



# Thermodynamics at the nanoscale: A new approach to the investigation of unique physicochemical properties of nanomaterials



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## ABSTRACT

An extension of the classic thermodynamics theory to nanometer scale has generated a new interdisciplinary theory – nanothermodynamics. It serves as a bridge between macroscopic and nanoscopic systems. Over the past decade, nanothermodynamics theories have developed rapidly owing to their critical role in investigating the size-dependent physicochemical properties of nanomaterials. This review examines up-to-date research results on this cutting-edge topic. The focus and emphasis are on the utilization of nanothermodynamics models to investigate the size-dependent thermal stability, magnetic properties, photoelectric behaviors, thermoelectric phenomena, mechanical properties, electrical properties, etc. of nanomaterials.

A range of properties have been studied with respect to the effects of size, dimensionality and composition through a quantitative nanothermodynamics model. It is found that (a) the size dependence of these properties can be universally reconciled to the effect of severe bond dangling; (b) for the same material size, the sequence of size effects on the properties, from strong to weak, is nanoparticles, nanowires and thin films; and (c) the composition effects on the properties of nanoalloys are substantial, having a nonlinear relationship. It also reveals that vacancy formation determined by the cohesive energy variation is one of the intrinsic factors which dominate the size-dependent physicochemical properties of nanomaterials.

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### List of symbols and abbreviations

$a, c$	lattice parameter
$a_h$	hole Bohr radius
$A_c$	a material constant
$A_m$	gram-atom ( $g$ -atom) surface area
$b$	bowing parameter
$B$	bulk modulus
BOLS	bond-order-length-strength
$c_G$	Gruneisen constant
$c_i$	coordination number-dependent reduction of bond length
$C$	a constant
$C_p$	heat capacity
$C_v$	equilibrium vacancy concentration
$C_0$	a size-independent pre-exponential coefficient
$d$	dimensionality of materials
$d_{hkl}$	inter-planar distance of ( $hkl$ )
$D$	thermal diffusivity

$D_d$	diffusion coefficient
DFT	density functional theory
$D_0$	a size-independent pre-exponential coefficient
$e$	electrical charge of one electron
$E_a$	first absorption peak energy
EAM	embedded-atom method
$E_c$	cohesive energy
$E_{ca}$	catalytic activation energy
$E_d$	diffusion activation energy
$E_{exc}$	spin–spin exchange interaction
$E_g$	bandgap energy
$E_{iv}$	lattice thermal vibrational energy
$E_r$	exciton Rydberg energy
$E_v$	vacancy formation energy
$f$	surface stress
$fwhm$	full width at half-maximum
FGS	fullerene-like graphite shells
$G$	Gibbs free energy

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