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Zi Wen

Thermodynamics of Materials

材料热力学 (英文版)



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Preface

As a classic theory dealing with energy and its transitions in matter, thermodynamics has always been a valuable theoretical tool, providing useful insights into all fields of science and technology since the 19th century. In this book, the basic underlying principles of thermodynamics are introduced concisely and their applicability to the behavior of all classes of materials, such as metals and alloys, ceramics, semiconductors, and polymers, is illustrated in detail. The book accentuates more physical thermodynamics and statistical physics closely tied to computer simulation results, which could deepen our present understanding of material's properties on a physical basis. This book acts also as an authored advanced text, including authors' findings on the new topics of nanothermodynamics or the size effect of thermodynamic functions. Thus, the book intends to provide an integrated approach to macro- (or classical), meso- and nano-, and microscopic (or statistical) thermodynamics within the framework of materials science, which helps us to see a natural connection between the molecular and nanometer level properties of systems and their collective properties on macroscopic scales, benefiting our current understanding of nanoscience and nanotechnology in 21st century. Since nanothermodynamics has only been recently developed, we emphasize the close relationship between the text and the new literature on this subject.

This book is intended for scientists, engineers and graduate students engaged in all disciplines of materials science.

Qing Jiang and Zi Wen
Jilin University, May 2010

Nomenclature

a_l	lattice constant
a_B	activity of material B
a_{emf}	thermal emf
a_{lc}	the lattice constants of cubic phase
a_{lt}	the lattice constants of tetragonal phase
A	surface or cross-sectional area
A'	material constant
A_0	surface atom density
$A_{AFM}(\infty)$	the exchange stiffness; $A_{AFM}(\infty) = 2J_{AFM}(\infty)s^2/a_l$
A_f	austenite transition finish temperature
A_L	area of two-dimensional unit cell of liquid
A_S	area of two-dimensional unit cell of solid
A_s	austenite transition start temperature
b	Burgers length
$\mathbf{b}$	Burgers vector
b'	cut-off distance
B	magnetic induction
$\mathbf{B}$	Bucky diamond
B'	$2S_{vib}(1 - \theta)/(3R\theta)$
B_m	bulk modulus
bcc	body centered cubic structure
c	$c = c'H'_v/H_v$
c_1	additional condition for different surface states
c_e	equilibrium concentration of vacancy
C	heat capacity
C'	concentration in the fluid for a particle of radius r
C'_0	bulk saturation concentration
C_B	magnetic contribution to the heat capacity
C_{Curie}	Curie constant
C_d	concentration for diffusion
$C_{H_{mag}}$	heat capacity at constant magnetic field
C_m	molar heat capacity
C_M	heat capacity at constant magnetic moment
$C_{P,m}$	molar heat capacity at constant pressure
$C_{V,m}$	molar heat capacity at constant volume
CN	coordination number
CNT	classical nucleation theory

ΔC_{pss}	heat capacity difference between polymorphous solid phases of the same substance
d	dimension of crystal
D	diameter
D	diamond
dc	diamond-type structure
e	$e = -4u' \Delta S / (3\lambda N_A^{1/3} V_s^{2/3})$
E	total energy
E^*	migration energy for diffusion
E_0	FM/AFM interfacial energy
E_c	bulk cohesive energy
$E_{ci}(N)$	cohesive energies of atoms at interior of cluster
E_{cr}	crystalline field
$E_{cs}(N)$	cohesive energies of atoms at surface of cluster
E_e	electric field in vacuum
E_{el}	elastic energy
E_{exc}	spin-spin exchange interaction energy
E_{fr}	frictional energy
E_g	band gap width
E_{mp}	magnetic potential energy
E_p	potential energy
E_{PA}	photoabsorption energy
E_{PL}	photoluminescence energy
E_s	energy for electron-phonon coupling
$E_{th}(T)$	thermal energy
E_v	van der Waals interlayer attraction
E_{vx}	the vacancy formation energy of the x site
E_Y	Young's modulus
f	surface or interface stress
$\bar{f}$	$\bar{f} = (f_f + f_r)/2$
f_B	activity coefficient of material B
f_c	fraction of electrons in the crystal
f_e	elastic force
f_f	interface stress of forward transition
f_o	force
f_r	interface stress of reverse transition
F	Helmholtz function
F	fullerenes
fcc	face centered cubic structure
fi	number of degree of freedom
g	degeneracy of the level
g'	geometry factor of the lattice type considered
$g_L(r)$	liquid radial distribution function
g_m	Gibbs free energy difference between bulk liquid and crystal
G	Gibbs function or Gibbs free energy
G	graphite
G'	magnetic Gibbs function
G_d	misfit dislocation energy

G_{el}	elastic Gibbs free energy
G_{i}	non-coherent interface Gibbs free energy
G_{s}	surface free energy
G_{shear}	shear modulus
G_{v}	volume Gibbs free energy
ΔG	Gibbs free energy change
h	atomic diameter
h and l	subscripts for high and low pressure phases
h_{f}	atomic diameter of films
h_{P}	Planck's constant (6.62×10^{-34} J-s)
h_{s}	atomic diameter of substrate
H	enthalpy
H'	magnetic enthalpy
H_{e}	exchange bias field
H_{e0}	exchange bias field at 0K, $E_0/(M_{\text{FM}}t_{\text{FM}})$
H_{eTb}	exchange bias at T_{b}
H_{mag}	magnetic field intensity
H_{s}	critical or threshold field required to destroy superconductivity in a metal
$H_{\text{s},0}$	critical field at 0K
hcp	hexagonal close packed structure
hr	hour
ΔH_{s}	solid transition enthalpy
ΔH_{sn}	superconductor transition enthalpy
ΔH_{v}	heat of evaporation at T_{m} or T_{b}
$\Delta H'_{\text{v}}$	heat of evaporation at $T = 0$ K
i	i -th level
I	current
I_{r}	moment of inertia
J	diffusing flux
J'	spin interact energy
J_{AFM}	the exchange integral
J_{d}	diffusing coefficient
J_{int}	interface coupling exchange between the FM and AFM spins
$J_{\text{i}}, J_{\text{s}}, J_{\text{sub}}$	exchange constant or exchange coefficient where subscripts "i", "s", and "sub" show interface, surface and substrate, respectively and $J_{\text{i}} = J_{\text{s}} + J_{\text{sub}}$
k	Boltzmann's constant
$\mathbf{k}$	scaling exponent
k'	rate of adsorption
k_{-1}	rate of evaporation from the completely covered surface at a certain T
k_{m}	a given macrostate
k_{r}	ratio of C_{P} and C_{V}
k_{s}	spring constant
K	$K = k'/k_{-1}$
K_{AFM}	the magnetic anisotropy constant
l_{ed}	electric displacement
l_{s}	length of step

L	liquid
ΔL	thickness of surface layer of nanoparticles
m^*	effective mass
m'	$m = (2 - v_1 - v_1^{1/2})/2$
M	magnetic moment
M_f	martensite transition finish temperature
M_{FM}	fixed saturation magnetization of the FM layer
M_s	martensite transition start temperature
M_w	molecular or atomic weight
min and max	minimum and maximum value
n	number of atoms in a molecule
n'	layer number of epitaxially grown films
n_0	number of energy level
n'_c	critical layer number
n_e	equilibrium number of vacancy
n_s	symmetry number
N	number of particles
N_A	Avogadro constant
N_d	dislocation number
O	carbon anions
P	pressure
$\overline{P}$	$\overline{P} = (P_f + P_r)/2$
P_d	electric polarization
P_e	external pressure
P_f	forward transition pressure
P_{in}	internal pressure
P_n	necessary pressure for the solid transition in thermodynamic equilibrium
P_r	reverse transition pressure
P_s	macroscopic spontaneous polarization
P_{ss}	surface spontaneous polarization
P_{sv}	interior spontaneous polarization
P_w	static pressure hysteresis width
q	$q = (d\rho_L/dT)[T_m/\rho_L(T_m)]$
Q	heat
Q_{ij}	electrostrictive coefficient
Q_P	heat at constant pressure
Q_V	heat at constant volume
r	radius, half thickness of film
r^*	critical radius of the nucleation
r_0	critical radius between solid and liquid
r_c	critical radius of nanocarbon for phase transition
r_e	effective dislocation stress field radius
r_g	grain size
r_h	radius of the hollow part of cylinder
$\mathbf{r}_i$	denote the vector position of the i -th link in the chain
R	ideal gas constant
$\mathbf{R}$	end-to-end vector
R_b	net displacement magnitude

R_c	radius of cylinder
R_e	equimolar radius
R_s	radius of surface tension
$\mathfrak{R}$	cell position
s	solid
s	spin value
s_{11}, s_{12}	elastic compliance constants
S	entropy
sa	atoms/molecules at the surface
sc	simple cubic structure
ΔS_b	bulk solid-vapor transition entropy
ΔS_{el}	electronic entropy
ΔS_m	melting entropy
ΔS_{pos}	positional entropy
ΔS_s	solid transition entropy
ΔS_{sn}	superconductor transition entropy
ΔS_{vib}	vibrational entropy
t	time
t_0	thickness of film that has firmly attached to a substrate
t_C	Celsius temperature
t_f	thickness of a monolayer
t_{FM}	thickness of FM layer
t_h	isotropic film of thickness
t_r	molecular relaxation time
t_s	surface melting layer thickness
T	absolute temperature
T_0	temperature at which the Gibbs free energy of austenite and martensitic phase are equal
T_{0b}	temperature at which the austenite and ferrite of the same composition have an identical G value
T_b	bulk solid-vapor transition temperature
T_{bl}	blocking temperature
T_c	the critical temperature
T_C	Curie temperature
T_f	freezing temperature
T_g	glass transition temperature
T_K	Kauzmann temperature
T_m	melting temperature
T_{mh}	melting temperature of high pressure phase
T_{ml}	melting temperature of low pressure phase
$T_m(r)$	size dependent melting temperature
T_n	critical temperature of the nucleation
T_N	the Néel temperature
T_r	reduced temperature
T_{room}	room temperature
T_s	solid transition temperature
$T_{s,0}$	superconductor transition temperature in the absence of a magnetic field
T_t	triple point temperature

u	potential difference
u'	$u' = (d\rho_L/dT)/\rho_L(T_m)$
$u(r)$	potential energy function
u_d	misfit dislocation energy of a single dislocation
u_e	elastic free energy of unit volume
U	internal energy
v	vibrational quantum number
v_1	$v_1 = Z_s/Z_b$
v'_1	$v'_1 = Z'_s/Z'_b$
v_u	ultrasound propagation velocity
V	volume
V_L	g-atom volume of liquid
V_s	g-atom volume of crystal
V_f	g-atom volume of the film
va	atoms/molecules within the particle
w	a critical exponent
w	$w = \gamma_{sv0}/\gamma_{Lv0}$
w'	weight fraction of the second polymer component
w_r	reversible work
W	mechanical work
W^*	useful work
Y	biaxial modulus, $Y = E_Y/(1 - \nu_P)$
Y_s	stability parameter
z	a number of order unity
z_b	coordinates without CN imperfection
z_i	coordinates with CN imperfection
Z	partition function
Z_b	coordination number (CN) of interior atom
Z'_b	next nearest CN of interior atom
Z_{hkl}	broken bond number
Z_s	coordination number of surface atom
$Z_{s'}$	next nearest CN of surface atom
α	coefficient of thermal expansion
α'	Lagrangian multiplier
α_F	ferrite phase
α_M	martensitic phase
α_r	σ_s^2/σ_v^2
α_s	σ_s^2/σ_v^2 for glass transition
β	compressibility
β'	Lagrangian multiplier
γ_A	austenitic phase
γ_{exp}	experimental values of interface energy
γ_i	non-coherent interface
γ_{Lv0}	bulk liquid-vapor interface energy
$\gamma'_{Lv0}(T)$	$\gamma'_{Lv0}(T) = d\gamma_{Lv0}(T)/dT$
γ_{sL0}	bulk solid-liquid interface energy
γ_{ss0}	bulk solid-solid interface energy
γ_{sv0}	bulk solid-vapor interface energy

γ_{TS}	solid-liquid interface energy based on the Turnbull-Spaepen relation
δ	Tolman's length, $\delta = R_e - R_s$
$\delta_{\min}$	minimum value of δ
δ_v	vertical distance from the surface of tension to the dividing surface
δ_{∞}	Tolman's length when $r \rightarrow \infty$
ε	bond energy
ε_0	permittivity of free space
ε_a	actual permittivity
ε_e	electronic energy
ε_{emf}	electromotive force
ε_F	Fermi energy
ε_i	the energy in level i
ε_n	nuclear energy
ε_n'	kinetic energy of the electrons
ε_p	kinetic energy of the holes
ε_r	relative permittivity
ε_{rt}	rotational energy
ε_t	translational energy
ε_v	vibrational energy
ζ	ratio of the surface volume to the entire volume
η	packing density
η_v	dynamic viscosity
θ	order parameter
θ_1	angle between direction of the nearest atoms at neighbor planes and that of the film surface
θ_a	contact angle
θ_c	$(T_m - T)/T_m$, degree of undercooling
θ_m	rotation angle of the magnetic dipole from its zero energy position $\pi/2$ to θ_m
θ_s	fraction of the surface occupied by gas molecules
ϑ_s and ϑ_L	electrical conductivity of the crystal and the melt
Θ	characteristic temperature
Θ_D	Debye temperature
Θ_E	Einstein temperature
κ	$\kappa = 1/[m'\Delta H_v/(T_m\Delta S) - 1]$
κ_s	$\kappa_s = \kappa - 2q/3$
λ	$2^{-1/6}\hbar$
λ'	$\lambda' = (8^{1/2}/3)(6\eta/\pi)^{2/3}$
λ_c	critical misfit
Λ	critical exponent
μ	chemical potential
μ'	$\mu' \cong 1/[4\pi(1 - \nu_P)]$
μ_0	permeability of free space
μ_B	1 Bohr magneton
μ_v	magnetization or magnetic moment per unit volume
ν	$\nu = m'\Delta H_v - T_m\Delta S$
ν_P	Poisson's ratio

ν_s, ν_L	characteristic vibration frequencies of the particles in the crystal and melt
ξ	correlation length
ξ_0	microscopic length
ξ_1	$J_{\text{int}}/(4K_{\text{AFM}}ra_1)$
Π	the number of phases presented
ρ	density
σ	root-mean-square (rms) average amplitude of atomic thermal vibration
ς	strain
τ	Turnbull coefficient
τ_{ij}	$\tau_{ij} = \partial\gamma_{sv}/\partial\varsigma_{ij}$
τ_s	shear stress
Γ	jump frequency of atom
Γ'	generic extensive property of a solution
v	a constant related to CN
Υ	mean-square root error between the predicted and the experimental results
φ	total bond strength ratio between next-nearest neighbor and the nearest one
φ_c	volume fraction of clusters at T_m
ϕ	geometric factor
Φ	total flux
χ	electric susceptibility
ψ	effective dislocation stress field radius
ω	interaction parameter
ϖ	$\varpi = \gamma_{Lv0}(T_m) - \gamma_{Lv0}^e(T_m) /\gamma_{Lv0}^e(T_m)$
Ω	the number of microstates
σ	stress
ν	$1/\nu_c$
$\Delta\varrho$	Peltier heat
∞	bulk size

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Chapter 1 Fundamentals of Thermodynamics

This chapter firstly looks back on the development of macroscopic thermodynamics during the last three hundred years and its historical contribution to the social evolvement. The present achievement and challenges are also discussed. To clearly understand the thermodynamic laws, the essential concepts of thermodynamics are defined and clarified. Further, the macroscopic thermodynamics of materials and the fundamental principles of four thermodynamics laws are introduced, which are the essential basis of the later chapters. The intrinsic relationships between these thermodynamics laws through a series of mathematical deductions are given, which additionally result in the acquirement of the most important physical amounts of materials.

1.1 Thermodynamics of Materials Science, Scope and Special Features of the Book

Classical thermodynamics is a branch of physics originating in the nineteenth century as scientists were first discovering how to build and operate steam engines [1], which primarily led to the industrial revolution. A steam engine is a heat engine that performs mechanical work using steam as its working fluid. Historically, thermodynamics developed just out of needs to understand the nature of these heat engines and to increase the efficiency of transition between heat and work [2]. With a deeper understanding of the relationship between heat, work and temperature, the design of engines of specific power output and efficiency became possible. Although the relationship between science and technology in this period is complex, it is fair to say that without the introduction of scientific thermodynamic methods, the development of the industrial revolution would not have been so swift.

The demands of the industrial revolution had put the “standard model” of physics in a crisis around the question of “what is energy?”. Energy as the capacity to do work is essentially an abstract concept. It cannot be measured directly and thus has no definite value. Thermodynamics, dealing with energy and its transitions, is based on two laws of nature, namely the first and the second laws of thermodynamics [3]. Thermodynamics tells us that the energy differences can be measured by heat and work removed or added.