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S. W. Koch

Dynamics of First-Order Phase Transitions in Equilibrium and Nonequilibrium Systems

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I. Introduction and Survey

The topic of this book[+] is the theoretical description of dynamical aspects of discontinuous phase transitions in physical systems. It includes effects like the development of phase separation - i.e. nucleation and spinodal decomposition - , freezing and melting, as well as phase transitions in systems which are far from thermal equilibrium. Examples are the formation of electron-hole droplets in highly laser excited semiconductors and transitions between different nonequilibrium states in optical systems like optical bistability.

The usual methods to describe these phase transitions is to treat only a few relevant variables explicitly. In such a macroscopic theory these relevant variables assume the role of order parameters. The other, nonrelevant variables lead to nonlinearities, dissipative effects, and to noise contributions in the equations of the order parameters. Hence, it is most appropriate to treat these processes within a probabilistic formalism. In this way one is able to investigate the dynamical evolution of a system after changing the external control parameters. If discontinuous phase transitions take place the initially stable states decay through build-up and growth of heterophase fluctuations. The probabilistic formalism is well suited to describe these stochastic processes.

It is one of the intentions of this book to point out some common aspects of the seemingly quite different physical problems presented in the various chapters. Especially, connections will be established between the discussed nonequilibrium transitions and phase transitions in the vicinity of thermal equilibrium. However, one may not expect a unified theory on the level of the theory of critical phenomena for continuous phase transitions. This theory utilizes the occurence of fluctuations on all length scales leading to universal behaviour. Such fluctuations do not occur in connection with discontinuous phase transitions. On the contrary, a well-defined length scale is set by the spatial extension of the heterophase fluctuations driving the respective transition. Especially these heterophase fluctuations and their consequences are a continuous theme of this book.

[+]This book is based on the habilitation thesis of the author, which has been accepted in December 1983 by the Physics Department of the University Frankfurt, Fed. Rep. Germany.

I.1 Basic Features of First-Order Phase Transitions

The basic features of first-order equilibrium phase transitions are discussed most easily in the framework of the Van der Waals theory for the liquid-gas transition. Historically, this theory is the first successful description of a discontinuous phase transformation. It dates back to the year 1873 when Van der Waals in his thesis [1] proposed the famous state equation for a classical liquid-gas system:

$$(p + \frac{a}{V^2})(V-b)=RT \quad . \qquad (I.1)$$

Here, V is the molecular volume, p is the pressure, T is the temperature, and a and b are material parameters. The pressure correction term a/V^2 is a consequence of the attractive part of the intermolecular interaction potential. The co-volume b takes into account the repulsive part. Fig.1 shows examples for the isotherms resulting from the Van der Waals equation.

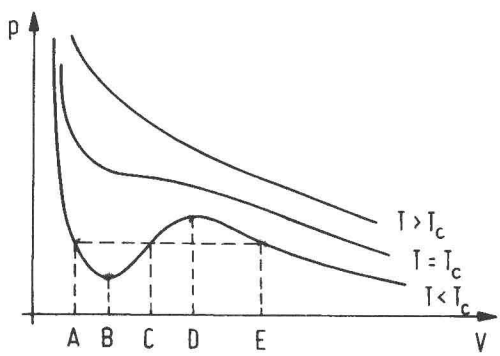

Fig. 1 : Isotherms of a Van der Waals system (schematically)

The function $p(V)\big|_{T=const}$ defined by Eq.(I.1) shows a cubic nonlinearity. Therefore, one has multiple solutions for $T<T_c$ which become degenerate at the so defined critical temperature T_c. For $T>T_c$ the isotherms become simply hyperbole, which are also described by the ideal gas state equation.

For $T\leq T_c$ the isotherms may be sub-devided into parts corresponding to different states of the system (see Fig.1). For $V<A$, the derivative

$\partial p/\partial V\big|_T$ is quite large and negative indicating that a small volume contraction leads to a large increase of the pressure. This characterizes the homogeneous fluid state. Correspondingly, for V>E the system is in the homogeneous gas state. The actual values of A and E, i.e. of V_{fluid} and V_{gas}, are determined with the help of the so-called Maxwell construction. This construction is a consequence of the condition, that in homogeneous systems the chemical potentials μ for coexisting phases have to be equal

$$\mu_{fluid} = \mu_{gas} \cdot$$

The increasing part of the isotherm (region B-D in Fig.1) describes states of the homogeneous system that are mechanically unstable

$$\frac{\partial p}{\partial V}\Big|_T > 0 \cdot$$

On the other hand, the states belonging to the regions A-B and D-E are mechanically stable. Nevertheless, they are no thermodynamic equilibrium states because they do not have the lowest free energy. However, due to their mechanical stability they have a finite lifetime and may very well be observed experimentally. The states of regions A-B and D-E are called over-heated fluid phase and over-saturated vapor phase, respectively.

From the p-V diagram (Fig.1) one may construct the binodal line in a T-V diagram by connecting the points of liquid-gas equilibrium .

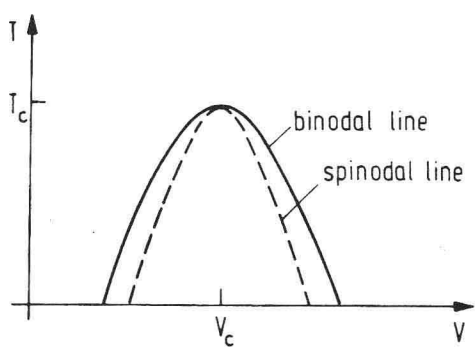

Fig. 2 : Phase diagram of a Van der Waals system (schematically).

The binodal line is also known as phase separation line, since it separates the homogeneous gas and liquid states. For parameters within

the binodal line the equilibrium system shows spatial two-phase coexistence. The dashed line in this coexistence region (see Fig.2) has been constructed from the p-V diagram for the condition $\partial p/\partial V\big|_T=0$. For this curve, Van der Waals introduced the name "spinodal line" [2] . In the region between binodal and spinodal, the homogeneous system is in a metastable state. At this point, it is important to mention, that such a strict distinction between metastability and instability is a direct consequence of the equation of state yielding isotherms of the form shown in Fig.1. Moreover, a rigorous treatment of these effects goes clearly beyond the framework of equilibrium thermodynamics. The corresponding states are nonequilibrium states which are characterized by a finite lifetime. Physically, this is a consequence of the characteristic fluctuations driving the system towards equilibrium.

The Van der Waals theory is a typical example of a mean-field theory. In Refs. [3-6] the respective authors show, that the state equation (I.1) is an exact description for systems with a potential U acting on a molecule at point r given by [3,5]

$$U(r)=\begin{cases}\infty & r<r_0\\ -|\bar{U}| & \text{otherwise}\end{cases} \qquad \text{(I.2a)}$$

or in the limit $\kappa\to 0$ by [7]

$$U(r)=\begin{cases}\infty & r<r_0\\ -|\kappa|e^{-|\kappa|r} & \text{otherwise}\end{cases} \quad . \qquad \text{(I.2b)}$$

The explicit expression for these potentials (e.g. Eq. I.2a) may be derived as effective selfconsistent-field approximation of the detailed many particle interaction [3] .

Other examples of successful mean-field theories are, e.g., the Weiss theory of ferromagnetism [8] and the Ginzburg-Landau theory of superconductivity [9] . These theories may be unified by introducing the concept of an order parameter. The order parameter can be any quantity representing an appropriate measure for the order arising at the phase transition. For the liquid-gas transition one usually chooses the density difference $\rho-\rho_c$ as an order parameter. Here, ρ_c is the density at the critical point.

In many cases, it is possible to expand the free energy in terms of the order parameter $\vec{q}$:

$$F(q,t)=F(0,T)+qF'(0,T)+\frac{q^2}{2}F''(0,T)+\frac{q^3}{3!}F'''(0,T)+\frac{q^4}{4!}F''''(0,T)+\ldots$$

$$=F(0,T)+\alpha q+\frac{\beta}{2}q^2+\frac{\gamma}{3}q^3+\frac{\delta}{4}q^4+\ldots \qquad (I.3)$$

This expanded form of F(q,T) is known as Ginzburg-Landau potential. It is one of the basic ingredients of the classical Landau theory of phase transitions [10]. In the framework of statistical mechanics the most probable value q_m of the order parameter is calculated by minimizing the free energy. Consequently, the probability distribution for q,

$$f(q,T)=Ne^{-F/k_BT},$$

(N is a normalization constant) has its maximum at $q=q_m$.

The various phase transitions are usually classified using the expanded form of F(q,T). Systems with

$$\alpha=0=\gamma$$

and

$$\beta=b(T-T_c)$$

exhibit continuous phase transitions. These transitions are also called phase transitions of second order. As shown in Fig. 3 , the minimum of F(q), i.e. q_m, shifts continuously from $q_m=0$ for $T>T_c$ to $q_m\neq 0$ for $T<T_c$.

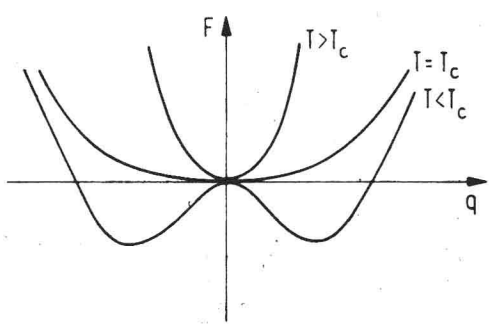

Fig. 3 : Free energy F versus order parameter q for a continuous phase transition (schematically).

If however the quantity γ is not equal to zero,

$$\gamma \neq 0 \ ,$$

the free energy may have the structure shown in Fig. 4 . In this case, the phase transformation appears discontinuously. A common feature of these first-order phase transitions is the appearance of two-phase coexistence (two simultaneous minima of F(q) at q=0 and $q \neq 0$), which gives rise to the phenomenon of hysteresis. In the case of temperature changes, the system may still remain in a metastable state (relative minimum of F) although this is not the state of lowest free energy. The potential barrier can only be surmounted with the help of random fluctuations which, however, are always present in a realistic system. They give rise to the observed finite lifetime of the metastable states.

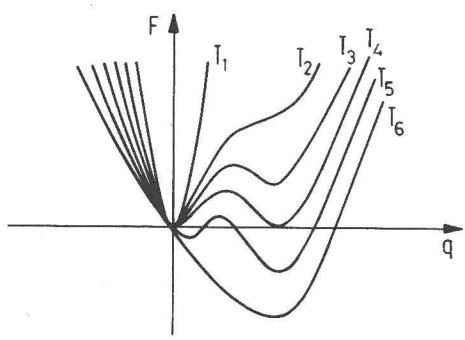

Fig. 4 : Free energy F versus order parameter q for a discontinuous phase transition (schematically). ($T_1 > T_2 > \ldots > T_6, T_4 = T_c$)

To summarize, the Van der Waals theory is a mean-field theory for a first-order phase transition in an equilibrium system. The transition is an equilibrium phase transition, since the state, into which the system evolves is a true equilibrium state in the sense of thermodynamics. Generally, equilibrium transitions occur in systems, which are (thermally) coupled to a reservoir (heatbath). Starting from thermal equlilibrium between bath and system, the bath temperature may be changed to destabilize the existing state initiating a transition to a new phase, which is again in equilibrium with the bath at the new temperature.

One distinguishes between these equilibrium phase transitions and the so-called nonequilibrium transitions. Although both show many common features (see e.g. the discussion in Ref. 11), nonequilibrium phase transitions take place in systems, which are coupled to more than one reservoir [12,13] . These reservoirs have to be at different temperatures preventing thermal equilibrium. At most, nonequilibrium steady states may be realized. By changing the bath parameters one can induce transitions between different nonequilibrium states. These transitions are called "nonequilibrium phase transitions". Completely analogous to the equilibrium case, they may be classified according to the behaviour of the respective order parameter. The Landau theory may be generalized: instead of the free energy, one discusses the so-called "generalized Ginzburg-Landau potentials" [11-14] . Explicit expressions for these potentials are calculated, e.g. in the framework of a Fokker-Planck equation for the probability distribution function $f(\vec{q},t)$:

$$\frac{\partial f}{\partial t} = -\sum \frac{\partial}{\partial q_i} K_i(\vec{q}) f + \frac{1}{2} \sum \frac{\partial^2}{\partial q_i \partial q_j} Q_{ij} f \quad . \tag{I.4}$$

In this equation, the drift term ($\propto \vec{K}$) contains the deterministic part of the order parameter dynamics. The diffusion term ($\propto \overleftrightarrow{Q}$) accounts for the influence of the stochastic fluctuations. The stationary solution of eq. (I.4)

$$f^{st}(\vec{q}) = f(\vec{q}, t=\infty)$$

defines the Ginzburg-Landau potential ϕ ,

$$f^{st}(\vec{q}) = N e^{-\phi(\vec{q})/k_B T} \quad .$$

Once ϕ is known, the terminology of equilibrium theory may be applied directly.

In some special cases (systems with detailed balance) ϕ may be calculated directly from the so-called potential conditions, yielding the stationary solution of the Fokker-Planck equation. Consequences of the detailed balance condition are discussed by Graham, e.g. , in Ref. 12. In more general cases however, the stationary Fokker-Planck equation usually cannot be solved analytically. Approximation schemes and/or numerical methods have to be applied. This becomes even more necessary when dealing eith dynamical phenomena, which arise, e.g. , in the context of nonequilibrium phase transitions.

At this point it is appropriate to emphasize the general importance of random fluctuations for equilibrium and nonequilibrium phase transitions. A central issue of the unified theory of continuous phase transitions is that critical fluctuations occur on all length scales. Hereby, the emphasis is shifted from properties specific for a particular system to universal properties [5,20] . Such fluctuations on all length scales do not appear in discontinuous phase transitions. In contrast, most fluctuations are well bounded in their spatial extension. These heterophase fluctuations represent local realizations of the phase into which the system evolves at the transition. A typical example is the formation of critical droplets in an oversaturated vapour (see section II.1 for more details). The appearance of these heterophase fluctuations is a characteristic feature in the decay of metastable states. They are the mechanism by which the potential barrier in the (generalized) Ginzburg-Landau potential may be crossed. Examples for these effects are found in nearly all topics discussed in this book.

I.2 Phase Transitions in Low Dimensional Systems

The distinction between continuous and discontinuous phase transitions is originally due to Ehrenfest [17] . According to his classification, a transition of order i, if the i-th derivative of the relevant thermodynamic potential is discontinuous at the phase transition, whereas all i-1 derivatives are continuous. For a system with p and T as independent variables, the free enthalpy is the relevant potential. If the first derivatives are not equal in both phases A and B, i.e.

$$v_A \neq v_B$$

and

$$s_A \neq s_B$$

(v volume per particle, s entropy per particle), the phase transition is of first order. In a second-order phase transition, on the other hand, one has

$$v_A = v_B \quad \text{and} \quad s_A = s_B \ ,$$

but the respective constant pressure specific heats

$$c_{p,A} \neq c_{p,B}$$

and the isothermal compressibilities

$$\kappa_{T,A} \neq \kappa_{T,B}$$

are unequal.

Generally, phase transitions are connected with discontinuities of thermodynamic potentials. Genuine discontinuities of these potentials can only occur for equilibrium systems in the thermodynamic limit ($N,V\to\infty,N/V=$finite) [18]. In finite systems, however, the thermodynamic potentials are always continuous functions of their independent variables [19]. In this sense, there are no phase transitions in finite systems. The changes of states in realistic (i.e. finite) systems should therefore, strictly speaking, not be identified as thermodynamic phase transitions. Nevertheless, for sufficiently large systems this may still be a very meaningful approximation. As an example, Fig.5 shows isotherms of Van der Waals systems of different sizes.

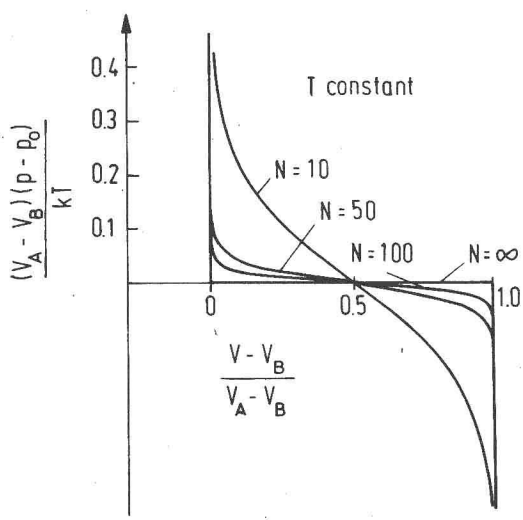

Fig.5: Equilibrium portion of the isotherms in Van der Waals systems ($T<T_C$) of different sizes. N is the number of particles. $N=\infty$ denotes the thermodynamic limit. v_A and v_B are the volumes of the liquid phase and the gas phase, respectively. p_0 is the pressure at the phase transition. (After Ref. 19.)