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Nucleation Theory

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One of the most striking phenomena in condensed matter physics is the occurrence of abrupt transitions in the structure of a substance at certain temperatures or pressures. These are first-order phase transitions, and examples such as the freezing of water and the condensation of vapors to form mist in the atmosphere are familiar in everyday life. A fascinating aspect of these phenomena is that the conditions at which the transformation takes place can sometimes vary. The freezing point of water is not always 0°C: the liquid can be supercooled considerably if it is pure enough and treated carefully. Similarly, it is possible to raise the pressure of a vapor above the so-called saturation vapor pressure, at which condensation ought to take place according to the thermodynamic properties of the separate phases. Both these phenomena occur because of the requirement for nucleation. In practice, the transformation takes place through the creation of small aggregates, or clusters, of the daughter phase out of the parent phase. In spite of the familiarity of the phenomena involved, accurate calculation of the rate of cluster formation for given conditions of the parent phase meets serious difficulties. This is because the properties of the small clusters are insufficiently well known.

The development from the 1980s onwards of increasingly accurate experimental measurements of the formation rate of droplets from metastable vapors has driven renewed interest in the problems of nucleation theory. Existing models, largely based upon versions of the classical nucleation theory developed in the 1920s–1940s, have on the whole explained the trends in nucleation behavior correctly, but have often failed spectacularly to account for this fresh data. The situation is more dramatic in the case of binary- or, more generally, multi-component nucleation where the trends predicted by the classical theory can be qualitatively in error leading to unphysical results.

This book, starting with the classical phenomenological description of nucleation, gives an overview of recent developments in nucleation theory. It also illustrates application of these various approaches to experimentally relevant problems focusing on the nonequilibrium gas–liquid transition, i.e., formation of liquid
droplets from a metastable vapor. A monograph on nucleation theory would be incomplete without presenting the recent advances in computer simulations of nucleation on a molecular level, which is a powerful research tool complementing both theory and experiment. I was glad that my colleague and friend Dr. Thomas Kraska from the University of Cologne accepted my invitation to write the chapter on Monte Carlo and Molecular Dynamics simulation of nucleation (Chap. 8)—the field to which he made a number of significant contributions.

Obviously, in view of the modest size of the book it was not possible to cover all new approaches formulated in recent years. The choice of the topics, therefore, reflects the background and prejudices of the author.

This monograph is an introduction as well as a compendium to researchers in soft condensed matter physics and chemical physics, graduate and postgraduate students in physics and chemistry starting on research in the area of nucleation, and to experimentalists wishing to gain a better understanding of the efforts being made to account for their data.

I am grateful to a number of colleagues who collaborated with me at various stages of the work. I benefitted greatly from discussions of fundamental problems of nucleation with Howard Reiss, Joe Katz, and Gerry Wilemski, which advanced my understanding of the subject. Several years spent in the group of Rini van Dongen in Eindhoven University will remain an unforgettable experience of a remarkable scientific atmosphere and friendly environment; special thanks are due to the former Ph.D. students Carlo Luijten, Geert Hofmans, and Dima Labetski for numerous discussions at the seminars and help in understanding the subtleties of nucleation experiments. It is a pleasure to thank Ian Ford, Barbara Wyslouzil, Judith Wölk, Jan Wedekind, Dennis van Putten, and Anshel Gleyzer for constructive criticisms. I am indebted to my colleagues and friends Jos Thijssen, Lev Goldenberg, Bob Prokofiev, Leonid Neishtadt, Andrey Morozov, Lyudmila Tsareva, Dmitry Bulahov, Kees Tjeenk Willink, and Marco Betting for encouragement and help without which this book would not have been written. But above all, I am grateful to my family—Esta and Maria—for the constant support during the almost endless process of thinking, writing, and editing of the manuscript.

Delft, May 2012

V. I. Kalikmanov
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Symbols

\( \mathcal{A}_i^v \)  Vapor phase activity of component \( i \)
\( \mathcal{A}_i^l \)  Liquid phase activity of component \( i \)
\( B_2 \)  Second virial coefficient
\( c_p \)  Specific heat at constant pressure
\( c_v \)  Specific heat at constant volume
\( \mathcal{F} \)  Helmholtz free energy of the system
\( \mathcal{F}_{\text{int}} \)  Intrinsic Helmholtz free energy
\( \mathcal{F}_d \)  Helmholtz free energy of hard spheres with diameter \( d \)
\( \mathcal{F}_n \)  Helmholtz free energy of the \( n \)-cluster
\( \mathcal{F}_{\text{conf}} \)  Configurational Helmholtz free energy of the \( n \)-cluster
\( \mathcal{F}^{(n)} \)  Helmholtz free energy of the gas of \( n \)-clusters
\( G \)  Gibbs free energy of the system
\( \Delta G(n) \)  Gibbs free energy of \( n \)-cluster formation
\( \Delta G^* \)  Nucleation barrier
\( h \)  Planck constant
\( J_n \)  Net rate of cluster formation \( (n \rightarrow n + 1) \)
\( J \)  Steady-state nucleation rate
\( J_0 \)  Pre-exponential factor for the steady-state nucleation rate
\( k_B \)  Boltzmann constant
\( m_1 \)  Mass of a molecule
\( n \)  Number of particles in a cluster
\( n_c; n^* \)  Number of particles in a critical cluster
\( N_1 \)  Coordination number in the liquid phase
\( p \)  Pressure
\( p^l \)  Liquid pressure
\( p^v \)  Vapor pressure
\( p_c \)  Critical pressure
\( p_d \)  Pressure of a hard sphere system
\( p_{\text{sat}} \)  Saturation pressure
\( q_n \)  Configuration integral of the \( n \)-cluster
\( q_{na,nb} \) Configuration integral of the binary \((n_a, n_b)\)-cluster
\( S \) Supersaturation
\( S' \) Entropy
\( S_n' \) Entropy of the \(n\)-cluster
\( S_n^{\text{conf}} \) Configurational entropy of the \(n\)-cluster
\( T \) Absolute temperature
\( T_c \) Critical temperature
\( \mu_{\text{LJ}}(r) \) Lennard–Jones interaction potential
\( U_N(r_1, \ldots, r_N) \) Microscopic potential energy of a configuration of \(N\) particles
\( Z' \) Compressibility factor in the liquid
\( Z'' \) Compressibility factor in the vapor
\( Z_n \) Partition function of the \(n\)-cluster
\( Z^{(n)} \) Partition function of the gas of \(n\)-clusters
\( Z_{na,nb} \) Partition function of the binary \((n_a, n_b)\)-cluster
\( \gamma \) Zeldovich factor
\( \beta = 1/(k_B T) \) Inverse temperature
\( \gamma_{\infty} \) Surface tension of a flat interface
\( \gamma_{\text{micro}} \) Helmholtz free energy per surface particle in the cluster (microscopic surface tension)
\( \delta_T \) Tolman length
\( \kappa = c_p/c_v \) Ratio of specific heats
\( \sigma_{\text{LJ}}, \sigma_{\text{LJ}} \) Parameters of a Lennard–Jones potential
\( \Lambda \) de Broglie wavelength of a particle
\( \mu \) Chemical potential
\( \mu_n \) Chemical potential of the \(n\)-cluster
\( \mu_d \) Chemical potential of a hard sphere with a diameter \(d\)
\( \mu_{\text{sat}} \) Chemical potential of a substance at vapor–liquid equilibrium (saturation chemical potential)
\( \nu \) Impingement rate per unit surface
\( \nu_i \) Impingement rate per unit surface of component \(i\) in binary nucleation
\( \nu_{\text{av}} \) Average impingement rate per unit surface in binary nucleation
\( \rho' \) Number density in the bulk liquid
\( \rho'' \) Number density in the bulk vapor
\( \rho_c \) Critical number density
\( \tau_i \) Line tension
\( \rho(n) \) Number density of \(n\)-clusters
\( \rho_{\text{sat}}(n) \) Number density of \(n\)-clusters at saturation
\( \Omega \) Grand potential of the system
\( \theta_{\infty} \) Reduced surface tension of a flat interface
\( \theta_{\text{micro}} \) Reduced Helmholtz free energy per surface particle (reduced microscopic surface tension)
CKE Classical Kelvin equation
CAMS Constant angle Mie scattering
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>CGNT</td>
<td>Coarse-grained nucleation theory</td>
</tr>
<tr>
<td>CNT</td>
<td>Classical nucleation theory</td>
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<tr>
<td>BCNT</td>
<td>Binary classical nucleation theory</td>
</tr>
<tr>
<td>MKNT</td>
<td>Mean-field kinetic nucleation theory</td>
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<tr>
<td>EoS</td>
<td>Equation of state</td>
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<tr>
<td>EMLD</td>
<td>Extended modified liquid drop model</td>
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<tr>
<td>DNT</td>
<td>Dynamic nucleation theory</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<tr>
<td>FPE</td>
<td>Fokker-Planck equation</td>
</tr>
<tr>
<td>GKE</td>
<td>Generalized Kelvin equation</td>
</tr>
<tr>
<td>HPS</td>
<td>High-pressure section of the shock tube</td>
</tr>
<tr>
<td>LPS</td>
<td>Low-pressure section of the shock tube</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
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<tr>
<td>MD</td>
<td>Molecular dynamics</td>
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<tr>
<td>NPC</td>
<td>Nucleation pulse chamber</td>
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<tr>
<td>NVT</td>
<td>Canonical (NVT) ensemble</td>
</tr>
<tr>
<td>NVE</td>
<td>Microcanonical (NVE) ensemble</td>
</tr>
<tr>
<td>RESS method</td>
<td>Rapid expansion of supercritical solution</td>
</tr>
<tr>
<td>tWF</td>
<td>ten Wolde–Frenkel cluster definition</td>
</tr>
<tr>
<td>SAFT</td>
<td>Statistical associating fluid theory</td>
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<tr>
<td>SANS</td>
<td>Small-angle neutron scattering</td>
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<tr>
<td>SAXS</td>
<td>Small-angle X-ray scattering</td>
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<tr>
<td>SSN</td>
<td>Laval supersonic nozzle</td>
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<tr>
<td>MFPT</td>
<td>Mean first passage time cluster definition</td>
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<td>WCA</td>
<td>Weeks–Chandler–Anderson theory</td>
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