the barrier, denoted commonly as the Gibbs number, G_*

$$G_* = \frac{W_*}{k_B T} \,. \tag{1.17}$$

The Gibbs number, G_* , plays an important role in the theory of homogeneous nucleation. It determines to a large extent the value of the steady-state nucleation rate, J. The nucleation rate, J, is determined as the mean number of viable nuclei formed in a unit volume at unit time. For steady-state conditions, the expression for J can be represented in the following way

$$J = N_1 B_1 \exp\left(-G_*\right) \,, \tag{1.18}$$

where N_1 is the number of molecules in a unit volume of the liquid and B_1 is a kinetic pre-factor characterizing the mean rate of passing the range of near-critical nucleus sizes in

cluster size space. For liquids with low viscosity, the parameter B_1 changes only slightly with an increase of the degree of supercooling, ΔT . By the order of magnitude, we have $N_1 \approx 10^{28} \text{ m}^{-3}$, $B_1 \approx 10^{10} - 10^{11} \text{ s}^{-1}$. From Eqs. (1.16)–(1.18) we may conclude that a small change of supercooling, ΔT , of the liquid significantly influences the nucleation rate, J. Thus, the value of J is increased by 9 orders of magnitude for mercury (Hg) and by 4 orders of magnitude for tin (Sn) when the supercooling is increased by 10 K starting from $\Delta T = 52$ K (for Hg) and 122 K (for Sn) [6].



Figure 1.3: Binodal curve (1), line of accessible superheating (2) and spinodal curve (3) of hexane. The circles on curve (2) refer to experimental measurements of the accessible superheating, C denotes the critical point.

The searches for the detailed expressions for J were connected with the construction and the solution of the set of kinetic equations describing the evolution of an ensemble of nuclei of subcritical sizes. This way of formulating homogeneous nucleation theory is described, for example, in the works of Volmer [5], Zeldovich [7], and Frenkel [8]. The model, based on the diffusion model of the nucleation process, turned out to be universal, independent with respect to the nature of the phases capable of coexistence and metastability. This general character is proven, for example, by the systematic investigations of homogeneous nucleation in superheated liquids [1] and supercooled melts [6].

Equations (1.15)–(1.18) clearly exhibit the strong nonlinear dependence of the nucleation rate on the "driving force" of the phase transition, $\Delta \mu$. It results in a very fast increase of J with an increase of $\Delta \mu$. By this reason, the process of homogeneous nucleation exhibits features widely similar to some threshold phenomenon. Only after some certain degree of

supersaturation is reached can perceptible nucleation be observed. Once this threshold is passed, the further increase of supersaturation leads to a dramatic increase of J.

Although the intensity of nucleation processes in a superheated liquid is increased with an approach to the spinodal, the degree of stability of the system with respect to discontinuous (heterophase) variations of its state is not directly determined by the stability of the system to relatively small homophase fluctuations. For processes of nucleation, connected with discontinuous (heterophase) fluctuations, the measure of stability is the mean waiting time, $\bar{\tau}$, for occurrence of a viable nucleus in a metastable system of a volume, V. This mean waiting time is connected with the nucleation rate via the relation [1,6]

$$\bar{\tau} = (J \cdot V)^{-1}$$
 (1.19)

It depends significantly on the interfacial tension, σ , and is not directly related to the isodynamic stability coefficients $-(\partial p/\partial v)_T$ and $(\partial T/\partial s)_p$.



Figure 1.4: Family of curves corresponding to an unstable equilibrium for a heterogeneous state consisting of a cluster in the otherwise homogeneous ambient phase for different values of the radius, r, of a spherical bubble in superheated hexane. By p_{LV} , the macroscopic binodal is specified corresponding to $r \rightarrow \infty$. The other curves are drawn for the following values of r: (1) r = 50 nm, (2) r = 10 nm, (3) r = 5 nm, (4) r = 3 nm. Curve (5) is the spinodal curve of liquid hexane.

In Fig. 1.3, the binodal and the spinodal curves and the line of accessible superheatings for liquid hexane are shown corresponding to the steady-state nucleation rate $J = 10^6 \text{ s}^{-1} \text{ cm}^{-3}$ [1]. Note that in supercooled single-component liquids there is no spinodal curve at all (see

Section 2.1); however, the nucleation kinetics is described by the same scheme as for the case of boiling of superheated liquids. The main condition of intensive spontaneous nucleation consists in a decrease of the nucleation barrier W_* to sufficiently low values, for example, when the Gibbs number is of the order

$$G_* = \frac{W_*}{k_B T} \approx 20-50 .$$
 (1.20)

Except for the case of very thin layers, the surface tension does not enter the conditions of phase equilibrium of two phases coexisting at planar interfaces. In the order of magnitude, the ratio of the interfacial energy of the system and the bulk contributions depends on the size of the newly evolving phase, l, as 1/l. For small particles ($l \approx r$) the surface energy gives a significant contribution to the conditions of their equilibrium with the environment (see Eq. (1.14)) and to the work of formation of an unstable equilibrium (critical) nucleus of the dispersed phase (cf. Eqs. (1.13) and (1.16)) in a sufficiently large volume of the parent (metastable) phase. If the radius of a new-phase particle, r, is taken as the size parameter, then one can plot a set of unstable equilibrium curves on a (T, p)-surface corresponding to different values of the size parameter, r. Each of these curves connects the temperature with the pressure of the external phase.

Figure 1.4 shows such a plot for gas bubbles in superheated hexane. With a decrease of r, the lines are shifted to the right along the temperature axis and to lower pressures as compared with the macroscopic binodal, p_{LV} . The latter curve corresponds to $(1/r) \rightarrow 0$. Note that for the line of accessible superheating of hexane (2), shown in Fig. 1.3, in the range p > 0 the radius of the critical nucleus increases with the increase of pressure (and temperature). By this reason, the line J(T, p) = constant does not belong to the family of curves r(T, p) = constant [1].

The phase boundary between the different phases consists, in general, of several molecular layers, its width, δ , is proportional to the correlation length. The minimal size of a new-phase particle also equals δ to an order of magnitude. The existence of a critical point in liquid–vapor equilibrium (or the liquid–liquid equilibrium in a solution) presupposes the growth of the correlation length and, consequently, also of the value of the parameter δ with the approach to the critical point. The absence of a critical point for crystal–liquid equilibrium in a single-component system makes the swelling of the transition layer impossible. Here its width is always limited in its extent to several intermolecular distances.