DYNAMICS OF FIRST-ORDER PHASE TRANSITIONS
IN MULTI-COMPONENT SYSTEMS:
A NEW THEORETICAL APPROACH

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1. Phase transformation kinetics and thermodynamics

Nucleation versus spinodal decomposition

The spinodal

⇒ Isotropic systems and spherical interfaces
⇒ Gibbs: Treatment is possible down to lowest sizes
\[ \Delta G \cong -n\Delta \mu + \sigma A, \quad A \propto n^{2/3} \propto R^2, \quad R_c \cong \frac{2\sigma}{\rho \Delta \mu}, \quad W_c = \frac{1}{3} \sigma A_c \]

\[ \Rightarrow \text{What are the approximations involved?} \]

\[ \Rightarrow \text{Is the classical model correct?} \]
• Steady-state nucleation rate

\[ J = J_0 \exp \left( -\frac{W_c}{k_BT} \right) \]

• Evolution of cluster size distributions

\[ \implies \text{Solution of the set of kinetic equations describing nucleation and cluster growth processes} \]

\[ \implies \text{One-component systems } N(n, t) \]

\[ \frac{\partial N(n, t)}{\partial t} = w^{(+)}(n - 1, t) \left\{ N(n - 1, t) - N(n, t) \exp \left[ \frac{\Delta G(n) - \Delta G(n - 1)}{k_BT} \right] \right\} \]

\[ -w^{(+)}(n, t) \left\{ N(n, t) - N(n + 1, t) \exp \left[ \frac{\Delta G(n + 1) - \Delta G(n)}{k_BT} \right] \right\} \]

\[ \implies \text{Thermodynamic description of critical, subcritical and supercritical clusters} \]
• Multi-component systems: \( N(n_1, n_2, \ldots, n_k, t) \)

Basic classical assumption: Clusters are small pieces of the macroscopic phase \( \Rightarrow N(n_1, n_2, \ldots, n_k, t) \Rightarrow N(n, t) \)

\( \Rightarrow \) Change of cluster properties with size

\( \Rightarrow \) Non-trivial problem from computational point of view

\( \Rightarrow \) Reduction of the dimensions highly desirable
Spinodal Decomposition (Gibbs’ footnote)

J. D. van der Waals (1893) ⇐⇒ Cahn & Hilliard (1958/59)
\[ \Delta G = G_{het} - G_{hom} = \int \left\{ \left[ g \left( T, p, c(\vec{r}) \right) - g \left( T, p, c_0 \right) \right] + \kappa (\nabla c)^2 \right\} dV \]

- The free energy density is a function not only of the local state parameters but also of the change of density (\( \nabla c \)).
- For small density gradients, the first non-zero term in the expansion is \( \propto (\nabla c)^2 \) (square gradient approximation).
- What is the situation, when the density changes are not small like in crystallization?
- By changing one (or several) state parameters, the free energy functional describes both phases and the states in the interface. Description requires the possibility of a continuous transition between both phases. Is then the theory applicable to crystallization?
Cahn and Hilliard

- Determination of the properties of critical clusters in metastable systems: The critical cluster size increases to infinity not only for small supersaturations but also for initial states near to the spinodal curve, its state depends significantly on supersaturation.

- Basic features of spinodal decomposition: Decomposition by amplification of initially small density perturbations.
  
  \[\Rightarrow\] Only fluctuations with spatial dimensions larger than some critical wave length are capable to grow.

  \[\Rightarrow\] Amplification of density or concentration differences proceeds basically for some given wave-length.

- Generation of the initial density profile by fluctuations (Cook)
The spinodal curve

![Spinodal Curve](image1.png)

van der Waals Equation of State

Maxwell Construction

Supersaturation, $x$

Reduced temperature, $T/T_c$

Volume
• Metastable states: $W/k_BT \geq 0$ (or 1): Nucleation
• Unstable states: $W/k_BT = 0$: Spinodal decomposition
• Problems:
  – Can a spinodal be determined uniquely (Binder)?
  – Experiments allow a precise determination of the spinodal for liquid-gas phase coexistence (Baidakov).
  – Does there exist a spinodal in any kind of phase formation?

⇒ There is no spinodal curve in melt crystallization (Skripov & Baidakov). What is the reason for and what are the consequences?

⇒ Gibbs and van der Waals methods contradict each other, in particular, in their predictions near the spinodal curve.
2. Gibbs’ Classical Theory of Surface Phenomena: Advantages and Shortcomings

\[ \Phi = \Phi_1 + \Phi_2 + \Phi_\sigma , \]
Postulate:

\[ dU_\sigma = T_\sigma dS_\sigma + \sum_{i=1}^{k} \mu_i \sigma d\nu_i + \sigma dA + C dc \]

Surface of tension: \( C = 0 \) \implies \( Ad\sigma + S_\sigma dT_\sigma + \sum_{i=1}^{k} n_i \sigma d\mu_i = 0 \)

\( \implies \) Surface tension depends on \((k+1)\) independent variables (what is the meaning of \( T_\sigma, \mu_i \sigma \), how these quantities can be determined?)

Gibbs: ”On the equilibrium of heterogeneous substances”

\( \implies \) In application to nucleation, restriction to the analysis of the properties of critical clusters

\( \implies \) Bulk properties of the critical clusters

\[ \mu_{i \alpha}(T_\alpha, \rho_{1 \alpha}, \ldots, \rho_{k \alpha}) = \mu_{i \beta}(T_\beta, \rho_{1 \beta}, \ldots, \rho_{k \beta}) = \mu_{i \sigma}, \quad T_\alpha = T_\beta = T_\sigma \]
Bulk properties of critical clusters - determined in such a way - are nearly the same (pressure corrections) as for the newly evolving ambient phase (essential ingredient of Gibbs’ theory). What is the relationship to the real critical cluster properties? Is the method applicable to very small clusters?

- Restricted applicability $\iff$ Always applicable!
  The properties are widely identical: Nucleation theorem!
- Gibbs: In application to spherical interfaces, the approach “will cause no difficulties if we regard the inner-mass phase as the one determined by the same relations ... when applying our formulae to a microscopic ball of water in vapor, we should regard the density and the pressure of the inner mass not as the actual density or pressure at the center of the ball but as the density of liquid water, which has the temperature and the potential of vapor ...”
Interfacial terms and size (surface of tension)

\[ p_\alpha - p_\beta = \frac{2\sigma}{R} \]

Work of formation of critical clusters

\[ W_c = \frac{16\pi}{3} \frac{\sigma^3}{(p_\alpha - p_\beta)^2} \]

- Gibbs’ theory does not allow us to determine the work of critical cluster formation without introducing further assumptions.
- Once \( W_c \) is known, the parameters of the Gibbs’ cluster can be determined uniquely leading to the same value of the work of critical cluster formation.
- The Gibbs’ and real critical clusters may hereby be very different in composition, shape and size!
⇒ Assumption 1: Incompressibility of the cluster phase
\[ p_{\alpha} - p_{\beta} \approx \sum_{i=1}^{k} c_i \alpha \left[ \mu_{i\beta}(T_{\beta}, p_{\beta}, \{x_{\beta}\}) - \mu_{i\alpha}(T_{\alpha}, p_{\beta}, \{x_{\alpha}\}) \right] \]
\[ \approx c_{\alpha} \Delta \mu(p, T, \{x_{\alpha}\}, \{x_{\beta}\}) \]
\[ W_c = \frac{16\pi}{3} \frac{\sigma^3}{[c_{\alpha} \Delta \mu(p, T, \{x_{\alpha}\}, \{x_{\beta}\})]^2} \]

⇒ Assumption 2: Composition \( \{x_{\alpha}\} \) of the critical clusters corresponds widely to the composition of the newly evolving phase
\[ \Delta \mu(p, T, \{x_{\alpha}\}, \{x_{\beta}\}) \Rightarrow \Delta \mu(T) \]

⇒ Assumption 3: Capillarity approximation (additional assumption in agreement with assumption 2)

- In some case, Gibbs’ theory gives a good description, in other cases enormous quantitative deviations may occur.
Gibbs’ theory always allows us to interpret nucleation phenomena by varying the surface tension. Physical explanation: curvature dependence of the surface tension

\[ W_c = \frac{16\pi}{3} \left( p_\alpha - p_\beta \right)^2, \quad \sigma = \sigma_\infty \left( 1 + \frac{\delta_0}{R} + \frac{\delta_1}{R^2} + \ldots \right) \]

Approach leads to other grave problems

\[ J = J_0 \exp \left( -\frac{W_c}{k_B T} \right), \quad \log \left( \frac{J_{\text{exp}}}{J_{\text{theor}}} \right) \leq 140 \]

Alternative approaches are possible leading to an increase of the surface tension with increasing temperature.

General result (independent on the method of interpretation):

\[ \Rightarrow \text{Estimates for } \sigma \text{ are too high!} \]
What is the origin of such trouble?

- Is Gibbs’ method correct for the determination of the bulk parameters of the critical clusters?
  \[\Rightarrow\] Gibbs says no!!!
  \[\Rightarrow\] van der Waals and modern density functional theories of nucleation: Bulk properties of critical clusters differ, in general, considerably from the properties of the newly evolving phase.
  \[\Rightarrow\] Origin of mentioned problems consists in the incorrect predictions of bulk properties of critical clusters in the framework of Gibbs’ theory!
  \[\Rightarrow\] Has Gibbs’ theory to be abandoned? No!

Generalization of Gibbs’ approach is possible avoiding mentioned and other shortcomings and retaining its advantages!!!
3. Generalized Gibbs’ approach: Basic ideas

Binary solutions: \[ W_c \propto \frac{\sigma^3(x, x_\alpha)}{(\Delta \mu(x, x_\alpha))^2}, \quad \sigma \propto (x - x_\alpha)^2 \]

Generalized Ostwald’s Rule of Stages in Nucleation:
*In phase transformation processes, the structure and properties of the critical nucleus may differ qualitatively from the properties both of the ambient and newly evolving macrophases. Those classes of critical clusters determine the process of the transformation, which correspond to a minimum of the work of critical cluster formation (as compared with all other possible structures and compositions, which may be formed at the given thermodynamic constraints). Two possibilities: Either equivalent to Gibbs (then useless) or different from Gibbs’ result (then what?)*
Gibbs

Although my results were in a large measure such as had been previously obtained by other methods, yet, as I readily obtained those which were to me before unknown, or by vaguely known, I was confirmed in my belief in the suitableness of the method adopted

Eugene Shchukin
Professor of Physical Chemistry, Moscow, Houston

Only Jesus and Gibbs never err, however, this statement has been proven strictly for Gibbs, only

Friedrich Schiller
It does not prove a thing to be right because the majority says it is so.
Shortcomings of Gibbs’ approach

- Gibbs restricted his analysis to *phase equilibria of heterogeneous substances*. He never even posed the problem to formulate thermodynamic potentials for thermodynamic non-equilibrium states.

Consequence: Employing Gibbs’ method, one has no rigorous basis so far for the description of cluster growth processes!

⇒ In describing cluster growth processes, different assumptions are commonly employed having no theoretical basis in Gibbs’ method ⇒ Argumentation

- Gibbs’ method is not correct in application to the determination of the bulk properties of the critical clusters.

⇒ What is the origin of the failure?
Search for saddles or extrema of (any landscape or) thermodynamic potentials

- Formulate the respective potential for any possible state including non-equilibrium states (not done by Gibbs)
- Search for the saddles by known methods

⇒ Can Gibbs’ classical theory be generalized to describe non-equilibrium states?
Gibbs’ fundamental equation (surface of tension)

\[ dU_\sigma = T_\sigma dS_\sigma + \sum_{j=1}^{k} \mu_{j\sigma} dn_{j\sigma} + \sigma dA \]

\[ S_\sigma dT_\sigma + Ad\sigma + \sum_{j=1}^{k} n_{j\sigma} d\mu_{j\sigma} = 0 \]

Consequences:

\[ \Rightarrow \] The surface tension depends - following Gibbs’ original method - exclusively on the \((k+1)\) state parameters of either the ambient phase or the cluster phase: Can be valid for equilibrium states, only (Gibbs’ phase rule) but not for clusters not in equilibrium with the ambient phase

\[ \Rightarrow \] The surface tension of clusters of arbitrary sizes has to depend, in general, on the state parameters of both ambient and newly evolving phases \((2(k+1)\) variables)
Generalization of Gibbs’ fundamental equation

\[ dU_\sigma = T_\sigma dS_\sigma + \sum_{j=1}^{k} \mu_{j\sigma} d\eta_{j\sigma} + \sigma dA + \sum_{i=1}^{k+1} \phi_{i\alpha} d\varphi_{i\alpha} \]

⇒ \( \{\varphi_{i\alpha}\} \) is a complete set of intensive variables, specifying the bulk state of the cluster phase;
⇒ Additional requirement

\[ \mu_{j\sigma} = \mu_{j\beta}, \quad T_\sigma = T_\beta \]

⇒ The general expressions for the thermodynamic potentials remain the same as derived in Gibbs’ classical approach, however, the surface tension has to be treated as a function of the state parameters of both ambient and cluster phase
⇒ Consistent description of thermodynamic non-equilibrium states - clusters in the ambient phase - as the basis for application to both nucleation and cluster growth processes
3.1 Generalized Gibbs’ Approach in Nucleation

Critical clusters: \( \{ \varphi_\alpha \} = \{ s_\alpha, \{ \rho_{i\alpha} \} \}; \{ \varphi_\beta \} = \{ s_\beta, \{ \rho_{i\beta} \} \} \)

\[
(T_\alpha - T_\beta) s_\alpha + (p_\beta - p_\alpha) + \sigma \frac{dA}{dV_\alpha} + \sum_{j=1}^{k} \rho_{j\alpha} (\mu_{j\alpha} - \mu_{j\beta}) = 0
\]

\[
\iff p_\alpha - p_\beta = \frac{2\sigma}{R}
\]

\[
(\mu_{j\beta} - \mu_{j\alpha}) = \frac{3}{Rs} \left( \frac{\partial \sigma}{\partial \rho_{j\alpha}} \right) \{ \rho_{i\beta} \}, T_\beta
\]

\[
\iff \mu_{j\beta} = \mu_{j\alpha}
\]

\[
(T_\beta - T_\alpha) = \frac{3}{Rs} \left( \frac{\partial \sigma}{\partial s_\alpha} \right) \{ \rho_{i\beta} \}, T_\beta
\]

\[
\iff T_\beta = T_\alpha
\]

\( \Rightarrow \) Surface tension

\[
\sigma = \sum_{i,j=1}^{k+1} \Theta_{i,j} (\varphi_{i\alpha} - \varphi_{i\beta}) (\varphi_{j\alpha} - \varphi_{j\beta})
\]
Work of critical cluster formation

- Expression for the work retains the same form, \( W_c = \frac{1}{3} \sigma A \)

- Classical Gibbs’ approach corresponds to a ridge point!!!
Example: Segregation in binary regular solutions

\( T_\alpha = T_\beta = 0.7T_c \)

\[
\Delta G = -n_\alpha \Delta \mu + \sigma A, \quad n_\alpha = \sum n_{j\alpha}, \quad c_\alpha = \frac{n_\alpha}{V_\alpha}
\]

\[
\Delta \mu = \sum_{j=1}^{k} \left[ \mu_{j\beta}(p, T, \{x_\beta\}) - \mu_{j\alpha}(p, T, \{x_\alpha\}) \right] x_{j\alpha}
\]
Critical clusters

\[ R_c = \frac{2\sigma}{c_\alpha \Delta \mu} , \quad \Delta G_c = \frac{16\pi}{3} \frac{\sigma^3}{(c_\alpha \Delta \mu)^2} \]

Thermodynamic properties of regular solutions

\[ \sigma(x, x_\alpha) = \sigma_0 \left( \frac{T}{T_c} \right) (x_\alpha - x)^2 , \quad \Delta \mu = -k_B T f(x, x_\alpha) \]

\[ f(x, x_\alpha) = (1 - x_\alpha) \left[ \ln \left( \frac{1 - x_\alpha}{1 - x} \right) + 2 \left( \frac{T_c}{T} \right) (x_\alpha^2 - x^2) \right] \]

\[ + x_\alpha \left\{ \ln \left( \frac{x_\alpha}{x} \right) + 2 \left( \frac{T_c}{T} \right) [(1 - x_\alpha)^2 - (1 - x)^2] \right\} \]

Requirements: Macroscopic surface tension and bulk properties of both phases in dependence on the state parameters
Properties of the critical clusters
Classical and generalized Gibbs’ approaches

![Graph showing cluster composition vs. supersaturation](image_url)
3.2 Generalized Gibbs’ Approach in Application to Cluster Growth and Dissolution

Basic postulate (tentative formulation):

The motion in the hypersurface of thermodynamic state parameters proceeds along the valley of the thermodynamic potential passing the saddle point.
1. A thermodynamically founded method of specification of the properties of sub- and supercritical clusters has been developed

2. Changes of the cluster properties occur basically in the range $0 \leq R/R_c \leq 3(R/R_c)$ (for the model considered)

3. Thermodynamic and kinetic properties of the clusters, derived from nucleation experiments, may dramatically fail for a description of the growth of larger clusters
• Change of surface tension and driving force for cluster growth

• Change of the effective diffusion coefficient

\[ \frac{1}{D} = k \sum_{i=1}^{k} \frac{x_{i\alpha}^2}{D_i x_{i\beta}} \]

• Change of growth rate

4. Vice versa, macroscopic properties may dramatically fail to describe cluster properties for nucleation

5. Diffusion coefficients and shapes of cluster size distributions: AgCl segregation

\[ \frac{D}{D_2} = \frac{D_1 x (1-x)}{D_2 x (1-x_{\alpha})^2 + D_1 (1-x) x_{\alpha}^2} \]
Cluster size distributions: Classical description

FIG. 1. Cluster size distribution function \( f(R,t) \): early stages of the AgCl precipitation at \( T = 457 \, ^\circ \text{C} \).

FIG. 2. Cluster size distribution function \( f(R,t) \): later stages of the AgCl precipitation at \( T = 457 \, ^\circ \text{C} \).

Experiment
Cluster size distributions: Motion along the specified by the basic postulate trajectory
Tatchev, Hoell, Kranold, Armyanov et al. (2005): Size distribution and composition of magnetic precipitates in amorphous Ni-P alloys
3.3 Further Consequences and Developments

3.3.1 The classical model of cluster formation and growth is, in general, not valid for segregation in solutions

⇒ The whole theory has to be reformulated from the very beginning!!!
3.3.2 Kinetics of nucleation in solid solutions proceeds not via the classical nucleation-growth scenario but via a scenario similar the Cahn-Hilliard picture of spinodal decomposition.
3.3.3 Is the classical model of cluster formation and growth valid for small supersaturations? Answer: No!
3.3.4 Incorporation of the kinetics into the determination of the most probable path of cluster evolution

Basic postulate (final version): Evolution proceeds via deterministic trajectory: Deterministic trajectory coincides with most probable stochastic trajectory of evolution

![Diagram](image1.png)

- Reduced radius, $R/R_c$
- Cluster composition, $x$
- $n_1/n_c$ vs $n_2/n_c$
3.3.5 Phase transition kinetics near the spinodal curve

Parameters of the critical clusters in the classical and generalized Gibbs’ approaches:

⇒ Saddle point approximation

⇒ Motion via the saddle is hard to realize: Infinite cluster sizes are required: Is motion via a ridge path eventually possible?
What is the composition and the work of formation of a ridge cluster in the generalized Gibbs approach having the same size as a critical cluster in Gibbs classical description?

Can the generalized Gibbs’ approach tell us anything about phase transitions in unstable initial states?
• The size of the critical clusters, determined via the generalized Gibbs’ approach for unstable initial states, behaves similarly as the size of the density fluctuations derived in the Cahn-Hilliard approach to spinodal decomposition.

\[ R_c \propto \left( 1 - \left( \frac{T}{4T_c} \right) \left( \frac{1}{x(1-x)} \right) \right)^{-1} \]

• In metastable states near the spinodal, ridge pathes to the new phase have comparable values of the work of cluster formation as compared with the saddle point. By kinetic reasons, the system will utilize then such ridge pathes to avoid the formation of large clusters as transient states.

• The system may follow such ridge pathes also starting from unstable initial states. This way, nucleation may be extended into the unstable region.
4. Future Developments: Application to Crystallization

First applications and supporting analyses:

- Determination of specific interfacial energy by measurements of the growth rate of near-critical clusters
- Interpretation of nucleation data for lithium disilicate
- A new perspective on the problem of ”metastable phases”
- P. Richet et al. (2005); D. Frenkel et al. (2004); Baidakov (2006)
  ...it turns out that the transition from the liquid to the fcc-crystal and back cannot be accomplished by just small shifts in the positions of the atoms: for such transitions a significant part of atoms should be moved by a distance about one atomic spacing...
Requirements:

- **Bulk properties**: Driving force in dependence on temperature, pressure (or density), composition and "degree of crystallinity"

  ⇒ Does the notation "degree of crystallinity" have any meaning?

- **Interfacial energy**

  \[ \sigma = A(p, T)(x_\alpha - x)^2 + B(p, T)(x_\alpha - x)(\rho_\alpha - \rho) + C(p, T)(\rho_\alpha - \rho)^2 + \ldots \]

  ⇒ What is the meaning and the value of \( \sigma \) for a macroscopic crystal-melt interface?!

  ⇒ How the "degree of crystallinity" has to be incorporated into this expression?
Analyzing the presently available experimental data about the melting of substances, one can derive the conclusion that the melting temperature increases infinitely with the increase of pressure and that a critical point on the equilibrium curve melt-crystal is absent. The absence of a critical point singularity is deeply connected with the essential discontinuity inherent in the properties of crystal and liquid. The properties of each of these condensed phases are described by its own equation of state. This property reflects the fact that there exist two qualitatively different modes of dense packing of atoms, the regular and the irregular packing modes, characterized by a different symmetry.
Symmetry-based concepts for the substantiation of the absence of an equilibrium critical point on the coexistence curve liquid-solid have been formulated first by Landau. According to his argumentation, in the transition from the solid to the liquid some symmetry elements characteristic to the crystal phase disappear. However, symmetry elements cannot disappear continuously. They are either present, or absent. Consequently, a continuous transition between different phases, which is characterized by a change of the symmetry of the system under consideration, is also impossible.

The difference between the liquid and the crystal does not consist only just in the absence of regularity in the mean positions of the molecules, i.e., in the existence of the long-range order of the crystal, but also in a large variety of
“basic units” of short range order in the liquids, and the resulting higher freedom in the coordination of the short-range neighbors. Latter difference is due to the fact that the liquid has no limitations with respect to the ordering of the molecules caused by the existence of a long-range ordering in a crystal. The development of such an approach to the interpretation of the structural properties of liquids has been initiated by the works of Bernal in contrast to concepts employing ideas of a quasi-crystalline structure of the liquids.

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.
Skripov and Faizullin:

\[ p < T < T_c \]

\[ p \]

\[ v \]

\[ p \]

\[ v \]
The difference of these figures is of principal importance and is in agreement with the concept of the absence of a crystal-liquid equilibrium critical point and the impossibility of a smooth transition between these two states of aggregation of matter. If this conclusion - as we believe - is true, then there cannot exist an universal continuous equation of state describing the different states of aggregation (i.e. of vapor, liquid, crystal) of simple substances in a correct way. The crystalline state has to be described by a separate \((T, v, p)\)-equation . . .

\[
\Delta G = G_{het} - G_{hom} = \int \left\{ \left[ g \left(T, p, c(\vec{r})\right) - g \left(T, p, c_0\right) \right] + \kappa (\nabla c)^2 \right\} dV
\]

⇒ The van der Waals and similar density functional methods are not applicable to crystallization
Basic conclusions

- A new theoretical concept has been developed allowing one to treat phase formation processes. In contrast to density functional methods, it allows to treat in a unique picture both phase formation and its further evolution.

- In application to the determination of the work of critical cluster formation, the method is qualitatively equivalent to van der Waals or more advanced density functional computations (as far as latter methods are applicable at all). It resolves in this way internal contradictions between two well-established theories.

In application to crystallization, the generalized Gibbs’ approach seems to be presently the only tool allowing one to go beyond Gibbs classical treatment in application both to nucleation and growth.
• The generalized Gibbs’ approach leads to values of the work of critical cluster formation (nucleation rate) smaller (larger) than the values obtained via the classical Gibbs’ approach.

• The generalized Gibbs approach allows one to determine the general scenario of evolution beyond nucleation. It turns out that the classical picture is not an appropriate model for segregation processes in solutions. Nucleation proceeds via a scenario similar to spinodal decomposition. In unstable states, nucleation in a generalized interpretation may be the dominating channel of evolution to the new phase.

Results have been obtained leaving the classical Gibbs’ approach: The classical Gibbs method of determination of the properties of critical clusters is incorrect!!!
Bertrand Russell
This is one of the views which are so absolutely absurd that only very learned men could possibly adopt them
References


