The background of the cover is a grayscale, high-magnification micrograph of a cell. A large, dark, circular nucleus is visible in the center, containing a lighter, dense nucleolus. The surrounding cytoplasm shows various organelles and a granular texture. The image is overlaid with a semi-transparent white horizontal band that serves as a background for the title text.

Mesosopic Thermodynamics for Scientists and Engineers

**Mikhail A. Anisimov
Thomas J. Longo**

WILEY

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To Our Families

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Preface

This book originates from an elective course that one of the authors (M.A.A.) has developed and offered at the University of Maryland, College Park, to senior undergraduate and entry-level graduate students in engineering and science programs. The motivation to develop a new course was a result of a certain dissatisfaction with the contents of the traditional thermodynamics course that he had been teaching in the Department of Chemical and Biomolecular Engineering for almost 30 years.

Thermodynamics is a keystone in science and engineering, bridging the gap between fundamentals and applications. However, when one compares the content of conventional courses in thermodynamics with what scientists and engineers often do in practice, one may notice a gap—one that is widening every year. New emerging technologies and products deal with subjects such as biomolecular and soft-matter engineering, micro-reactor chemistry and microcapsule drug delivery, micro-fluidics and porous media, nanoparticles and nanostructures, supercritical-fluid extraction, and systems at the edge of stability. Engineers often must design processes or products under conditions where traditional thermodynamics may become insufficient, as in the case of strongly fluctuating and nano-size systems, or dissipative structures away from equilibrium. The scientific basis for such issues is not commonly addressed in traditional engineering thermodynamics and transport courses. The aim of *Mesoscopic Thermodynamics for Scientists and Engineers* is to fill this gap, at least partially.

Mesoscopic thermodynamics can be defined as a semi-phenomenological approach to phenomena in systems where a mesoscopic length-scale, intermediate between the atomistic scale and the macroscopic scale, emerges and where such a length explicitly affects the thermodynamic properties and phase behavior. There are numerous topics to be considered in mesoscale thermodynamics (equilibrium and nonequilibrium): finite-size and confined systems, fluctuations, wetting and adsorption, interfacial phenomena, microphase separation and nucleation, molecular self-assembly, self-organized criticality, and mesoscale dissipative structures. It would be unrealistic to expect from an introductory-level book to address all or even most of them. Each of these topics deserves a special monograph. Instead, this book emphasizes two major universal features (described in Part I) that must be introduced into the traditional thermodynamic framework in order to address mesoscopic phenomena. These features are fluctuations and local (spatially dependent) properties. To make the text self-sufficient for the readers, Part I also includes a summary of classical equilibrium and nonequilibrium thermodynamics (Chapter 2). Chapter 2 serves as an important background and guide to the core material of the book, but cannot substitute a comprehensive textbook on thermodynamics. In Part II, a universal thermodynamic approach to meso-heterogeneous systems is specified through examples, which are relevant to

modern research and engineering practice. Most examples deal with meso-heterogeneous fluid systems. Each chapter in both parts is supplemented by exercises.

The readers are assumed to have an undergraduate background in thermodynamics, calculus, physics, and chemistry. Acquaintance with statistical mechanics would be useful, but is not required for comprehension of the material. All chapters include references to textbooks, monographs, and journal research articles for further, more advanced reading. Although the description of the topics is self-sufficient within the book, a supplementary conventional undergraduate text on thermodynamics would be useful, especially in solving the problems provided at the end of each chapter.

We are grateful to our colleague and collaborator Jan V. Sengers, Distinguished University Professor Emeritus at the University of Maryland, for fruitful discussions and his valuable comments on this text prior to publication. M.A.A. appreciates important contributions from his colleagues, collaborators, and former students, especially Christopher E. Bertrand (PhD, 2010), who helped in clarifying a number of issues addressed in this book.

College Park, MD
December 2023

Mikhail A. Anisimov and Thomas J. Longo

Notations, Acronyms, and Units

General Notations

Symbols	Designates (units)
\mathcal{A}	surface area (m^2)
A_t	total Helmholtz energy (J)
$A = A_t/n$ or A_t/N	Helmholtz energy per mole or per molecule (J/mol)
$A_0, B_0, \Gamma_0, D_0, \xi_0, \sigma_0$	asymptotic critical amplitudes of weak susceptibility, spontaneous order parameter, strong susceptibility, ordering field, correlation length, and surface tension, respectively
a and b	van der Waals constants ($\text{J} \cdot \text{m}^3/\text{mol}^2$) and (m^3/mol)
a_0, b_0, u_0, e_0, g_0	coefficients of the Landau expansion in the meanfield theory of phase transitions
\mathbf{a}_i	monomer random step (vector)
B	second virial coefficient (m^3/mol)
\tilde{b}	mobility of a Brownian particle ($\text{m}^2 \cdot \text{K}/\text{s} \cdot \text{J}$)
c	molar concentration (mol/L); also, speed of light (m/s)
c_0	gradient-term coefficient in the Landau-Ginzburg functional
C	third virial coefficient (m^3/mol^2)
C_p	isobaric molar or molecular heat capacity ($\text{J}/\text{mol} \cdot \text{K}$)
C_v	isochoric molar or molecular heat capacity ($\text{J}/\text{mol} \cdot \text{K}$)
$C(r)$	spatial correlation function
$C(t)$	temporal correlation function
D	mutual diffusion coefficient in a binary solution (m^2/s)
D_T	thermal diffusion coefficient (m^2/s)
d	number of dimensions (dimensionality) of space
E_t	total energy (J)
E_k	kinetic energy (J)
E_p	potential energy (J)
\mathbf{F}	force (vector) (N)
G_t	total Gibbs energy (J)
$G = G_t/n$ or G_t/N	Gibbs energy per mole or per molecule (J/mol)

$g = \mathbf{g} $	free-fall acceleration (m/s^2)
H_t	total enthalpy (J)
$H = H_t/n$ or H_t/N	enthalpy per mole or per molecule (J/K)
\mathbf{h}	magnetic field (vector) (A/m)
h	generalized field variable
h	reduced (by 2π) Planck's constant ($1.0546 \times 10^{-34} \text{ J} \cdot \text{s}$)
\mathbf{j}_D	mutual diffusion flux ($\text{mol/m}^2 \cdot \text{s}$)
\mathbf{j}_Q	heat flux ($\text{J/m}^2 \cdot \text{s}$)
\mathcal{K}_0	Krichevskii parameter
\mathcal{K}	generalized Krichevskii parameter
K	reaction equilibrium constant
$k_B = R/N_A$	Boltzmann's constant per molecule ($1.38 \times 10^{-23} \text{ J/K}$)
k_p	baro-diffusion ratio
k_T	thermo-diffusion ratio
ℓ	length (m)
\mathbf{M}	magnetization (vector) (A/m)
M_w	molecular weight (g/mol)
m	mass (kg)
n	number of moles
n_i	number of moles for species i
$N = nN_A$	number of molecules
N_A	Avogadro's number (6.02×10^{23} molecules per mole)
$N_i = n_i N_A$	number of molecules for species i
\mathcal{N}	degree of polymerization
n_λ	refractive index
N_G	Ginzburg number
P	pressure (Pa; J/m^3 ; N/m^2)
P_r	probability
Q	heat (J)
Q_{ij}	components of a tensor order parameter
\mathbf{q}	wave number (vector) (m^{-1})
R	gas constant ($8.314 \text{ J/mol} \cdot \text{K}$)
R_g	radius of gyration (m)
R_h	hydrodynamic radius of a Brownian particle
r	distance
\bar{r}	average intermolecular distance
r_0	molecular radius
S_t	total entropy (J/K)

$S = S_t/n$ or S_t/N	entropy per mole or per molecule (J/K)
T	temperature (K)
t	time
U_t	total Internal energy (J)
$U = U_t/n$ or U_t/N	internal energy per mole or per molecule (J/K)
$u = \mathbf{u} $	velocity (speed) (m/s)
u_s	thermodynamic speed of sound (m/s)
V_t	total volume (m ³)
$V = V_t/n$ (or $V = V_t/N$)	volume per mole or per molecule (m ³)
W	work (J)
w	probability density
$x \equiv x_2$	mole or molecular fraction of solute in a binary mixture
x_i	mole or molecular fraction of species i
y	effective “activity” of species
z	vertical coordinate
z_n	molecular coordination number
z_r	dynamic critical exponent

Greek Notations

α_p	isobaric or volumetric expansivity (K ⁻¹)
α_H	Joule–Thompson coefficient (K/Pa)
α_s	sound attenuation (m ⁻¹)
$\alpha, \beta, \gamma, \delta, \nu, \vartheta, \eta$	critical exponents of weak susceptibility, spontaneous order parameter, strong susceptibility, ordering field, correlation length, surface tension, and correlation function, respectively
$\check{\alpha}$	Onsager’s molar transport coefficient (mol/[m · s · J])
$\check{\beta}$	Onsager’s cross transport coefficient (mol/[m · s · K])
$\check{\gamma}$	Onsager’s heat transport coefficient (J/[m · s · K])
γ_i	activity coefficient of species i
$\check{\delta}$	Reaction kinetic coefficient (mol/[m ³ · s · J])
δ'	Tolman’s length (m)
ϵ	dielectric constant
ϵ	energy of intermolecular interactions (J)
$\check{\zeta}$	bulk viscosity (Pa · s)
ζ	interfacial thickness (m); also, extent of reaction
$\check{\eta}$	dynamic shear viscosity (Pa · s)
θ	scattering angle
Θ	Theta (Flory) temperature
κ	thermal conductivity (J/m · s · K)
κ_T	isothermal compressibility (Pa ⁻¹)

κ_{Π}	osmotic compressibility (Pa^{-1})
λ	wavelength (m); also, a coupling constant
λ_s	sound wavelength (m)
μ	chemical potential of a pure substance (J/mol), equal to the Gibbs energy per molecule G in a single-component system
μ_{cxc}	chemical potential along phase coexistence (J/mol)
μ_0	chemical potential in zero-field ($\mu_0 = \mu_{\text{cxc}}$ for fluids for $T < T_c$)
μ_i	chemical potential of species i (J/mol)
$\mu_{21} = \mu_2 - \mu_1$	exchange chemical potential (J/mol)
ξ	correlation length of order-parameter fluctuations (m)
ξ_{ψ}	de Gennes correlation length of polymer-chain fluctuations (m)
Π	osmotic pressure (Pa)
$\rho = n/V_t$ or N/V_t	molecular or molar density (mol/m^3)
$\rho_i = \rho x_i$	partial molar density (molar concentration) of species i (mol/m^3)
$\rho A = A_t/V_t$	density of Helmholtz energy (J/m^3)
$\rho S = S_t/V_t$	density of entropy ($\text{J}/\text{m}^3 \cdot \text{K}$)
σ	surface tension (J/m^2 ; N/m)
τ	relaxation time (s)
v_0	volume of a molecule (m^3)
ϕ_i	volume fraction of species i
$\phi \equiv \phi_2$	volume fraction of polymers in a polymer solution
φ	order parameter; generalized density
φ_0	spontaneous order parameter (in zero ordering field)
$\hat{\chi}$	generalized dimensionless susceptibility
$\hat{\chi}_1$	strong scaling susceptibility
$\hat{\chi}_2$	weak scaling susceptibility
$\hat{\chi}_{12}$	cross scaling susceptibility
$\boldsymbol{\psi}$	de Gennes polymer-chain order parameter (vector)
ψ	critical exponent of shear viscosity
ϖ	Flory interaction parameter
$\Omega_t = -PV_t$	grand thermodynamic potential (J)

Special Notations

- In subscripts and superscripts: roman fonts indicate words, while italicized fonts indicate variables or functions.
- Circumflex (as in $\hat{\mu}$) designates reduced (dimensionless) thermodynamic properties.
- The inverted circumflex (as in $\check{\alpha}$) is used for Onsager transport coefficients.
- Over bar (as in \bar{N}) designates average equilibrium properties
- Subscript c (as in T_c) designates critical parameters.
- Superscript \circ (as in μ_1°) designates a reference state.
- Bold (as in \mathbf{h} or \mathbf{r}) designate vectors.

- Variation δ (as in $\delta\rho$) designates fluctuation or variation.
- Total differential d and partial differential ∂ indicate derivatives.
- Differential with a bar d (as in dW) designates an inexact differential quantity of work or heat.
- Symbol Δ (as in ΔU) designates a property change or excess (as in ΔC_V).
- Symbol \AA designates angstrom ($1\text{\AA} = 0.1\text{ nm} = 10^{-10}\text{ m}$).
- Brackets $\langle \rangle$ (as in $\langle \delta\rho \rangle$) designate statistical average of fluctuations or variations.
- The summation symbol, \sum , assumes a summation over the index i , such as in $\sum \mu_i N_i$.
- The symbol \sim indicates “scales as” or “order of,” the symbol \approx indicates an approximate value, while the symbol \cong indicates a rounded quantity.

Acronyms

$\bar{n}\bar{O}\bar{m}$	4- <i>n</i> -alkyloxyphenyl-4'- <i>n</i> -alkyloxybenzoates (\bar{n} and \bar{m} are the number of carbon atoms in the alkyl groups)
$\bar{6}\bar{O}\bar{6}\bar{N}\bar{O}_2$	4- <i>n</i> -hexyloxyphenyl-4'- <i>n</i> -hexyloxynitrobenzoate
BMOAB	4- <i>n</i> -butyl-4'-methoxyazoxybenzene
CHX	cyclohexane
CMC	critical micelle concentration
CP	critical point
DAG	dysprosium aluminum garnet
DCP	double critical point
DDAB	didodecyldimethylammonium bromide
DLS	dynamic light scattering
EOS	equation of state
Freon-113	trichlorotrifluoroethane
HLM	Halperin–Lubensky–Ma
LGCL	liquid–gas critical line (locus)
LLCL	liquid–liquid critical line (locus)
LGCP	liquid–gas critical point
LLCP	liquid–liquid critical point
LCEP	lower critical end point
LP	Lifshitz point
MBBA	4-methoxybenzylidene-4'- <i>n</i> -butylaniline
MC	Monte Carlo
MD	molecular dynamics
MFCP	meanfield critical point
NAC	nematic-smectic A-smectic C multicritical point
PBMA	poly(butyl methacrylate)
PEO	polyethylene oxide
PMMA	polymethylmethacrylate
PS	polystyrene
RG	renormalization group
RMS	root mean squared

SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SLS	static light scattering
SmA, SmC	smectic A, smectic C
S,S-MBBPC	S,S-(+)-4''-(methylbutyl) phenyl-4'-(methylbutyl) biphenyl carboxylate
TBA	tertiary butanol
TCP	tricritical point
TP	triple point
UCEP	upper critical end point
VDW	van der Waals

Greek Alphabet

A	α	alpha	N	ν	nu
B	β	beta	Ξ	ξ	xi
Γ	γ	gamma	O	o	omicron
Δ	δ	delta	Π	π	pi
E	ϵ	epsilon	P	ρ	rho
Z	ζ	zeta	Σ	σ	sigma
H	η	eta	T	τ	tau
Θ	θ	theta	Υ	υ	upsilon
I	ι	iota	Φ	ϕ	phi
K	κ	kappa	X	χ	chi
Λ	λ	lambda	Ψ	ψ	psi
M	μ	mu	Ω	ω	omega

Expansions of Basic Functions

$$\frac{1}{1 \pm x} = 1 \mp x + x^2 \pm x^3 + \dots$$

$$e^{\pm x} = 1 \pm x + \frac{1}{2!}x^2 \pm \frac{1}{3!}x^3 + \dots$$

$$\ln(1 \pm x) = \pm x - \frac{1}{2}x^2 \pm \frac{1}{3}x^3 - \frac{1}{4}x^4 \dots$$

$$\sin x = x - \frac{1}{3!}x^3 + \frac{1}{5!}x^5 \dots$$

$$\cos x = 1 - \frac{1}{2!}x^2 + \frac{1}{4!}x^4 \dots$$

$$\tan x = x + \frac{1}{3}x^3 + \frac{1}{15}x^5 + \dots$$

$$\tanh x = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 + \dots$$

Out of Intense Complexities, Intense Simplicities Emerge
– Winston Churchill

Part I

Thermodynamic Approach to Meso-Heterogeneous Systems

1

Macro, Meso, Micro

This chapter includes:

- Definition of “mesoscale”
- Definition of “meso-thermodynamics”
- Typical objects of meso-thermodynamics
- Probing mesoscales by scattering techniques

1.1 Thinner than a Hair

One can roughly consider a length scale less than 10 μm (10,000 nm) and larger than 1 nm as mesoscopic. This is a huge range. The upper boundary is about 10 times smaller than the thickness of a human hair (Figure 1.1), and, usually, one needs a microscope, optical or electronic, to see objects smaller than that.

Below one micron, one enters a sub-micron world. A size between 1 and 100 nm can also be defined as nanoscopic. It should be noted that any classification is conditional and circumstantial: sometimes “thinner-than-a-hair” objects can be treated macroscopically, while some macroscopic objects, like polymer solutions or complex fluids, may require a mesoscopic approach.

A natural atomistic length scale is 1 \AA = 0.1 nm. This is (approximately) the size of a hydrogen atom and the length of a carbon–carbon covalent bond. Whatever happens at the atomistic scale will be dominated by the material’s intramolecular structure and by the details of the intermolecular interactions. Phenomena at the atomistic scale cannot be treated by thermodynamics. Yet, how could one describe a single polymer molecule which consists of millions of carbon–carbon bonds? Is this a thermodynamic system?

The principal question arises: is traditional (macro-scale) thermodynamics sufficient enough to describe mesoscale systems? Can one apply, without restriction, the laws and equations of classical thermodynamics to calculate the chemical reaction equilibria and design a micro-reactor, which is only 100 nm thick, or to describe a transition between the alternative structures of a protein molecule? What would be the definition of a “phase” in such systems? All biological cells are natural micro-reactors. Can we still use the concepts of chemical potential, osmotic pressure, surface tension, etc. for such objects? A microchip can contain only hundreds of atoms. What is the limiting size for which thermodynamics is still applicable? In a micro-porous medium, not only does the surface energy dominate over the bulk energy, but also the surface itself may be poorly defined. Is there still room for thermodynamics, beyond the trivial mass and energy balances?

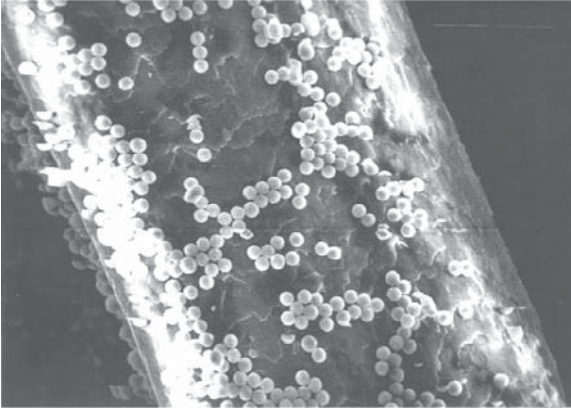


Figure 1.1 Electron microscopy image of polystyrene particles (3.4 μm diameter) on a human hair (Courtesy of Spherotech, Inc.). The hair (with a thickness of about 100 μm) can still be considered as a macroscopic object in most applications, while the polystyrene particles are mesoscopic.

1.2 Where Does the Size Matter?

Classical thermodynamics is essentially macroscopic. To define thermodynamic states and thermodynamic properties, one needs systems with a huge number of individual particles, such as atoms or molecules [1, 2]. Statistical mechanics defines thermodynamic states and properties only in the so-called “thermodynamic limit”, where the total volume (V_t) and the number of particles (N) must tend to infinity, while the molecular number density of the substance, $\rho = N/V_t$, remains finite. Even a cubic millimeter of liquid water (1 mg) contains 3×10^{19} molecules. It is sufficient to regard such a small droplet of water as a macroscopic body and neglect the surface effects in considering its bulk properties. If the characteristic size of the object is ℓ , the surface energy is proportional to ℓ^2 , while the bulk energy is proportional to ℓ^3 . This is why one can measure the temperature of steam condensation as well as the vapor pressure in a small tube, and use these data in the design of an upscale distillation column, taller than 100 m.

Macroscopic thermodynamics eliminates the size of the system by reducing the extensive thermodynamic properties (which depend on size) by the number of particles, the number of kilograms, or the volume. Equations of thermodynamics usually operate with intensive properties, such as density, concentration, molar or specific volume, etc., which do not depend on the size. The actual length scale is restored only in the final stage of engineering design. The equations of state implicitly depend on atomistic length scales, the molecular size, and the range of intermolecular interactions. However, since these microscopic characteristics are integrated over a huge number of molecules, the parameters of common equations of state (EOS) are independent of the length scale.

There are at least three categories of popular objects in which macro-scale size-independent thermodynamics may breakdown:

1. Soft condensed-matter materials, such as complex fluids (polymer solutions and melts, micro-emulsions, gels, and liquid crystals) [3–15]. Most food and cosmetics are soft matter [16]. Humans (like other living organisms) are “soft-matter machines.” All soft-matter materials, even being themselves macroscopic, have some kind of mesoscopic structure which is characterized by the existence of one or more mesoscales.
2. Systems that are essentially finite (practically speaking, sub-micron or nano-size) in one or more dimensions [17–19]. Examples include nanoparticles (if the particle is considered as a separate system), pores, films and layers, fibers, and threads. Meso-heterogeneous interfaces with

a thickness from 1 nm to microns also belong to this category. Sometimes such systems can be truly microscopic in a certain dimension, and they should thus be treated as two- or even one-dimensional objects. Here, the size really matters!

3. Systems in a near-critical state (i.e. in the vicinity of a critical point or a second-order phase-transition) [20–28]. Such systems are mesoscopically inhomogeneous as a result of strong thermal fluctuations. The mesoscopic length scale associated with these fluctuations is known as the “correlation length.”

1.3 What Is Meso-Thermodynamics?

Each of these categories has been a subject of extensive experimental and theoretical investigations for the last 50 or more years. Thermodynamics of adsorption [29], wetting transitions [30], micro-phase separation in polymers [31], gelation [32, 33], and phase equilibria in confined fluids [34, 35] are just a few examples. Computer simulations of mesoscale systems become increasingly informative (see, for example, Refs. [36–41]). The existence and dominant role of mesoscale inhomogeneities is a common feature of all the systems mentioned above.

Mesosopic thermodynamics (or in short, “*meso-thermodynamics*”) can be defined as a semi-phenomenological approach to systems and phenomena in which a length, intermediate between the atomic scale and the macroscopic scale, emerges and where such a length explicitly affects the thermodynamic properties [42]. This science is still thermodynamics, as its objects are still governed by statistical mechanics but, in contrast to “macro-thermodynamics,” it explicitly contains a mesoscopic length scale associated either with the structure of materials or with the actual finite size. Many ideas and concepts of mesoscopic thermodynamics were developed and explored in colloid and interface science long ago [42–44]. However, only more recently, a high degree of *universality* (and thus “simplicity”), originating from the very existence of the mesoscopic length scale, has been fully recognized.

Meso-thermodynamics also includes thermal fluctuations – spontaneous deviations from average (equilibrium) properties, assigned by thermodynamics. Fluctuations emerge in the apparent “violation” of the second law of thermodynamics. A famous astrophysicist Sir Arthur Eddington wrote: “... if your theory is found to be against the second law of thermodynamics I can offer you no hope...” [45]. However, the existence of fluctuations just demonstrates the statistical meaning of the second law. In fact, the statement of Sir Eddington is unconditionally correct only in the thermodynamic limit (for an infinite number of molecules).

Representation of a micro-heterogeneous system as an “ensemble” of small open systems was introduced and elaborated by Hill [46, 47]. This approach is important for small systems, where the surface energy plays a significant role and for the analysis of computer simulations that usually involve a relatively small number of molecules. In this book, we provide a different approach to unify the description of mesoscopic phenomena. This approach is based on the concept of a “local” coordinate-dependent free energy, known as the “Landau–Ginzburg functional” [1, 2], allowing for the unified treatment of “apparently” physically different mesoscopic heterogeneous systems, whose properties depend on an appropriate mesoscopic length scale.

The approach to introduce a mesoscale in thermodynamic properties goes back to van der Waals [48] and is sometimes referred to as “quasi-thermodynamics,” “local thermodynamics,” or “point-thermodynamics” [49]. This approach was generalized by Landau and Lifshitz [1, 2, 50] and was later elaborated for fluid interfaces by Cahn and Hilliard [51] and by Rowlinson and

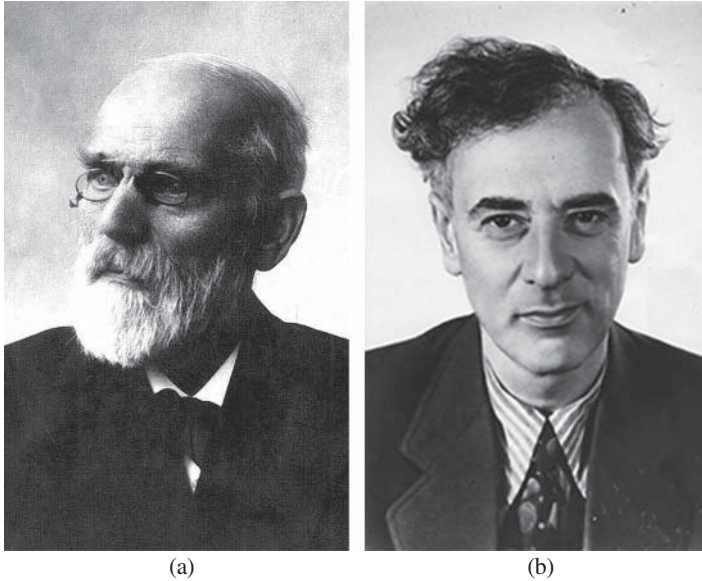


Figure 1.2 Two founders of mesoscopic thermodynamics: Johannes Diderik van der Waals (a) and Lev Davydovich Landau (b), see more information in the footnote. Source: Unknown author/Wikimedia Commons/Public Domain.

Widom [49]. Arguably, van der Waals and Landau (see Figure 1.2) may be viewed as the fathers of this branch of thermodynamics.¹

A theory elaborating toward the microscopic description of condensed-matter systems is referred to as “density functional theory” (DFT) [52]. Unlike the microscopic description provided by DFT, the approach adopted in this book is semi-phenomenological, addressing the microscopic complexity through a few mesoscopic parameters (e.g. the correlation length). In short, the motto of this book is “finding simplicity in complexity.” Typical models of meso-thermodynamics are coarse-grained models that do not have to account for every detail on the atomistic scale. Instead, such models emphasize universality. For example, the behavior of polymer solutions is basically determined not by a particular structure of the monomer units but by the fact that the polymer molecule is often a long, flexible curve in three-dimensional space. Another example is the near-critical state. The origin of critical-point universality lies in long-range correlations that involve a large number of molecules, so that the details of direct intermolecular interactions become unimportant.

In many cases, more than one mesoscale determines the properties of meso-heterogeneous systems. One of the mesoscales could be an instrumental scale, such as the wavelength of radiation, or the actual finite-size scale, such as the radius of a droplet. Another one could be inherent to the meso-heterogeneous structure, such as the size of a polymer molecule or the correlation length of density fluctuations. A competition of these mesoscales, which may produce new phenomena and modify the thermodynamic properties, can also be treated within the universal framework of meso-thermodynamics [42].

¹ Van der Waals (1827–1923) was a Dutch physicist who won a Nobel Prize in 1910 for his work on equations of state for fluids. Landau (1908–1968) was a Soviet physicist who won a Nobel Prize in 1962 for his pioneering theoretical works on condensed matter, in particular, for the classical theory of phase transitions.