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Generalized Ehrenfest's approach to phase transitions in multicomponent systems in the presence of an electromagnetic field

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Abstract. The path of a transformation is defined and discussed in the framework of classical thermodynamics. The Ehrenfest's approach to the theory of higher order transition is generalized to heterogeneous systems of r components in the presence and in the absence of electromagnetic fields. By introducing a state label the phase transitions, in proximity of singular points, are analysed in terms of the stability theory. Systems, in the presence and in the absence of a magnetic field are discussed in some detail. It is shown that the Ehrenfest approximation about the transition of 2nd order is physically unstable.

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1 Introduction

Generally, macroscopic processes are studied in a single phase system which is assumed to be so large that the boundaries do not affect the physical phenomenon of interest. Obviously, this is an idealization of the reality even though reasonable for several situations. Notwithstanding natural phenomena involve always a number of phases (or subsystems) and hence the global system is heterogeneous.

It is not surprising, therefore, that phase equilibrium thermodynamics is of paramount importance for processes development in the chemical industry and play an important role in the phase equilibria thermodynamics of condensed matter [1].

It is common knowledge that the postulates of thermodynamics give us the possibility to describe the macroscopic state of a system independently of molecular considerations: classical thermodynamics is restricted to equilibrium situations [2–4]. It deals with reversible processes, i.e. transitions between equilibrium states. This is a crucial point and can be synthesized with the following question: "*if thermodynamics studies isolated systems, how is it possible to determine the equilibrium conditions*?" The question can be overcome in two ways which correspond to two different formulations of thermodynamics. The first, due to Gibbs, is phenomenological and uses the concept of "*virtual displacement*" [5–7]. The second one, due to Charatheodory, is axiomatic and exploits the idea of "*partition*" [8–10].

In Gibbs approach a thermodynamic transformation is studied by discriminating among extensive and intensive variables. Extensive variables characterize the system while the intensive variables indicate the interactions of the system with its surroundings. A full knowledge of a system is obtained by the *fundamental equation* and, as Gibbs himself realized [5], it can be generalized to include any extensive variable associated with the work done by the system. Thus, one assumes that all thermodynamic characteristics of a system are contained in the fundamental equation, which is a surface in the *Gibbs space*, termed *primitive surface* [6].

It is the aim of this paper to formulate, for heterogeneous systems, a concept of *thermodynamic path* unambiguously beginning from topological properties of the primitive surface and to study some its general consequences. We take an approach in which the global evolution, in the Gibbs space, is derived from a *state label* which is strictly connected to the homogeneity of the fundamental equation. Such a parameter could be a helpful tool to select one among the possible paths that the system can cover. It enables one to investigate the analytical properties of Gibbs space also in proximity of a phase transition. It is well known that the first attempt at classifying phase transitions was Ehrenfest classification scheme [11,12]. According to this scheme phase transitions were labeled by the lowest derivative of the free

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energy that is discontinuous at the transition. The Ehrenfest scheme is inaccurate in the neighborhood of phase transitions, as it neglects the role of thermodynamic fluctuations [13]. An interesting aspect of our approach consists in the possibility to study the analytical properties of *critical points* that, in this context, are the singular points of the transformation. The equations derived also provide a mathematical means to investigate the stability of a transformation in the neighborhood of singular points (*continuous transitions*). Among the phase transitions, the onset of the superconductivity in a zero magnetic field is, without doubt, the most known [14,15], therefore we focus on thermodynamics in the presence of a magnetic field. In any case, the treatment can be extended to more complex physical situations where magnetic and electric fields are simultaneously present and several chemical reactions can occur. Some systems, particularly soft matter systems, exhibit phenomena that can be regarded as phase transitions, but are quite different from the ordinary ones [1]. Theoretical analyses of such transitions have been presented in the literature. Such theories are essentially theories where the two "phases" are not regarded as truly different phases, but simply as conditions on the two side of a region where physical properties change very rapidly with slight changes of the state variables. Then such theories are not truly phase-transitions since the abruptness of the transition is not retained [4]. The present formulation can be seen also as a preliminary attempt to describe these phenomena in terms of equilibrium thermodynamics. Finally, in order to illustrate the method, one-component two-phase systems have been investigated both in the absence and in the presence of magnetic field.

2 Thermodynamics in the presence of electromagnetic fields

When a material is embedded in a field, its thermodynamic properties are affected. The sources of the field may be in the surroundings or included in the system. In either case, the properties of material affect the value of effective field in any point in the material.

It is customary in the treatment of these systems to make a nonoperational decomposition of internal energy into two parts [18,19]:

$$d\tilde{U} = dU + dU_{\text{field}} \tag{1}$$

where $d\tilde{U}$ is the differential change in the internal energy of the system, dU is the differential change of internal energy in absence of field and dU_{field} is associated with the differential change in the field energy. This term, according to the classic electrodynamics, is given by [15]

$$dU_{\text{field}} = \mathbf{H} \cdot d(\mathbf{B}V) \tag{2}$$

where

$$\mathbf{B} = \eta \cdot \mathbf{H} \tag{3}$$

is the magnetic induction, $\mathbf{H}$ is the magnetizing field and η is the permeability of the contents in the volume V. The induction field depends on the magnetization $\boldsymbol{M}$ of the matter in V according to the relationship

$$\mathbf{B} = \eta_0 \left(\mathbf{H} + \boldsymbol{M}\right) \tag{4}$$

being the permeability of free space. The decomposition in equation (1) does not imply that dU is independent of the magnetostatic potential, we shall, however, make the additional assumption that dU depends only on the temperature, pressure and composition.

By employing equations (2) and (4), we can put equation (1) into the form

$$dU^* = TdS - P^*dV + \sum_{i=1}^{r} \mu_i dn_i + \eta_0 \mathbf{H} d(\mathbf{M}) \tag{5}$$

where U^* is the excess of internal energy over the background field energy associated with the volume V of space

$$U^* = \tilde{U} - \frac{\eta_0}{2}\mathbf{H}^2 V \tag{6}$$

P^* is a pressure-like variable

$$P^* = P - \frac{\eta_0}{2}\mathbf{H}^2 \tag{7}$$

$\mathbf{M} = \boldsymbol{M}V$ is the total magnetic moment, S is the entropy and μ_j, n_j are the chemical potential and mole number of the component j.

We consider a linearly isotropic and uniform continuum uniformly magnetized so that η in equation (3) is independent of $\mathbf{H}$. Thus we may write

$$\mathbf{M} = \boldsymbol{M}V = \frac{\eta - \eta_0}{\eta_0} V\mathbf{H} = \chi \mathbf{H} \tag{8}$$

where χ is the volumetric magnetic susceptibility.

Equation (5) can be considered an operational definition of the internal energy function for the system of interest. Such a function (*fundamental equation*) contains all needed information about the system in thermodynamic equilibrium and is a first order homogeneous function of its variables so that the Euler theorem yields

$$SdT - VdP^* + \sum_{i=1}^{r} n_i d\mu_i + \eta_0 \mathbf{M} d\mathbf{H} = 0 \tag{9}$$

or, equivalently,

$$sdT - vdP^* + \sum_{i=1}^{r} x_i d\mu_i + \eta_0 \mathbf{m} d\mathbf{H} = 0 \tag{10}$$

where

$$s = S/n;\ v = V/n;\ x_i = n_i/n;\ \mathbf{m} = \mathbf{M}/n \tag{11}$$

are average molar quantities and $n = \sum_{k=1}^{r} n$ is the total number of moles.

To extend these results over heterogeneous systems, we consider a multicomponent, heterogeneous system made up of number ν of homogeneous and magnetizable phases and in which no chemical reaction occurs. Originally each phase, in internal equilibrium, is separated from each other by boundaries that are permeable to the magnetic field but impermeable to the flow of heat or diffusing species. When the separation surfaces are removed, transfer of heat and mass, displacements of phase boundaries and redistributions of magnetic or electric field energy may take place. Since U^*, S, V and n_k are extensive properties, their total value is approximately the sum of internal energy, entropy, volume and mole number, of the different phases, that is they are *additive invariants*. In reality one should also include the surface effects and interfacial boundaries tensions. However, we assume that the phases are so large and of such a shape that the surface contribution can be neglected as compared with the bulk-volume effects.

Under this approximation, the criterion for equilibrium takes the form

$$(\delta U^*)_{S,V,n_1,\dots n_r\mathbf{M}} \geq 0 \tag{12}$$

where δ is a virtual variation [7]. The equilibrium conditions, for the whole system, can be obtained by considering the phases pairwise [21] to reach the conclusion that

$$\begin{array}{ll} T^{(\alpha)} = T & \text{for } \alpha = 1,\, \dots,\, \nu \\ P^{*(\alpha)} = P^* & \text{for } \alpha = 1,\, \dots,\, \nu \\ \mu_i^{(\alpha)} = \mu & \text{for } \alpha = 1,\, \dots,\, \nu \text{ and } i = 1,\, \dots,\, r \\ \mathbf{H}^{(\alpha)} = \mathbf{H} & \text{for } \alpha = 1,\, \dots,\, \nu. \end{array} \tag{13}$$

These conditions represent the necessary and sufficient conditions for equilibrium when all interphase surfaces are deformable, permeable to all components, heat-conducting and permeable to magnetic flux.

3 Phase-diagram space

Equilibrium conditions (13) allow us to write the Gibbs-Duhem equation, relatively to an arbitrary phase α, as

$$s^{(\alpha)}dT - v^{(\alpha)}dP^* + \sum_{i=1}^{r} x_i^{(\alpha)} d\mu_i + \eta_0 \mathbf{m}^{(\alpha)} d\mathbf{H} = 0$$

$$\alpha = 1,\, 2,\, \dots,\, \nu. \tag{14}$$

This equation is generally studied to derive a relationship between the variables in the phase-diagram of the system and describe the states of coexistence of any pairs of phases. Indeed, many authors have discussed the existence and characteristics of the solutions of this equation, particularly illuminating is the treatment of Mistura [17], who studied the solution of the Gibbs-Duhem equation in the contact space where all densities and fields are regarded as independent variables. Throughout this paper, we use a different approach in order to emphasize some properties inherent in the phase transitions near the singular points.

In order to obtain information about the *thermodynamic state* of the system it is convenient to exploit the mass balance in each phase

$$\sum_{i=1}^{r} x_i^{(\alpha)} = 1 \tag{15}$$

and to rewrite equation (14) as

$$s^{(\alpha)}dT - \nu^{(\alpha)}dP^* + \sum_{i=1}^{r-1} x_i^{(\alpha)} d(\mu_i - \mu_r) + d\mu_r + \eta_0 \mathbf{m}^{(\alpha)} d\mathbf{H} = 0 \tag{16}$$

where equation (15) has been used.

Now, we take an arbitrary phase β of the system as reference phase so that equation (16) becomes

$$\sum_{i=1}^{r-1} {}_\beta\left[x_i\right]^\alpha dY_i + {}_\beta\left[s\right]^\alpha dT - {}_\beta\left[v\right]^\alpha dP^* + \eta_{0\,\beta}\left[\mathbf{m}\right]^\alpha d\mathbf{H} = 0$$

$$\text{with } \alpha,\, \beta = 1,\, 2,\, \dots,\, \nu \text{ and } \alpha \neq \beta \tag{17}$$

where $Y_i = \mu_i - \mu_r$ is the chemical potential relative to the component r and

$${}_\beta\left[s\right]^\alpha = s^{(\beta)} - s^{(\alpha)}, \quad {}_\beta\left[v\right]^\alpha = v^{(\beta)} - v^{(\alpha)},$$
$${}_\beta\left[\mathbf{m}\right]^\alpha = \mathbf{m}^{(\beta)} - \mathbf{m}^{(\alpha)}, \quad {}_\beta[x_i]^\alpha = x_i^{(\beta)} - x_i^{(\alpha)} \tag{18}$$

are, respectively, the jumps of entropy, volume, magnetization and mole fraction of component i across the surface separating the phases α and β.

Sets of observed phase behaviors are often presented as phase diagrams where some thermodynamic parameters are varied while others are fixed [3]. It is found experimentally [4] that the properties of systems in heterogeneous equilibrium are modified in the presence of a magnetic field. Equilibrium compositions, then, are expected to vary with the strength of magnetic field. However, the effect is so slight that extremely high field are necessary for any appreciable change of the system. On the other hand, for linear materials the magnetic susceptivity is independent of the field strength, therefore we assume that $\mathbf{H}$ is a function of temperature and pressure only. As a consequence the method could be helpful to study the phase behaviors exhibited by hydrocarbon mixtures, the phase diagram of oxides at high temperatures, the phase transitions in semiconductors induced by external fields as well as the shape transition in magnetic field of sensitive polymer gels.

Thus, by substituting for pressure P^* the expression (7), and assuming for simplicity, that $\mathbf{H}$ is dependent on T and P equation (21) can be put in the form

$$\sum_{i=1}^{r-1} {}_\beta[x_i]^\alpha dY_i + {}_\beta\left[s^*\right]^\alpha dT - {}_\beta\left[v^*\right]^\alpha dP = 0$$

$$\text{with } \alpha,\, \beta = 1,\, 2,\, \dots,\, \nu \text{ and } \alpha \neq \beta \tag{19}$$

with

$${}_\beta\left[s^*\right]^\alpha = {}_\beta\left[s\right]^\alpha + \eta_{0\,\beta}\left[\mathbf{m} + v\mathbf{H}\right]^\alpha \left(\frac{\partial \mathbf{H}}{\partial T}\right)_P \tag{20}$$

and

$${}_\beta\left[v^*\right]^\alpha = {}_\beta\left[v\right]^\alpha - \eta_{0\,\beta}\left[\mathbf{m} + v\mathbf{H}\right]^\alpha \left(\frac{\partial \mathbf{H}}{\partial P}\right)_T. \tag{21}$$

Since $\beta \neq \alpha$ there are only $\nu(\nu-1)$ equations of type (19), each describing the states of coexistence of a pair of phases. For each value of β we define a matrix of order $(\nu-1)\times(r+1)$ by

$$\begin{aligned} {}_{\beta}\mathrm{L}_i^{\alpha} &= {}_{\beta}\left[x_i\right]^{\alpha} \quad \text{for} \quad i=1,\,2,\,...,\,r-1 \\ {}_{\beta}\mathrm{L}_r^{\alpha} &= {}_{\beta}\left[s^*\right]^{\alpha}\,; \quad {}_{\beta}\mathrm{L}_{r+1}^{\alpha} = -{}_{\beta}\left[v^*\right]^{\alpha}. \end{aligned} \tag{22}$$

By defining

$$Y_r = T; \quad Y_{r+1} = P \tag{23}$$

we cast equation (19) into

$$\sum_{j=1}^{r+1} {}_{\beta}\mathrm{L}_j^{(\alpha)} dY_j = 0 \quad \alpha = 1,\ldots,\nu \quad \text{and} \quad \alpha \neq \beta. \tag{24}$$

Thus, for a fixed value of β, we have a set of $\nu-1$ homogeneous linear equations in $r+1$ unknowns whose solution can be determined to within an arbitrary parameter [23].

Indeed, let ${}^{\alpha}_{\beta}\Delta_j$ be the determinant obtained by striking out the column j from the matrix ${}_{\beta}\mathrm{L}_j^{\alpha}$, such solution can be written as a sequence of proportions

$$\frac{dY_1}{{}^{\alpha}_{\beta}\Delta_1} = \frac{dY_2}{{}^{\alpha}_{\beta}\Delta_2} = \cdots = \frac{dY_r}{{}^{\alpha}_{\beta}\Delta_r} = \frac{dY_{r+1}}{{}^{\alpha}_{\beta}\Delta_{r+1}} = dt \tag{25}$$

dt being a constant of proportionality.

From (25) it follows

$$\frac{dY_j}{dt} = {}^{\alpha}_{\beta}\Delta_j(Y_1,\,Y_2,\,...,\,Y_{r+1}) \qquad \begin{array}{l} j=1,\,2,\,...,\,r+1 \\ \beta = 1,\,2,\,...,\nu-1. \end{array} \tag{26}$$

Thus the Gibbs-Duhem equations (14) have been transformed into $\nu(\nu-1)$ sets of first-order differential equations of $r+1$ variables, each set describing a particular pair of phases. We note that is ${}_{\beta}\left[\cdots\right]^{\alpha} = -{}_{\alpha}\left[\cdots\right]^{\beta}$ so that one has to resolve only $\nu(\nu-1)/2$ sets of equations. Of course these sets of equations contain the same physical information of the Gibbs-Duhem equations (14), nevertheless in this form the parameter t makes it possible to rationalize the concept of thermodynamic path.

4 Thermodynamic paths

Given an heterogeneous system with f degrees of freedom, described by equation (26), and known the values of Y_i for $t = t_0$

$$Y_i(0) = Y_i^0 \tag{27}$$

it is possible to determine the value of Y_i at any other t

$$Y_i = \psi_i(t, Y_1^0,\,...,\,Y_{r+1}^0). \tag{28}$$

We know that if ${}^{\alpha}_{\beta}\Delta_j$ are continuous and Lipschitzian functions this solution is unique. It may be easily inverted. Indeed, if we take Y_i as a new initial condition and solve equation (26) for $(-t)$ we come back to Y_i^0

$$Y_i^0 = \psi_i(-t, Y_1, ...Y_{r+1}). \tag{29}$$

This is a consequence of the reversibility of equilibrium processes.

We may look at these equations in an alternative way. We have found $r+1$ functions, ψ_i, of the phase-space variables Y_i, which have the property of being constant along any *path* of the transformation. If we eliminate the variable t among these $r+1$ equations, we are then left with a set of r functions of the phase-space variables alone, which have the property of being constant along any trajectory. We may denote them with symbols $\Phi_j(Y_1, Y_2, ..., Y_r)$ $j=1$, $2, \ldots, r$; these functions may be called *invariants of the transformation.* Attributing a set of numerical values c_j to these constants

$$\Phi_j(Y_1(t), Y_2(t), ..., Y_r(t)) = c_j \qquad j = 1, 2, ..., r \tag{30}$$

is equivalent to determine the *path* of the system in phase space, that is the *trajectory* of the transformation.

From a geometrical standpoint each of the r equations (30) for given c_j defines an r-dimensional hypersurface in the $(r+1)$-dimensional phase-space. The path of the transformation must lie entirely on each of these surfaces, and therefore is simply the intersection of r surfaces. Thus the knowledge of an integral allows us to get rid of one dimension. Hence, determining more integrals reduces the problem further until we arrive at a one-dimensional line that is precisely the path (or *trajectory*) of the thermodynamic transformation, consisting of equilibrium states. Although the procedure looks very attractive the situation is actually much more complex since equations (26) are, generally, extraordinarily non linear equations. In order to investigate how the transformation takes place, without knowing the solutions of equation (26), it necessary to have information about the topology of phase space.

5 Topology of phase-space

Consider a system described by equations (26) whose solutions are given by equation (28). In order to obtain a geometric picture of the solution, it is useful to consider the vector

$$\mathbf{\Gamma}(t) = \begin{pmatrix} Y_1 \\ \vdots \\ Y_{r+1} \end{pmatrix} \tag{31}$$

as a point of an $(r+1)$-dimensional space. The value of $\mathbf{\Gamma}(t)$ represents *the state* of the system at a given t and when t increases $\mathbf{\Gamma}(t)$ describes a curve in this $(r+1)$-dimensional space. At each point, the vector

$$\mathbf{V}(t) = \begin{pmatrix} dY_1/dt \\ \vdots \\ dY_{r+1}/dt \end{pmatrix} = \begin{pmatrix} {}^{\alpha}_{\beta}\Delta_1 \\ \vdots \\ {}^{\alpha}_{\beta}\Delta_{r+1} \end{pmatrix} \tag{32}$$

is tangent to the curve, and the collection of all such tangent vectors defines the *flow field.*

Formally the solution of equation (26) can be written as $\mathbf{\Gamma}(t) = \mathrm{U}(t, t_0)\mathbf{\Gamma}(t_0)$, where $\mathrm{U}(t, t_0)$ is the *propagator* of the transformation that generates the line defined by $\mathbf{\Gamma}(t)$, starting from an initial state $\mathbf{\Gamma}(t_0)$. The formal expression of U is obtained by integrating between t_0 and t equation (26):

$$\mathbf{\Gamma}(t) = \mathbf{\Gamma}(0) + \int_{t_0}^{t} \mathbf{V}(\mathbf{\Gamma}(t'))dt' \tag{33}$$

replacing by $\mathbf{\Gamma}(t') = \mathbf{\Gamma}(0) + \int_{t_0}^{t'} \mathbf{V}(\mathbf{\Gamma}(t''))dt''$ and $\mathbf{\Gamma}(t'')$ by $\mathbf{\Gamma}(t'') = \mathbf{\Gamma}(0) + \int_{t_0}^{t''} \mathbf{V}(\mathbf{\Gamma}(t'''))dt'''$ and so on. This recursive process defines U as a t-ordered multiple integral which helps us to prove in a constructive way the existence and uniqueness of solutions by Picard's method of successive approximations [24]. The crucial point now is the following: for a given initial condition, what is the topological nature of the *trajectory*? Clearly the problem at hand is to study the various types of flows in the phase space. The simplest way of doing this is to calculate the volume of a certain domain Ω

$$\mathbf{D}\left[\Omega(t)\right] = \int_{\Omega} dY_1 \cdot dY_2 \cdots dY_{r+1}. \tag{34}$$

Any point in $\mathbf{D}\left[\Omega(t_0)\right]$ can be regarded as a possible initial condition, and as t increases each point describes a curve which is generated by the application of $\mathrm{U}(t_0, t)$. Each point $\mathbf{\Gamma}(t_0)$ "evolves" uniquely in a new point $\mathbf{\Gamma}(t)$ in the volume $\mathbf{D}\left[\Omega(t)\right]$. In general, both the shape and volume of $\mathbf{D}\left[\Omega(t)\right]$ change during the transformation, therefore we have

$$\begin{aligned} \frac{d\mathbf{D}\left[\Omega(t)\right]}{dt} &= \frac{d}{dt}\int_{\Omega} dY_1 \cdot dY_2 \cdots dY_{r+1} \\ &= \int_{\Omega} \frac{d\mathbf{J}(t)}{dt} dY_1(0) \cdot dY_2(0) \cdots dY_{r+1}(0) \end{aligned} \tag{35}$$

where

$$\mathbf{J}(t) = \frac{\partial\left[Y_1(t), Y_2(t), ..., Y_{r+1}(t)\right]}{\partial\left[Y_1(t_0), Y_2(t_0), ..., Y_{r+1}(t_0)\right]} \tag{36}$$

is the Jacobian of the transformation. In appendix I we show that

$$\frac{d\mathbf{J}}{dt} = \sum_{i=1}^{r+1} \frac{\partial \dot{Y}_i(t)}{\partial Y_i(t)} \mathbf{J}(t) \tag{37}$$

$\dot{Y}_i(t)$ being the derivative with respect to the t. With this equation we transform equation (35) into

$$\frac{d\mathbf{D}\left[\Omega(t)\right]}{dt} = \nabla \cdot \mathbf{V}\mathbf{D}\left[\Omega(t)\right] \tag{38}$$

where

$$\nabla \cdot \mathbf{V} = \sum_{i=1}^{r+1} \frac{\partial \dot{Y}_i(t)}{\partial Y_i(t)} \tag{39}$$

is the divergence of $\mathbf{V}$ in the phase-space. It follows that the volume of any domain in the phase-space is preserved by the transformation if $\nabla \cdot \mathbf{V} = 0$ everywhere so that $|\mathbf{J}(t)| = |\mathbf{J}(0)| = 1$. On the contrary if $\nabla \cdot \mathbf{V} < 0$ the original set of points contained in the volume $\mathbf{D}\left[\Omega(0)\right]$ contracts to a set of zero volume in the phase space.

Note that $\nabla \cdot \mathbf{V}$ can be evaluated directly from equation (26), without computing explicitly $\Gamma(t)$. However, we are now faced with the problem to determine the evolution of a small perturbation in the initial conditions dictated by equations (26). This problem can be approached in two different ways depending on the particular range of the parameter t. Specifically, if $t_0 \leq t \leq t_1$ the theorem of the continuous dependence on the initial conditions can be used, otherwise if t can increase to infinity one can tackle the problem by using the stability theory [25].

The parameter t, is a label individuating the different equilibrium states occupied by as system in a transformation, therefore, it can considered, in principle, an unlimited variable. This allows us to investigate about the stability of solutions of equations (26)

6 Linear stability

A point $(\bar{Y}_1, \bar{Y}_2, ..., \bar{Y}_{r+1})$, such that ${}^{\alpha}_{\beta}\Delta_j(\bar{Y}_1, \bar{Y}_2, ..., \bar{Y}_{r+1}) = 0$ for all $j = 1, 2, \ldots, r+1$, where equation (25) becomes meaningless, is called singular point. In this section, we investigate the analytical properties of a thermodynamic transformation in proximity of these points.

Consider the autonomous set of equation (26), without knowing the solution, it is possible to obtain much qualitative information about the flow by plotting the *phase portrait* [25]. If the derivatives $\partial^{\alpha}_{\beta}\Delta_i/\partial Y_j$, $i, j = 1, 2, \ldots, r+1$ do not all vanish identically at the singular point, then we can also solve locally for $\Gamma(t)$, near $\bar{\mathbf{\Gamma}}(t)$, performing a linear stability analysis near a singular point. To this aim we expand the functions ${}^{\alpha}_{\beta}\Delta_j(Y_1, Y_2, ..., Y_{r+1})$ in Taylor series.

To first order in the displacement $\delta Y_i = Y_i - \bar{Y}_i$ we obtain the well-known variational equations

$$\frac{d\delta Y_i}{dt} = \sum_{j=1}^{r+1} {}^{\alpha}_{\beta}A_{ij}\delta Y_j \tag{40}$$

that are linear equations in the displacements δY_i^*, since the Jacobi matrix of the transformation

$${}^{\alpha}_{\beta}\mathbf{A} = {}^{\alpha}_{\beta}\mathrm{A}_{ij} = \left(\frac{\partial^{\alpha}_{\beta}\Delta_i}{\partial Y_j^*}\right)_{Y_k = \bar{Y}_k} \tag{41}$$

has constant entries.

Therefore near a singular point equation (26), becomes

$$\frac{d\delta\mathbf{\Gamma}}{dt} = {}^{\alpha}_{\beta}\mathbf{A}\delta\mathbf{\Gamma}(t) \tag{42}$$

whose solution can be obtained explicitly from the Picard's method, which yields

$$\delta\mathbf{\Gamma}(t) = \left(\mathbf{I} + \sum_{\mathrm{k}=1}^{\infty} \frac{t^{\mathrm{k}}}{\mathrm{k}!}{}^{\alpha}_{\beta}\mathbf{A}^{\mathrm{k}}\right)\delta\mathbf{\Gamma}(0) = \exp({}^{\alpha}_{\beta}\mathbf{A}t)\delta\mathbf{\Gamma}(0) \tag{43}$$

where $\mathbf{I}$ denotes the identity matrix and the sum of the series is by definition the exponential of the matrix ${}^{\alpha}_{\beta}\mathbf{A}$. The evaluation of this exponential is more easily performed after the structure of ${}^{\alpha}_{\beta}\mathbf{A}$ has been resolved. In general, if ${}^{\alpha}_{\beta}\mathbf{A}$ can be diagonalized, then we can write

$$\delta\boldsymbol{\Gamma}(t)=\sum_{\mathrm{i}=1}^{r+1} c_i e^{{}^{\alpha}_{\beta}\lambda_i t}\,{}^{\alpha}_{\beta}\mathbf{e}_i \tag{44}$$

where ${}^{\alpha}_{\beta}\mathbf{e}_i$ is the eigenvector of ${}^{\alpha}_{\beta}\mathbf{A}$ corresponding to eigenvalue ${}^{\alpha}_{\beta}\lambda_i$ and the constants c_i are to be determined by the initial conditions. If ${}^{\alpha}_{\beta}\mathbf{A}$ is not diagonalizable, one still may be able to obtain the right eigenvalues of ${}^{\alpha}_{\beta}\mathbf{A}$ provided that the eigenvectors of ${}^{\alpha}_{\beta}\mathbf{A}$ form a complete set spanning the $(r+1)$-dimensional tangent space near the singular point $\bar{\boldsymbol{\Gamma}}$ [25].

We are, now, in position to define the linear stability of a singular point $\bar{\boldsymbol{\Gamma}}$. A point is a stable point if $\mathrm{Re}\left\{{}^{\alpha}_{\beta}\lambda_{\mathrm{j}}\right\} \leq 0$ for all indices j while it is an unstable point if $\mathrm{Re}\left\{{}^{\beta}_{\alpha}\lambda_{\mathrm{j}}\right\} > 0$ for at least one index j. Obviously the global phase portrait will consist of some distribution of various singularity, with flow lines determined by the non linear vector $\mathbf{V}$ connecting the various local portraits. Clearly, by varying the initial conditions, it is possible to shift the system from a *basin of attraction* to another. Nevertheless such investigation can be performed only if the ${}^{\alpha}_{\beta}\Delta_j(Y_1, Y_2, ..., Y_{r+1})$ are analytical functions in a neighbourhood of the singular points. It is well known, however, that the physical properties near singular points cannot be treated analytically. Indeed these studies have been used to define critical exponents which provide an insight into the nature of a singular transition. The discrepancy between theory and experiment indicates the these state cannot be treated analytically [26–31].

Although this point will be the subject of a complete study in a forthcoming paper, here, we anticipate that in such conditions the stability can be analysed by choosing for $\mathbf{D}[\Omega]$ an infinitesimal $(r+1)$-dimensional sphere of radius ${}^{\alpha}_{\beta}\varepsilon_i(0)$, which in the course of the transformation deforms into an infinitesimal ellipsoid whose principal axes $\varepsilon_i(t)$ are given by

$${}^{\alpha}_{\beta}\varepsilon_i(t) = {}^{\alpha}_{\beta}\varepsilon_i(0) e^{{}^{\alpha}_{\beta}\lambda_i t}. \tag{45}$$

In the limit ${}^{\alpha}_{\beta}\varepsilon_i(0) \to 0$ this relationship holds for arbitrarily long t so that ${}^{\alpha}_{\beta}\lambda_i$ can be defined by

$${}^{\alpha}_{\beta}\lambda_i(t) = \lim_{t\to\infty} \lim_{{}^{\alpha}_{\beta}\varepsilon(0)\to 0} \frac{1}{t} \ln\left[\frac{{}^{\alpha}_{\beta}\varepsilon_i(t)}{{}^{\alpha}_{\beta}\varepsilon_i(0)}\right]. \tag{46}$$

The basic idea of equation (46) is that small perturbations in the *initial conditions* are exponentially fast so that a path can be computed only for particular values of t such that ${}^{\alpha}_{\beta}\varepsilon_i(0) e^{{}^{\alpha}_{\beta}\lambda_i t} \ll L$ where $L \sim$ the extent of the phase space where the transformation occurs.

7 Discussion

In this section we apply the general treatment stated in the previous sections to a study of the properties of one-component two-phase systems. This application has to be considered a simple example which allows us to compare the method results with known physical situations [4]. For the sake of clarity, the discussion about the phase transitions of a material, in presence and in absence of an external magnetic field, shall be developed in two distinct cases.

Case 1. *One- component system in* the *absence of an external magnetic field*

For a one-component system, $r = 1$ and $\nu = 2$. Let us consider 1 as the reference phase, whereby equation (26) reduces to

$$\begin{aligned}\frac{dP}{dt} &= {}_1[s]^2\\ \frac{dT}{dt} &= {}_1[v]^2\end{aligned} \tag{47}$$

where ${}_1[s]^2$ and ${}_1[v]^2$ are nonlinear functions of T and P.

For ${}_1[s]^2 \neq 0$ and ${}_1[v]^2 \neq 0$ the set of equations (47) correspond to the classic Clausius-Clayperon equation whose solution can be obtained explicitly:

$$\int_{P_0}^{P} \frac{dP}{{}_1[s]^2} = \int_{T_0}^{T} \frac{dT}{{}_1[v]^2} = t - t_0. \tag{48}$$

This formal procedure implies that the initial conditions T_0, P_0 at $t = t_0$ are not taken among the set $\{T, P\}$ of points of ${}_1[s]^2$ and ${}_1[v]^2$, such that ${}_1[s]^2 = 0$ and ${}_1[v]^2 = 0$, i.e. the transformation is not singular. More precisely a transformation is entirely determined by the position and nature of its singular points. In this context a singular point corresponds to a transformation where the volume is not discontinuous and the latent heat of transformation is zero. There are only two well-established instances of transitions which show no discontinuity of either volume or enthalpy: glass transition in polymers and onset of superconductivity in a zero magnetic field [31,32]. Let $\bar{T}, \bar{P}$ be the singular point, by expanding the right-hand side of equation (47) in Taylor series around this point we obtain:

$$\begin{aligned}{}_1[s]^2 &= \frac{{}_1[c_{\mathrm{P}}]^2}{T}\delta T - {}_1[V\beta]^2\,\delta P + ...\\ {}_1[v]^2 &= {}_1[\beta V]^2\,\delta T - {}_1[V K_{\mathrm{T}}]^2\,\delta P + ...\end{aligned} \tag{49}$$

where $K_{\mathrm{T}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{\mathrm{T}}, \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P}}$.

The coefficients in these equations have been evaluated using Maxwell's equations [2] and taking into account the commutability of the operators ${}_1[\,]^2$ and $\partial/\partial x$.

The perturbation equations, at the first order approximation, are then

$$\begin{aligned}\frac{d(\delta P)}{dt} &= -{}_1[\beta V]^2\,\delta P + \frac{{}_1[c_\mathrm{P}]^2}{T}\delta T\\ \frac{d(\delta T)}{dt} &= -{}_1[VK_\mathrm{T}]^2\,\delta P + {}_1[\beta V]^2\,\delta T\end{aligned} \tag{50}$$

where it is evident that $\nabla\cdot\mathbf{V} = trace({}^2_1\mathbf{A}) = 0$ and consequently $|\mathbf{J}(t)| = 1$. Thus the volume in the phase space is preserved during the transformation.

Since the matrix is traceless, its eigenvalues can be easily evaluated by the relation

$$\lambda^2 + \left|{}^2_1\mathbf{A}\right| = 0 \tag{51}$$

$|{}^2_1\mathbf{A}|$ being the determinant of ${}^2_1\mathbf{A}$.

The solutions are stable only if

$$\left|{}^2_1\mathbf{A}\right| = \frac{{}_1[c_\mathrm{P}]^2}{T}\,{}_1[VK_\mathrm{T}]^2 - \left({}_1[V\beta]^2\right)^2 > 0 \tag{52}$$

more precisely, in a singular point the solutions may only to oscillate around the equilibrium values $\bar{T}, \bar{P}$. Maybe that these oscillations make the phases macroscopically indistinguishable in a continuous transformation (e.g. critical opalescence). Inequality (52) implies that

$$\frac{{}_1[c_\mathrm{P}]^2}{T}\,{}_1[VK_\mathrm{T}]^2 > 0 \tag{53}$$

so that the transformation can occur only if ${}_1[c_\mathrm{P}]^2$ and ${}_1[VK_\mathrm{T}]^2$ have the same sign, that is to say c_p and $V\mathrm{K}_\mathrm{T}$ have a finite discontinuity at equilibrium. This also implies that

$$\begin{aligned}&{}_1[VK_\mathrm{T}]^2 \to 0 \Rightarrow {}_1[c_\mathrm{P}]^2 \to \infty\\ &{}_1[c_\mathrm{P}]^2 \to 0, \;\Rightarrow {}_1[VK_\mathrm{T}]^2 \to \infty.\end{aligned} \tag{54}$$

In other words a λ-transition may be seen as a consequence of the stability conditions.

If, following Ehrenfest [11,12], one assumes that both volumes and entropy do not suffer any discontinuities, it is found

$$\left|{}^2_1\mathbf{A}\right| = 0 \tag{55}$$

or equivalently

$$\frac{{}_1[c_\mathrm{P}]^2}{T}\,{}_1[K_\mathrm{T}]^2 = \left({}_1[\beta]^2\right)^2 V \tag{56}$$

that is the Prigogine-Defay relation [32].

Taking into account equation (52) one deduces that the solution may be stable only if $\delta T =$ const. and $\delta P =$ const. We conclude, therefore, that the Prigogine-Defay relation, often used to analyse the problems of phase transitions, is an intrinsically unstable solution. This conclusion seems in agreement with the fact that equation (56) is not experimentally confirmed [4]. Thus the initial Ehrenfest's hypothesis on the continuity of entropy and volume is generally not valid. Finally, we observe that, with equations (14) and (17), the chemical potential (that in this case is the molar Gibbs free energy), can be written as

$$\frac{d\mu}{dt} = -s^{(1)}{}_1[v]^2 + v^{(1)}{}_1[s]^2 \tag{57}$$

and, making use of equation (47) one arrives at

$$\frac{d\mu}{dt} = -s^{(1)}\frac{dT}{dt} + v^{(1)}\frac{dP}{dt}. \tag{58}$$

This equation states that the singularity of the transformation are "extreme" points of μ which is the basic idea of Erhenfest's approach to phase transitions [28]. From this point of view, we can say that equation (26) is a sort of generalized Erhenfest's approach, to systems with $f > 1$ degrees of freedom. We notice that the method allows to interpret the so-called higher-order phase transitions in terms of only equilibrium thermodynamics.

Case 2. S*ystem of one-component in the presence of an external magnetic field*

In this case equation (26) becomes

$$\begin{aligned}\frac{dP}{dt} &= {}_1[s^*]^2\\ \frac{dT}{dt} &= {}_1[v^*]^2.\end{aligned} \tag{59}$$

Making use of equations (20) and (21) one finds

$${}_1[s^*]^2 = {}_1[s]^2 + {}_1[\chi^*]^2\left(\frac{\partial\mathbf{H}^2/2}{\partial T}\right)_P \tag{60}$$

$${}_1[v^*]^2 = {}_1[v]^2 - {}_1[\chi^*]^2\left(\frac{\partial\mathbf{H}^2/2}{\partial P}\right)_T \tag{61}$$

where

$${}_1[\chi^*]^2 = \eta_{01}[\chi+\nu]^2 \tag{62}$$

and the definition (8) has been used.

It is clear that a singular point is individuated by the solutions of the following equations

$${}_1[s]^2 + {}_1[\chi^*]^2\left(\frac{\partial\mathbf{H}^2/2}{\partial T}\right)_P = 0 \tag{63}$$

$${}_1[v]^2 - {}_1[\chi^*]^2\left(\frac{\partial\mathbf{H}^2/2}{\partial P}\right)_T = 0. \tag{64}$$

It is easily shown that a nontrivial solution exists only if

$${}_1[s]^2 = 0;\, {}_1[v]^2 = 0;\, {}_1[\chi^*]^2 = 0. \tag{65}$$

Therefore equation (50) can be used to evaluate the perturbation equation near the singular point, obtaining

$$\begin{aligned}\frac{d\delta P}{dt} &= \left\{-{}_1\left[\beta V\right]^2 + \frac{\partial_1\left[\chi^*\right]^2}{\partial P}\frac{\partial\left(\mathrm{H}^2/2\right)}{\partial T}\right\}\delta P\\ &\quad+\left\{\frac{{}_1[c_\mathrm{P}]^2}{T}+\frac{\partial_1[\chi^*]^2}{\partial T}\frac{\partial\left(\mathrm{H}^2/2\right)}{\partial T}\right\}\delta T\\ \frac{d\delta T}{dt} &= -\left\{{}_1\left[K_\mathrm{T}V\right]^2+\frac{\partial_1\left[\chi^*\right]^2}{\partial P}\frac{\partial\left(\mathrm{H}^2/2\right)}{\partial P}\right\}\delta P\\ &\quad+\left\{{}_1\left[\beta V\right]^2-\frac{\partial_1[\chi^*]^2}{\partial T}\frac{\partial\left(\mathrm{H}^2/2\right)}{\partial P}\right\}\delta T. \end{aligned}\tag{66}$$

We note that

$$\nabla\cdot{}^2_1\mathbf{A} = \frac{\partial_1\left[\chi^*\right]^2}{\partial P}\frac{\partial\left(\mathbf{H}^2/2\right)}{\partial T} - \frac{\partial_1\left[\chi^*\right]^2}{\partial T}\frac{\partial\left(\mathbf{H}^2/2\right)}{\partial P}\tag{67}$$

Hence the phase-volume is dependent on magnetic properties of the phases. In other words, for diamagnetic or paramagnetic materials the phase-volume varies differently during the transformation.

In this case the eigenvalues of matrix ${}^2_1\mathbf{A}$ can be calculated by solving the quadratic equation

$$\left({}^2_1\lambda\right)^2 + \nabla\cdot{}^2_1\mathbf{A}{}^2_1\lambda + \left|{}^2_1\mathbf{A}\right| = 0\tag{68}$$

where the determinant $|{}^2_1\mathbf{A}|$ can be evaluated directly from equation (66). Thus the study of the behaviour in a singular point is reduced to an algebraic problem. If for instance, $\chi^* = \chi^*(T)$ and $\mathbf{H} = \mathbf{H}(T)$, then $\nabla\cdot\mathbf{A} = 0$ so that

$$\begin{aligned}\left|{}^2_1\mathbf{A}\right| &= \frac{{}_1\left[c_\mathrm{P}\right]^2}{T}{}_1\left[VK_\mathrm{T}\right]^2 - \left({}_1\left[V\beta\right]^2\right)^2\\ &\quad+{}_1\left[VK_\mathrm{T}\right]^2\frac{d_1\left[c_\mathrm{P}\right]^2}{dT}\frac{d\left(\mathrm{H}^2/2\right)}{dT}\end{aligned}\tag{69}$$

and the stability analysis is the same of case1. Finally, we note that if P or T are kept constant during the transformation, the equations (59)–(61) give

$$\left(\frac{\partial\left(\mathbf{H}^2/2\right)}{\partial T}\right)_P = -\frac{{}_1\left[s\right]^2}{{}_1\left[\chi^*\right]^2}\tag{70}$$

and

$$\left(\frac{\partial\left(\mathbf{H}^2/2\right)}{\partial P}\right)_T = \frac{{}_1\left[v\right]^2}{{}_1\left[\chi^*\right]^2}\tag{71}$$

which are the expressions used in textbooks to explain the transition from a normal conductor to a superconductor [33].

Thus equations (59) synthesize fully the phase behaviour of a one-component system in a magnetic field. It is important thus to underline that the results discussed in this section are a consequence of development (49), that is to say they are valid for systems with da *classical behaviour*. The discussion about the phase behaviour of a *nonclassical system*, in the presence and absence of a magnetic field, where equation (60) is no longer valid will be treated separately in a forthcoming paper. Here we conclude observing that by introducing a state label the phase transitions in proximity of singular points may be analysed in terms of the stability theory. This label allows to extend the Ehrenfest's approach to multi-component systems.

For one-component systems the method is particularly simple because it is reducible to an algebraic problem.

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Appendix A

The object is to study the derivative $\frac{d\mathbf{J}(t)}{dt}$, where $\mathbf{J}(t)$ is defined in equation (40). To obtain this derivative one differentiates, e.g. row by row:

$$\begin{aligned}\frac{d\mathbf{J}(t)}{dt} &= \frac{\partial\left[\dot{Y}_1(t),Y_2(t),...,Y_{r+1}(t)\right]}{\partial\left[Y_1(t_0),Y_2(t_0),...,Y_{r+1}(t_0)\right]}\\ &\quad+\frac{\partial\left[Y_1(t),\dot{Y}_2(t),...,Y_{r+1}(t)\right]}{\partial\left[Y_1(t_0),Y_2(t_0),...,Y_{r+1}(t_0)\right]}\\ &\quad+\cdots+\frac{\partial\left[Y_1(t),Y_2(t),...,\dot{Y}_{r+1}(t)\right]}{\partial\left[Y_1(t_0),Y_2(t_0),...,Y_{r+1}(t_0)\right]}.\end{aligned}\tag{A.1}$$

Applying the chain rule for Jacobians, we obtain

$$\begin{aligned}&\frac{\partial\left[Y_1(t),...,\dot{Y}_j(t),...,Y_{r+1}(t)\right]}{\partial\left[Y_1(t_0),...,Y_{r+1}(t_0)\right]} =\\ &\qquad\frac{\partial\left[Y_1(t),...,\dot{Y}_j(t),...,Y_{r+1}(t)\right]}{\partial\left[Y_1(t),...,Y_{r+1}(t)\right]}\\ &\qquad\times\frac{\partial\left[Y_1(t),...,Y_j(t),...,Y^*_{r+1}(t)\right]}{\partial\left[Y_1(t_0),...,Y_{r+1}(t_0)\right]}\\ &\qquad=\frac{\partial\left[Y_1(t),...,\dot{Y}_j(t),...,Y_{r+1}(t)\right]}{\partial\left[Y_1(t),...,Y_{r+1}(t)\right]}\mathbf{J}(t).\end{aligned}\tag{A.2}$$

It is easy to show that

$$\frac{\partial\left[x_1,x_2\right]}{\partial\left[x_1,t\right]} = \frac{\partial x_2}{\partial t}\tag{A.3}$$

and this generalizes to

$$\frac{\partial\left[Y_1(t),...,\dot{Y}_j(t),...,Y_{r+1}(t)\right]}{\partial\left[Y_1(t),...,Y_{r+1}(t)\right]} = \frac{\partial\dot{Y}_j(t)}{\partial Y_j(t)}\tag{A.4}$$

With the substitution of equations (A.2) and (A.4) into (A.1) we arrive at

$$\frac{d\mathbf{J}(t)}{dt} = \sum_{\mathrm{j}=1}^{r+1} \frac{\partial \dot{Y}_j(t)}{\partial Y_j(t)} \mathbf{J}(t) \tag{A.5}$$

which is equation (37).

References

1. P.W. Anderson, *Basic Notions of Condensed Matter Physics* (Perseus Publishing, 1997)
2. A.B. Pippard, *Classical Thermodynamic* (Cambridge University Press, Cambridge, 1957)
3. H. Callen, *Thermodynamics and an Introduction to Thermostatics* 2nd edn. (Wiley, New York, 1985)
4. G. Astarita, *Thermodynamics: an advanced textbook for chemical engineers* (Plenum Press, New York, 1989)
5. J.W. Gibbs, *Collected Works* (Longman Green & Co. Inc., New York, 1928)
6. J.W. Gibbs, *Commentary on Collected Works* (Yale University Press, New Haven, Conn., 1928)
7. Sommerfeld, *Thermodynamics and statistical mechanics* (Academic Press. Inc. Publisher, New York, 1950)
8. C. Charatheodory, Math. Ann. **67**, 335 (1909)
9. J.A. Schouten, W. van der Kulk, *Pfaff's problem and its generalizations* (Oxford University Press, New York, 1949)
10. P.T. Landsberg, *Thermodynamics with Quantum Statistical Illustrations* (Interscience, New York, 1961)
11. P. Ehrenfest, Leiden Comm. Suppl. **75**b (1933)
12. G. Jaeger, Arch. Hist. Exact Sci. **53**, 51 (1998)
13. N. Goldenfeld, *Lectures on Phase Transitions and Renormalization Group* (Perseus Publishing, 1992)
14. V.L. Newhouse, *Applied Superconductivity* (John Wiley & Sons, Inc., New York, 1964)
15. D. Shoenberg, *Superconductivity* (Cambridge University Press, London, 1960)
16. R.N. Haward, *The Physics of Glassy Polymers* (Applied Science Publ., London, 1973)
17. P.G. de Gennes, J. Prost, *The physics of Liquid Crystals* (Clarendon Press, 1995)
18. Y. Zimmels, Phys. Rev. E **52**, 1452 (1995)
19. E.M, Lifshitz, L.D. Landau, L.P. Pitaevskii, *Electrodynamics of Continous Media*, 2nd edn. (Butterworth-Heinemann, 1984)
20. I.A. Privorotskii, Rep. Prog. Phys. **35**, 115 (1972)
21. J.G. Kirkwood, I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961)
22. L. Mistura, J. Phys. A **12**, 1527 (1979)
23. V.I. Smirnov, *A Course in Higher Mathematics* (Pergamon Press, Oxford, 1964)
24. E.A. Coddington, N. Levinson, *Theory of ordinary differential equations* (McGraw-Hill Press, 1955)
25. V.I. Arnold, *Ordinary Differential Equations* (M.I.T. Press, 1973)
26. R.L. Scott, Ber. Bunsenges, Phys. Chem. **76**, 296 (1972)
27. J.S. Rowlinson, F.L. Swinton, *Liquids and Liquids mixtures*, 2nd edn. (Butterworths, London, 1982)
28. S.B. Kiselev, J.C. Rainwater, Fluid Phase Equilib. **141**, 129 (1977)
29. J. Jiang, J.M. Prausnitz, J. Chem. Phys. **111**, 5964 (1999)
30. V.A. Agayan, M.A. Anisimov, J.V. Sengers, Phys. Rev. E **64**, 6125 (2001)
31. J.M.H. Levelt Senger, R.F. Chang, G. Morrison., ACS Symp. Ser. **300**, 110 (1986)
32. I. Prigogine, R. Defay, *Chemical Thermodynamics* (Longmans, New York, 1954)
33. M.W. Zemansky, Heat and Thermodynamics (McGraw-Hill, 1968)