

Two-phase core-shell nanoparticle model

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ABSTRACT A two-phase core-shell model for nanoparticle melting is proposed, in which a solid core is surrounded by a quasi-liquid shell. The model provides self-consistent analytical expressions for the size-dependent melting temperature and effective surface tension, along with kinetic equations describing the temporal evolution of the shrinking solid core under external heating. The analysis identifies distinct melting regimes, including a pronounced acceleration in the final stage caused by curvature-induced melting-point depression. Numerical estimates for silver and copper nanoparticles demonstrate that size effects can significantly reduce melting time. The results offer simple and physically transparent relations that clarify nanoscale melting behavior, provide an intuitive interpretation of the Tolman length, and explain the overheating observed in molecular dynamics simulations.

KEYWORDS core-shell nanoparticles, two-phase model, melting kinetics, thermodynamic equilibrium, surface effects, size-dependent properties, phase transition

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1. Introduction

The design of nanomaterials with tailored physicochemical properties remains a central challenge in modern materials science and nanotechnology [1, 2]. At the nanoscale, material properties undergo profound changes due to the dominant influence of surface effects [3–12]. Unlike bulk materials, where the fraction of surface atoms is negligible, in nanoparticles, it can reach 50 % or more. Therefore, the heterogeneous structure and size-dependent effects must be explicitly considered when describing both thermodynamic and kinetic behavior.

Classical thermodynamics, particularly Gibbs' theory, provides a powerful framework for describing equilibrium in macroscopic systems, but its direct application to nanoparticles is limited. The Laplace equation, which relates the pressure difference across a curved interface to the surface tension, depends on the choice of the dividing surface, such as the equimolar surface or the surface of tension, complicating the description of interfacial phenomena [13, 14]. In this classical picture, the interface is usually treated as infinitely thin, neglecting its finite thickness and the detailed molecular structure. As a result, several key quantities in the theory, including the Tolman length [15], which measures the offset between the surface of tension and the equimolar surface, are not uniquely defined and remain difficult to determine both theoretically and experimentally. These ambiguities often lead to discrepancies between macroscopic thermodynamic predictions and molecular dynamics simulations, particularly for very small nanoparticles where surface effects and molecular-scale fluctuations are significant [16–19]. Most previous studies have focused on the size dependence of melting temperature and surface tension, while the kinetics of the melting process has remained largely unexplored. This gap highlights the need for analytical models capable of describing both equilibrium properties and the time-dependent behavior of melting in nanoscale systems.

In this work, we develop a two-phase core-shell model of nanoparticles, in which the solid core is surrounded by a shell treated as a melted or quasi-liquid layer, consistent with the concept of surface premelting [20–25]. This approach reflects the enhanced mobility of surface atoms even below the bulk melting temperature. The core and shell are treated as coupled thermodynamic subsystems, enabling the description of both equilibrium conditions and melting kinetics, specifically the temporal evolution of the core radius under external heating.

In developing the present model, we focus on the thermodynamically controlled regime of nanoparticle melting, where the characteristic timescale of heat transfer through the shell is much shorter than that of atomic diffusion. Under such conditions, typical for nanoparticles with radii below several tens of nanometers, mass transport can be neglected, and the melting dynamics are governed primarily by interfacial curvature and heat conduction. This assumption enables a consistent analytical description of the melting process without introducing additional kinetic coefficients or diffusion terms.

Analytical expressions are derived for the radius-dependent melting temperature and the effective surface tension. In the limiting cases of large particle radius or vanishing shell thickness, the model reproduces the classical Laplace and

Gibbs–Thomson relations, ensuring consistency with macroscopic thermodynamics. This integrated framework thus provides a versatile theoretical tool for analyzing both equilibrium properties and dynamic melting behavior of nanoparticles, emphasizing the decisive role of the surface layer.

2. Thermodynamic analysis of a core-shell nanoparticle

We consider a single nanoparticle represented as a two-phase system, consisting of a solid core surrounded by a liquid shell. The core and shell are treated as coupled phases capable of mass exchange, with the shell having a finite thickness δ comparable to the particle radius R . This formulation assumes that each phase maintains a uniform, bulk-like density (or molar volume) despite the nanoscale confinement, so that the solid and liquid can be characterized by constant material parameters. The surface layer is modeled as a melted or quasi-liquid phase, consistent with the concept of surface premelting, reflecting the enhanced mobility of surface atoms compared to the bulk.

Subscripts c and s denote the core and shell phases, respectively. For thermodynamic stability, the chemical potentials in both phases must be equal

$$\mu_c = \mu_s, \quad (1)$$

which implies that there is no net transfer of atoms or molecules between the core and the shell. It should be noted that strictly speaking, the chemical potential of a solid component is tensorial due to mechanical stress anisotropy [26]. For a spherical nanoparticle under isotropic surface stress and absent external shear fields, the stress tensor in the core reduces to a hydrostatic pressure. In this specific symmetric case, the tensorial chemical potential condition simplifies to the scalar equality of Eq. (1), which is widely used in nanothermodynamics of spherical particles [26]. We emphasize that this is a simplification: strictly speaking, in a crystalline solid core the chemical potential is a tensor and may vary with distance from the center. However, for the present model we adopt the hydrostatic (fluid-like) approximation for the solid core. This simplification is justified for spherical particles whose radius is much larger than the interatomic spacing, and is sufficient for the analytical description of the melting kinetics. We employ this approximation to maintain the transparency of the model. Within this fluid-like description, the distinction between thermodynamic surface energy and mechanical surface stress is neglected as a higher-order correction, consistent with standard treatments of isotropic solid–liquid interfaces [26, 27].

Expanding the chemical potentials linearly in pressure around the bulk phases at zero pressure within this hydrostatic approximation gives the equilibrium relation

$$\mu_{0c} + v_c p_c = \mu_{0s} + v_s p_s. \quad (2)$$

Here, p_c and p_s are the pressures in the core and shell; v_c and v_s denote the molar volumes of the core (solid) and shell (liquid) phases; μ_{0c} and μ_{0s} are the chemical potentials of the bulk phases at the same temperature T and zero pressure. At the core-shell interface, the Laplace equation describes the pressure difference due to surface curvature:

$$p_s = p_c - \frac{2\sigma_i}{R_c}, \quad (3)$$

where σ_i is the solid-liquid interfacial tension (σ_{SL}), $R_c = R - \delta$ is the core radius. This relation shows that the pressure in the core is always higher than in the shell. The quantity σ_i in Eq. (3) denotes the interfacial tension defined at the surface of tension, for which the Laplace relation holds exactly without terms involving $\partial\sigma/\partial R$ [13, 14]. Substituting (3) into (2) gives one

$$\Delta\mu + p_c \Delta v + \frac{2\sigma_i v_s}{R_c} = 0. \quad (4)$$

where $\Delta\mu = \mu_{0c} - \mu_{0s}$ and $\Delta v = v_c - v_s$. Eq. (4) is the fundamental equilibrium condition, relating the properties of the core and shell, their molar volumes, pressures, and the core radius.

The model predicts a decrease in the melting point for the nanoparticle. Near the bulk melting temperature T_{m0} , the difference between the chemical potentials of the bulk solid and liquid phases can be expressed as

$$\Delta\mu \approx T\Delta S_m - \Delta H_m \approx -\Delta H_m \left(1 - \frac{T}{T_{m0}}\right), \quad (5)$$

where ΔS_m and ΔH_m are the bulk molar entropy and enthalpy of fusion, respectively. Here, $\Delta S_m = \Delta H_m/T_{m0}$ represents the increase in disorder per mole as the solid melts into the liquid phase in the bulk material. Substituting (5) into (4) and solving for the equilibrium melting temperature $T_m(R_c)$ leads to the formula

$$T_m(R_c) = T_{m0} \left[1 - \frac{1}{\Delta H_m} \left(p_c \Delta v + \frac{2\sigma_i v_s}{R_c}\right)\right]. \quad (6)$$

Equation (6) shows that the melting temperature decreases with decreasing core radius R_c , primarily due to the surface curvature term proportional to R_c^{-1} . When the volume change Δv between the solid and liquid phases is negligible, Eq. (6) reduces to the classical Gibbs–Thomson relation. This expression quantitatively describes the melting-point depression in small particles. In such particles, the enhanced surface-to-volume ratio and interfacial curvature promote surface premelting and increase the thermodynamic instability of the solid phase.

Equation (6) contains two contributions that control the shift of the nanoparticle melting temperature relative to the bulk value: the curvature term $2\sigma_i v_s / R_c$ and the volumetric term $p_c \Delta v$. Here we adopt the notation $\Delta v = v_c - v_s$ (solid minus liquid). For most metals, melting is accompanied by an increase of the molar volume of the substance, so that $v_c < v_s$ and therefore $\Delta v < 0$. Under compressive internal pressure ($p_c > 0$), the product $p_c \Delta v$ is negative, which reduces the quantity subtracted in Eq. (6) and thus produces an *effective elevation* of the apparent bulk melting temperature. Defining

$$T_\infty = T_{m0} \left(1 - \frac{p_c \Delta v}{\Delta H_m} \right), \quad (7)$$

one recovers the conventional Gibbs–Thomson form

$$T_m(R_c) \approx T_\infty \left(1 - \frac{2\sigma_i v_s}{\Delta H_m R_c} \right). \quad (8)$$

Strict substitution of Eq. (7) into Eq. (6) yields $T_m = T_\infty - 2\sigma_i v_s T_{m0} / (\Delta H_m R_c)$. Since $|T_\infty - T_{m0}| / T_{m0} \ll 1$ ($\sim 3 - 6\%$ for Ag, Cu), replacing $T_{m0} \rightarrow T_\infty$ in the curvature term introduces a second-order correction ($\lesssim 1\%$). The compact form (8) is therefore retained without affecting quantitative results. Because $\Delta v < 0$ in the usual solid $\rightarrow$ liquid volume-increase case, $T_\infty > T_{m0}$, which provides a simple and physically transparent explanation for the systematic overestimation of the “bulk” melting point often reported in molecular-dynamics studies carried out at (effectively) fixed volume. For example, fitting the Gibbs–Thomson relation to the silver nanoparticle data [23] yields an extrapolated bulk temperature $T_\infty = 1303 \pm 12$ K (cf. the experimental value $T_{m0} = 1234$ K), i.e. an apparent overheating of about 70 K that can be attributed to the volumetric contribution $p_c \Delta v$. From the fitted curvature parameter $K = 1.07 \pm 0.06$ K nm and $\sigma_i = K \Delta H_m / (2v_s)$, we estimate the solid-liquid interfacial energy $\sigma_i = 0.55 \pm 0.03$ N/m. These results therefore indicate that both the observed overheating and the high effective interfacial energy are consistent with the volume-change contribution ($\Delta v < 0$) inherent to the melting of silver. This effect is illustrated in Fig. 1.

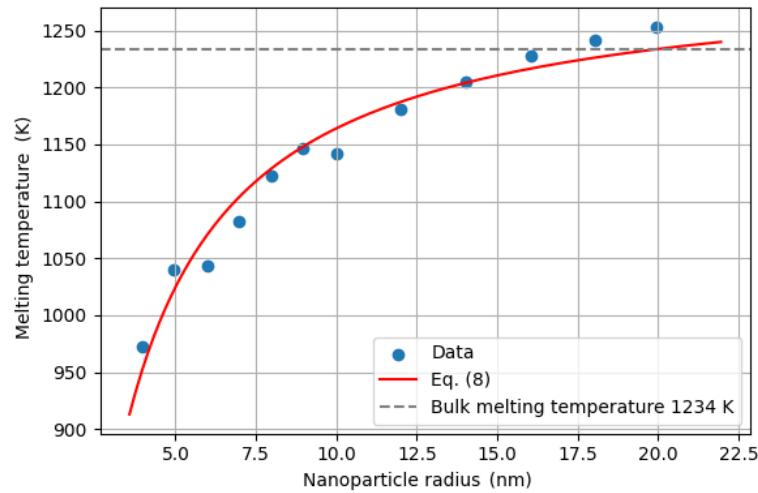


FIG. 1. Size dependence of the melting temperature of silver nanoparticles. Symbols – MD simulation data from Ref. [23]; solid line – fit to the Gibbs–Thomson relation, Eq. (8). The extrapolated bulk value $T_\infty = 1303$ K exceeds the experimental melting temperature $T_{m0} = 1234$ K, indicating an apparent overheating due to the negative volume change ($\Delta v < 0$) upon melting

For a core-shell particle, the total excess free energy associated with interfaces can be expressed as the sum of the inner and outer surface contributions

$$F_{\text{surf}} = 4\pi R^2 \sigma_s + 4\pi R_c^2 \sigma_i, \quad (9)$$

where σ_s is the liquid-vapor surface tension (σ_{LV}). To describe the overall thermodynamic behavior of the nanoparticle, it is convenient to introduce an effective surface tension σ that gives the same total excess energy as if the entire particle were homogeneous

$$F_{\text{surf}} = 4\pi R^2 \sigma. \quad (10)$$

Equating (9) and (10) yields

$$\sigma(R) = \sigma_s + \sigma_i \left(1 - \frac{\delta}{R} \right)^2 \approx \sigma_s + \sigma_i \left(1 - \frac{2\delta}{R} \right), \quad (11)$$

where the linear approximation is valid for thin shells, i.e., when $\delta \ll R$.

Equations (9)–(11) treat the liquid shell as a macroscopic phase with bulk-like properties and additive interfacial contributions. For ultrathin shells ($\delta \sim 1$ nm), one might in principle need to consider corrections such as the distinction between mechanical surface stress and thermodynamic surface energy [26, 27], or the difference between the Helmholtz

free energy and the grand thermodynamic potential that arises in open systems [28], as well as effects specific to confined liquid films [29]. However, in our model the system is closed (total number of particles $N = \text{const}$) and the Helmholtz free energy $F(T, V, N)$ is the natural thermodynamic potential. The surface tensions σ_s and σ_i are defined as the excess Helmholtz free energy per unit area of the corresponding interfaces at fixed T , V , N . Since our system is closed, no transition to the grand canonical ensemble or to the grand thermodynamic potential Ω is required. Moreover, our system consists of a solid core and a liquid shell in direct contact, with no thin film confined between two surfaces; therefore, disjoining pressure effects are not present. The additive approximation, Eq. (9), is adopted for all shell thicknesses considered in this work, while noting that for $\delta \sim 1$ nm additional molecular-scale effects may become relevant.

Although the model explicitly describes a two-phase solid-liquid system, it can equally be interpreted as an effective solid-vapor interface, with the liquid layer serving as the intrinsic transition region between the solid core and the vapor environment. In this interpretation, the effective surface tension defined by Eqs. (9)–(11) must be identified with the curvature-dependent surface tension in the Tolman formula [13–15]:

$$\sigma(R) \approx \sigma_\infty \left(1 - \frac{2\delta_T}{R} \right), \quad (12)$$

where σ_∞ is the surface tension of the corresponding flat interface and δ_T is the Tolman length. For a pure substance, the flat-limit interfacial energy of the effective solid-vapor boundary satisfies $\sigma_\infty = \sigma_{SV} = \sigma_{LV} + \sigma_{SL} = \sigma_s + \sigma_i$ by Young's equation with zero contact angle [29]. Matching the curvature-dependent term in Eq. (11) with the Tolman expansion (12) yields

$$\delta_T = \delta \frac{\sigma_i}{\sigma_s + \sigma_i} = \delta \frac{\sigma_{SL}}{\sigma_{SV}}, \quad (13)$$

which provides a direct physical meaning to the Tolman length: it is proportional to the equilibrium thickness of the premelted liquid layer, with a dimensionless factor determined by the relative interfacial tensions. According to thermodynamic models and experimental estimates for typical metals, the ratio σ_{SL}/σ_{SV} lies within 0.15 ± 0.03 [30]; consequently, the Tolman length is approximately one-seventh of the premelted layer thickness. Within this framework, δ_T is necessarily positive for the solid-core/liquid-shell morphology; a sign reversal would require an inverted structure (e.g., a liquid core surrounded by a solid shell), which lies outside the present scope.

Thus, the effective surface tension (11) provides a unified description that incorporates both geometric confinement and interfacial curvature effects across the full size range from bulk to nanoscale.

While the classical Gibbs phase rule ($F = C - P + 2$) predicts a unique melting temperature for bulk systems, its application to nanoparticles requires modification due to the significant contribution of curved interfaces. The generalized form $F = C - P + 3$, which includes curvature as an additional parameter, explains the continuous dependence $T_m(R_c)$ derived in our model. This extended thermodynamic framework naturally accommodates the size-induced melting point depression and validates the physical consistency of our core-shell approach.

3. Melting kinetics of core-shell nanoparticle

Building on the thermodynamic framework established above, we now turn to the kinetics of nanoparticle melting. In the core-shell model, melting is treated as a dynamic process in which the solid core gradually transforms into the surrounding liquid shell. The temporal evolution of the core radius $R_c(t)$ is governed by the rate of mass transfer across the core-shell interface, which depends on the local thermodynamic driving force, i.e., the difference in chemical potentials between the solid and liquid phases.

The heat balance at the core-shell interface can be expressed as

$$L_v \frac{dV_c}{dt} = -(Q - P), \quad (14)$$

where $V_c = 4\pi R_c^3/3$ is the core volume, $L_v = \Delta H_m/v_c$ is the volumetric latent heat of fusion (energy per unit volume), Q is the heat flux through the shell to the core, and P represents the power dissipated in the liquid shell due to convective mixing and viscous effects.

Equation for the heat flux is obtained from the steady-state heat conduction equation in a spherical shell. For radial symmetry, the temperature profile satisfies

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) = 0, \quad (15)$$

with boundary conditions $T(R_c) = T_m(R_c)$ and $T(R) = T_p$. The solution gives

$$T(r) = T_m + (T_p - T_m) \frac{1/R_c - 1/r}{1/R_c - 1/R}, \quad (16)$$

and the total heat flux through the shell is

$$Q = -4\pi r^2 \lambda_s \frac{dT}{dr}, \quad (17)$$

which yields

$$Q = 4\pi\lambda_s \frac{T_p - T_m(R_c)}{R_c^{-1} - R^{-1}} = 4\pi\lambda_s \Delta T(R_c) \frac{RR_c}{R - R_c}, \quad (18)$$

where $\Delta T(R_c) = T_p - T_m(R_c)$ is the overheating, T_p is the temperature of the external heat source, λ_s is the thermal conductivity of the liquid shell.

To complete the energy balance, we must account for dissipative losses in the liquid shell. Within the framework of nonequilibrium thermodynamics, the rate of energy dissipation P is defined as the product of a generalized flux and its conjugate thermodynamic force. For the moving core-shell interface, the generalized flux is identified with the interface velocity $J = |dR_c/dt|$, which characterizes the rate of the phase transformation. The conjugate thermodynamic force represents the total resistive force exerted by the liquid shell against the interface motion. Since the hydrodynamic flow and mixing effects induced by the boundary displacement occupy the entire liquid region, the total resistance scales proportionally with the volume of the shell. Thus, we model the generalized force as $F_{\text{diss}} = \gamma(R^3 - R_c^3)$, where γ is an effective coefficient characterizing the specific resistance per unit volume due to fluid motion and viscous losses. The product of this force and the flux yields the dissipative power:

$$P = \gamma(R^3 - R_c^3) \left| \frac{dR_c}{dt} \right|, \quad (19)$$

The use of the absolute value for the velocity ensures that the dissipation power remains positive definite ($P \geq 0$) regardless of the direction of the interface motion (melting or solidification), thereby satisfying the Second Law of Thermodynamics. This phenomenological relation captures the essential scaling of energy losses with both the active fluid volume and the kinetics of the phase boundary.

Combining (14), (18) and (19), and noting that $dV_c/dt = 4\pi R_c^2(dR_c/dt)$, we obtain the governing differential equation for the core radius evolution:

$$\frac{dR_c}{dt} = -\frac{R\lambda_s}{L_v} \frac{T_p - T_m(R_c)}{(R - R_c) \left[R_c + \frac{\gamma}{4\pi L_v R_c} (R^3 - R_c^3) \right]}. \quad (20)$$

The kinetic equation (20) describes the evolution of the solid core radius down to the nanoscale. However, the continuum thermodynamics framework underlying Eq. (8) breaks down when the core radius becomes comparable to the characteristic length $l_c = 2\sigma_i v_s / \Delta H_m$. For copper this gives $l_c \approx 0.15$ nm, i.e., of the order of the interatomic distance. This scale marks the natural lower limit of the present continuum model.

Formally, Eq. (8) predicts $T_m \rightarrow 0$ at $R_c = l_c$, and the dissipation term in Eq. (20) diverges as $R_c \rightarrow 0$. To ensure physical consistency, we integrate the kinetic equation from the initial radius $R_c(0) = R$ down to a final cutoff radius $R_c \sim l_c$. Below this size, the distinction between solid and liquid phases becomes ambiguous due to strong finite-size effects and thermal fluctuations. Since the volume of the remaining core scales as l_c^3 , the contribution of the final stage to the total melting time is negligible for $R \gg l_c$. Thus, the melting time is defined as the time required to reduce the core to the l_c . Under the assumptions $R \gg R_c, l_c$ and constant overheating ΔT , equation (20) can be simplified by approximating $(R - R_c) \approx R$ and $(R^3 - R_c^3) \approx R^3$. This yields:

$$t_m \approx \frac{L_v R^2}{2\lambda_s \Delta T} + \frac{\gamma R^3}{4\pi L_v} \log \left(\frac{R}{l_c} \right). \quad (21)$$

The first term represents the conventional diffusion-limited melting time, while the second term accounts for the additional delay due to viscous dissipation in the liquid shell. The cutoff at $R \sim l_c$ ensures the physical consistency of the solution by avoiding the divergence of the dissipation term at vanishing core radius.

Let us now proceed to the exact solution of equation (20) taking into account (8). We introduce the following notations

$$x = \frac{R_c}{R}, \quad \tau = \frac{\lambda_s T_{m0}}{L_v R^2} t, \quad x_0 = \frac{2\sigma_i v_s}{R \Delta H_m}, \quad \theta = \frac{T_p}{T_\infty} - 1, \quad \Gamma = \frac{\gamma R}{4\pi L_v}.$$

Taking this into account, we obtain an ordinary differential equation with separable variables

$$\frac{dx}{d\tau} = -\frac{x_0 + \theta x}{(1 - x)[x^2 + \Gamma(1 - x^3)]}, \quad x \in [1, x_0]. \quad (22)$$

The melting time τ_m for $\Gamma = 0$ is given by

$$\tau_m = \frac{x_0^3 - 1}{3\theta} - \frac{(x_0 + \theta)(x_0^2 - 1)}{2\theta^2} + \frac{x_0(x_0 + \theta)(x_0 - 1)}{\theta^3} + \frac{x_0^2(x_0 + \theta)}{\theta^4} \log \left[\frac{x_0 + \theta}{x_0(1 + \theta)} \right]. \quad (23)$$

Taking the limit $x_0 \rightarrow 0$ in equation (23) yields $\tau_m = 1/(6\theta)$.

For a copper nanoparticle [31–34] with $R = 10$ nm, $\Delta T = 10$ K, and material parameters $L_v = 2 \cdot 10^9$ J/m³, $\lambda_s = 150$ W/(m·K), $\sigma_i = 0.13$ N/m, $\Delta H_m = 13.2$ kJ/mol, and $T_\infty = 1356$ K, Eq. (23) yields $t_m \approx 4$ ps. This result is significantly smaller than the estimate from Eq. (21), confirming the extremely rapid melting in nanoscale particles and highlighting the critical importance of self-consistently accounting for the size-dependent melting temperature when

modeling ultrafast phase transitions. Accounting for energy dissipation in the liquid shell allows, through the adjustment of the parameter $\Gamma > 0$, for achieving complete agreement with molecular dynamics simulation results for the melting time (tens to hundreds of ps [31–34]).

An explicit solution $x = x(\tau)$ of eq. (22) is not available, making numerical methods the preferred approach. Numerical solution of eq. (22) is conveniently implemented in block-diagram simulation tools (e.g., Simulink, Scilab Xcos, SimInTech, or similar environments). The integral formulation allows building intuitive graphical models that visually represent the melting kinetics and enable efficient parameter variation studies. Eq. (22) can be rewritten in integral form as

$$x(\tau) = 1 - \int_0^\tau \frac{(x_0 + \theta x(s)) ds}{(1 - x(s)) [x^2(s) + \Gamma(1 - x^3(s))]} \quad (24)$$

The integration is performed until $x(\tau) = x_0$, indicating complete melting. The numerical implementation utilizes basic arithmetic blocks, a single integrator, and feedback based on $x(\tau)$. In addition, a PL software block is employed to stop the calculation when the core reaches complete melting.

Figure 2 presents the block diagram and the resulting numerical solution. The parameters for the calculation were chosen as representative values typical for metallic nanoparticles. The numerical integration was carried out using the RK45 method (Dormand–Prince adaptive step-size control). The temporal evolution of the core radius reveals three well-defined kinetic stages, each governed by distinct physical mechanisms. The process initiates with a rapid, nearly exponential decrease in radius, driven by the large initial core size and the applied overheating, which promote fast interface propagation. This initial transient gradually transitions into a quasi-linear regime, where the melting rate remains approximately constant as heat conduction through the growing liquid shell becomes rate-limiting. The final stage exhibits marked acceleration, characterized by a progressively increasing melting rate. This terminal acceleration arises directly from the size-dependent melting temperature depression described by the Gibbs–Thomson relation: as the core radius diminishes, the thermodynamic driving force $T_p - T_m(R_c)$ intensifies nonlinearly, creating an autocatalytic effect that rapidly completes the phase transformation.

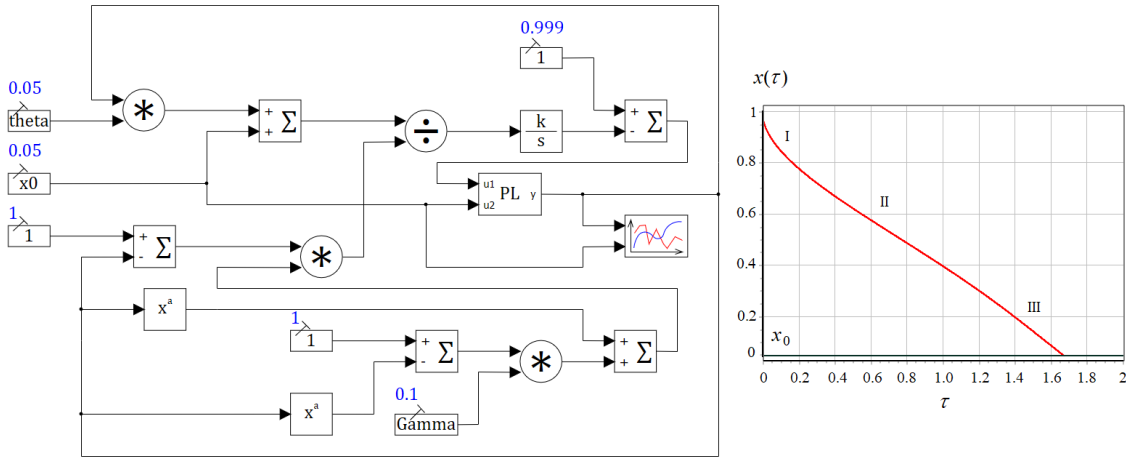


FIG. 2. Melting kinetics of a nanoparticle ($x_0 = 0.05$, $\theta = 0.05 > 0$, $\Gamma = 0.1$): block diagram of the SimInTech simulation model and temporal evolution of the normalized core radius showing distinct melting regimes

The influence of the size dependence of the melting temperature can be quantitatively assessed by comparing two melting kinetics: one assuming a constant melting temperature and the other accounting for the size-dependent decrease of T_m with decreasing core radius. This comparison is most clearly demonstrated within the $\Gamma = 0$ approximation. For the constant-temperature case, the evolution of the core radius is described by

$$\frac{dx}{d\tau} = -\frac{\theta}{x(1-x)}, \quad x \in [1, 0], \quad (25)$$

with the analytical solution

$$\tau = \frac{1 - 3x^2 + 2x^3}{6\theta}, \quad \tau_m = \frac{1}{6\theta}, \quad (26)$$

which corresponds to the classical description with a fixed driving force for phase transformation.

Figure 3 shows the calculated $x(\tau)$ curves for both cases, highlighting the fundamental differences in process dynamics. The model with a constant melting temperature (red dashed line) exhibits a smooth deceleration of the melting rate as the core radius decreases, and the linear melting stage is noticeably prolonged. In contrast, the model accounting for size

dependence (blue solid line) reveals a pronounced acceleration in the final stage, which is associated with the decrease in $T_m(R_c)$ during core melting. This acceleration significantly reduces the total melting time, underscoring the critical importance of considering surface curvature when modeling phase transitions in nanoparticles. A comparison of the calculations in Figs. 2 and 3 further reveals that viscous dissipation significantly retards the melting process, particularly during its final stage, thereby partially counteracting the curvature-induced acceleration.

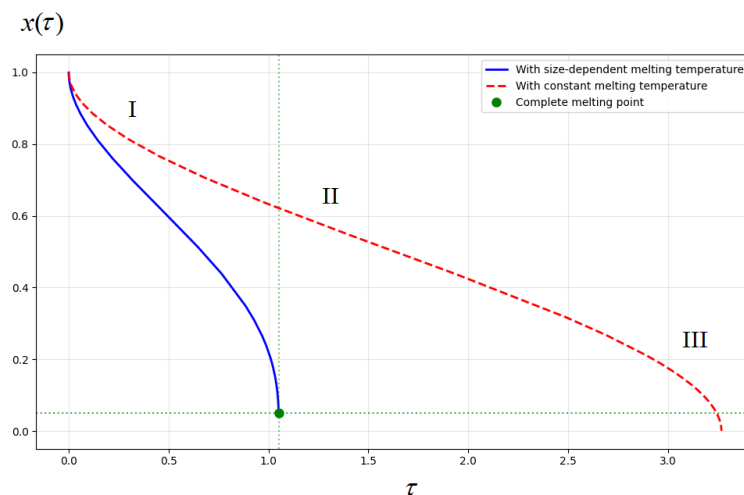


FIG. 3. Quantitative comparison of melting models: size-dependent versus constant melting temperature ($x_0 = 0.05$, $\theta = 0.05 > 0$, $\Gamma = 0$). The more than threefold reduction in melting time demonstrates the significant impact of curvature-induced melting point depression on nanoscale phase transformation kinetics

4. Conclusion

A consistent thermodynamic–kinetic framework for nanoparticle melting has been developed based on a two-phase core-shell model. The theory explicitly incorporates the finite thickness and physical properties of the quasi-liquid surface layer, providing a natural extension of classical thermodynamics to nanoscale systems. Analytical expressions for the size-dependent melting temperature and effective surface tension clarify the physical meaning of the Tolman correction, linking it directly to the structural thickness of the liquid shell.

The kinetic formulation demonstrates that melting proceeds through distinct stages governed by the interplay between interfacial curvature and heat conduction. The model predicts a pronounced size dependence of the melting time, with characteristic acceleration at the final stage due to curvature-enhanced overheating. These predictions quantitatively account for the fast melting observed in molecular dynamics simulations and pump-probe experiments.

The proposed framework unifies equilibrium and dynamic descriptions of phase transitions in nanoparticles, yielding compact analytical relations and transparent physical insight. It provides a basis for predicting the thermal stability of nanostructured materials and for guiding the design of thermally robust nanodevices.

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