Modelling the mechanosynthesis of gold nanoparticles using a structural-phase-field-crystal model with ballistic driving

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Abstract

Mechanochemistry is becoming an established method for the sustainable, solid-phase synthesis of scores of materials and molecules, ranging from active pharmaceutical ingredients to materials for cleantech. Yet we are still lacking a good model to rationalize experimental observations and develop a mechanistic understanding of
the factors at play during mechanically assisted, solid-phase synthesis. We propose herein a structural-phase-field-crystal (XPFC) model with a ballistic driving force to describe such a process, with the specific example of the growth of gold nanoparticles in a two component mixture. The reaction path is described in the context of free energy landscape of the model, and dynamical simulations are performed based on phenomenological model parameters closely corresponding to the experimental conditions, so as to draw conclusions on nanoparticle growth dynamics. It is shown that the ballistic term lowers the activation energy barrier of reaction, enabling the reaction in a temperature regime compatible with experimental observations. The model also explains the mechanism of precipitated grain size reduction that is consistent with experimental observations. Our simulation results afford novel mechanistic insights into mechanosynthesis with far-reaching implications beyond nanomaterials.

**Keywords**

Mechanosynthesis, Nanoparticles, Phase field method, Structural-phase-field-crystal model, Reaction path

1 **Introduction**

Mechanochemistry is defined as the field of chemical transformations initiated or sustained by mechanical force, the kind of which is experienced during mechanical milling or grinding or extrusion.\(^1\) Although it is an ancient method,\(^2\) compared to conventional solution-based chemical synthesis, mechanosynthesis has seen a resurgence recently in a variety of applications including towards the synthesis of metal-organic frameworks,\(^3,4\) metalloids,\(^5,6\) perovskites,\(^7,8\) and nanoparticles (NP).\(^9,10\) As reactions in mechanoochemistry occur in the solid phase, reagent solubilization is not necessary. This prevents the use of large amounts of solvents, while the alternative energy delivery is also associated with energy input reduction,
two aspects making this method attractive from a sustainability point of view.\textsuperscript{11-12} An additional benefit resides in the ability to scale mechanochemical methods,\textsuperscript{13} often with more ease than when solvents are involved, and the possibility to perform reactions impossible to perform otherwise.\textsuperscript{14-17} In the context of NP synthesis, the use of mechanochemistry was first reported by Geckeler and coworkers who demonstrated the controlled growth of Au NP (6-28 nm) in the solid phase.\textsuperscript{18} Many examples were developed since,\textsuperscript{16,19} including from our group where we demonstrated that ultra-small Au NPs could be formed in the presence of long chain amines with excellent size control and a dependence of the NP size over ligand chain length.\textsuperscript{9} Since then, other metal-based and binary systems were reported along the same principles.\textsuperscript{12,20,21} Recently, efforts were made by the group of Camargo and Emmerling to follow the formation of such Au NPs in situ using X-ray absorption and diffraction spectroscopies, which shed light into the kinetics of Au reduction accompanying NP growth.\textsuperscript{22,23}

The homogeneous seeding and growth of metal nanoparticle in solution has long been rationalized theoretically by the model proposed by LaMer and Dinegar in 1950,\textsuperscript{24} and used extensively during the past 2 decades of intense NP synthesis exploration.\textsuperscript{25} Yet the concepts developed therein are hardly applicable to solid phase syntheses as the notions of compositions and supersaturations, central to NPs growth, can not be translated directly from the liquid phase. Additionally, while reactions in solution rely solely on the use of thermal energy, in the solid phase, mechanical energy needs to be accounted for as well. The mechanism of mechanochemical reactions is often discussed from a microscopic point of view in the context of two widely accepted views. The first, “hot spot” model, posits that there are short-lived microscopic areas of very high temperature, which can be induced by mechanical force.\textsuperscript{26,27} The second, so-called “magma-plasma” model, asserts that local dislocations and plastic deformation, bond-rupture and crystallographic defects, are related to the mechanical force.\textsuperscript{28-30} These models can be used to offer qualitative mechanistic explanations of different reactions and both rely on the local microscopic environment being altered dynamically and/or structurally.\textsuperscript{31,32} However, these models describe reactions in which the mechanical
forces at play are much larger than the ones considered in the examples described above. In particular, in the synthesis of Au NPs, notions that high temperatures the kind of which would degrade organic ligands or even cause gold melting, are incompatible with experimental evidence. Furthermore, there have been no models to date that describe the spatio-temporal properties of nucleation and nano-crystalline precipitate evolution in mechanochemical, solid phase, reactions.

The phase field crystal (PFC)\textsuperscript{33} method is a field theoretic approach whose form is motivated from classical density functional theory (CDFT),\textsuperscript{34} but which typically replaces microscopic parameters arising from the original CDFT with effective parameters that make spatio-temporal microstructure simulations tractable on diffusional times scales. The starting point of a PFC model is a free energy of a system expressed in terms of a local order parameter field. The free energy captures the local thermodynamic driving forces that characterize reactions between possible phases in the system, as well the energy cost associated with nanoscale interfaces between phases. Microstructure dynamics is described by the evolution of the order parameter field, driven by the dissipative dynamical minimization of said free energy, subject to mass conservation. Greenwood\textit{ et al.}\textsuperscript{35} extend the original PFC method to the so-called “structural” phase field crystal (XPFC)\textsuperscript{35} method, where the “X” emphasizes the use of specific density-density correlation functions in the free energy to control the crystal symmetries that emerge during crystallization. PFC and XPFC methods has been successfully used in recent years in the description of solidification,\textsuperscript{36,37} structural phase transitions in pure and alloy materials,\textsuperscript{38,39} clustering and precipitation.\textsuperscript{40,41} These phase field crystal models are based purely on thermal energy input to drive reactions. Recently, Ofori-Opoku\textit{ et al.}\textsuperscript{42} incorporated into an XPFC model a procedure to treat external neutron bombardment by including a ballistic energy term developed by Enrique and Bellon\textsuperscript{43,44} and used it to study microstructural stability in irradiation-driven nanocrystalline systems.\textsuperscript{42}

Herein we propose to apply a similar XPFC framework to that of Ref.\textsuperscript{42} to gain mechanistic insight into mechanochemical NP synthesis. In doing so, we considered two necessary
modifications arising from the specific nature of NP mechanosynthesis: the form of driving force (neutron irradiation vs mechanical input), and the reaction environment. In particular, the ballistic term was altered to mimic the mechanical milling taking place while growing AuNPs by reduction of HAuCl$_4$ in a stainless steel ball milling apparatus. Also, the XPFC model was adapted to account for the effect of ligand type (mass and length) as the NP grow in the presence of excess long-chain amine ligands. The model was used to elucidate the mechanism of AuNPs precipitation and growth in the solid phase. This was made possible by the newly developed XPFC ballistic term, which provided for the first time a framework for tuning the milling frequency and the ligand type. An analysis of the model’s thermodynamics helped elucidate how mechanical energy delivery affects the free energy of the reaction, and thus how a NP precipitation reaction is feasible under normal room-temperature experimental conditions. Moreover, spatio-temporal microstructure evolution using the XPFC model made it possible to simulate the nucleation and growth of nanoparticles in the solid phase and to analyze their size. Our results reproduced experimental trends, and helped develop a deeper understanding of potential mechanisms for the growth of nanoparticles in the solid phase.

2 XPFC Model for Nanoparticle Mechanosynthesis

In our previous work, we have shown that Au NPs could be obtained with excellent size control by reacting with an Au precursor, hydrochloroauric acid, with long chain amines, in the solid phase, by milling them in a stainless steel reactor. This reaction can be viewed as a two step process with first the reduction of Au(III) species into atomic Au(0), and second the assembly of atomic Au(0) into nanoparticles (Fig. 1). We elected to model the second step, namely the formation of Au NPs as a precipitation phase transition, described in a two component (Au(0)-ligands) monotectic system. This modelled reaction is denoted $l_1 \rightarrow \alpha + l_2$, where $l_1$ (e.g. Au(0)-ligands mixture before reaction) and $l_2$ (e.g. Au(0)-ligands...
mixture after reaction) are two disordered phases, and \( \alpha \) (e.g. Au NPs) is the precipitated solid phase. This describes solid precipitation from disordered phase \( l_1 \) to a solute-poor crystalline phase \( \alpha \) and a solute-rich disordered phase \( l_2 \). In the developed XPFC model, we used \( c \) as the local composition at a given point in space, where \( c = 0 \) at locations solely composed of ligands, and \( c = 1 \) in regions of pure Au phase. The parameters of our model free energy are chosen such that the crystalline phase of Au forms at composition \( c = 1 \). As purely atomistic molecular treatment could not be handled in the XPFC formalism, the reduction of Au(III) to Au(0) was not considered, so as to focus on the role of Au(0) in Au NP formation. The model is studied in 2D in order to enable faster computer simulation efficiency but without losing the model’s ability in elucidating the salient mechanisms of Au NP formation. We chose the <111> direction to represent NP crystallography, leading to hexagonal closed packed atomic packing of Au crystals in 2D.
The energy functional for the XPFC model for nanoparticle mechanosynthesis (XPFC-NanoMecha) was established using the monotectic mixture XPFC model developed by Smith and Provatas\textsuperscript{41} as a starting point. The latter model though only considers thermal energy input, so we proceeded with adding another term called “ballistic term”, following the approach of Enrique and Bellon\textsuperscript{43,44}. The resulting energy functional is provided here:

\[
\frac{\Delta F [n(\vec{x}), c(\vec{x})]}{k_B T \rho_0} = \left( \frac{\Delta F_{id} [n(\vec{x})]}{k_B T \rho_0} + \frac{\Delta F_{mix} [n(\vec{x}), c(\vec{x})]}{k_B T \rho_0} + \frac{\Delta F_{ex} [n(\vec{x}), c(\vec{x})]}{k_B T \rho_0} \right) + \frac{\Delta F_{ballistic} [n(\vec{x}), c(\vec{x})]}{k_B T \rho_0}
\]

(1)

where \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, and \( \rho_0 \) is the total system reference density. The free energy functional has been broken into the ideal \( \Delta F_{id} [n(\vec{x})] \),
mixing $\Delta F_{\text{mix}}[n(\vec{x}), c(\vec{x})]$, excess $\Delta F_{\text{ex}}[n(\vec{x}), c(\vec{x})]$ and ballistic $\Delta F_{\text{ballistic}}[n(\vec{x}), c(\vec{x})]$ parts, respectively. The function $n(\vec{x})$ is a normalized term for the density, defined as $n(\vec{x}) = (\rho(\vec{x}) - \rho_0) / \rho_0$ where $\vec{x}$ denotes the position, $\rho(\vec{x})$ is the local mass density, and $\rho_0$ is the reference mass density. The function $c(\vec{x})$ is the local composition, as defined above, which varies with respect to position $\vec{x}$. By adopting a series of reasonable approximations (which are described in the supplementary information) for each term, the free energy form is developed in terms of $\{n(\vec{x}), c(\vec{x})\}$. To simplify mathematical expressions, a dimensionless free energy is often introduced in PFC models, given by

$$\mathcal{E} = \frac{\Delta F}{k_B T \rho_0 V}$$

(2)

### 2.1 Incorporating ballistic energy in the XPFC model

The ballistic term $\Delta F_{\text{ballistic}}$ accounts for the energy dissipated into the system by the external mechanical force applied during a mechanochemical reaction, which is expressed as $\Delta F_{\text{ballistic}} = \gamma \mathcal{G}$, where $\mathcal{G}$ accounts for mechanically induced interactions between parts of the system, and $\gamma = \Gamma / M$ where $\Gamma$ is the scaled forcing frequency on system particles while $M$ is the particle mobility. It is worth mentioning that $\gamma$ is a phenomenological parameter in this model, as microscopic information on the energy input associated with each ball hitting event is not easy available. Adapting the work of Enrique and Bellon\textsuperscript{43}, the specific form of $\mathcal{G}$ proposed in this work is

$$\mathcal{G} = \frac{\Pi(c(\vec{x}))}{2} \int d\vec{x} \ d\vec{x}^\prime \ n(\vec{x}) \ g(\vec{x} - \vec{x}^\prime) \ n(\vec{x}^\prime),$$

(3)

where $\Pi(c(\vec{x}))$ modulates the mechanical energy dissipated into the system at a point $\vec{x}$ (represented by the integral in Eq. (3)) as a function of the local composition $c(\vec{x})$. The kernel
for the ballistic exchange $g$ satisfies a Poisson’s equation, i.e.,

$$\nabla^2 g(\vec{x} - \vec{x}') = - [\delta(\vec{x} - \vec{x}') - w_R(\vec{x} - \vec{x}')], \quad (4)$$

where the source delta function $\delta(\vec{x} - \vec{x}')$ accounts for short-range ballistic interactions between particles, while the weight function $w_R(\vec{x} - \vec{x}')$ accounts for interactions between points in the system dissipated over longer spatio-temporal scales, the form of which depends on the energy dissipation length $R$. Further details on $w_R(x)$ are available in supplementary information.

2.2 The interpolation function $\Pi(c)$

The interpolation function $\Pi(c)$ allows us to modulate the amount of ballistic energy input into the system as a function of the local distribution of particles, which in turn is represented in the PFC model by the local composition $c(\vec{x})$. Specifically, the energy absorbed by a ligand-rich volume element is different from that absorbed by a gold-rich volume. This can be quantified by considering the an elastic collision analogy wherein a stationary ball with a small mass $m$ is hit by a heavy ball of $M$ ($m/M \ll 1$) moving at speed $\vec{u}$. After the collision, the small ball will move at a velocity of $\vec{v} = \left[2m/(M + m)\right] \vec{u}$ and a kinetic energy

$$E_m = \frac{2m}{1 + m/M} |\vec{u}|^2 \approx 2m|\vec{u}|^2 \quad (5)$$

In mechanosynthesis, the milling ball (ball milling process) or the pestle (grinding process) can be regarded as the “heavy ball”, while the particles can be regarded as instances of the “light ball”. Thus, it is reasonable to approximate the energy input locally into a small volume of the system as being proportional to the integrated mass around the small local
volume, modulated by the type of mass via the composition \( c \) according to

\[
\Pi(c) = 1 - \left( 1 - \frac{m_{B(\text{gold})}}{m_{A(\text{ligand})}} \right) c
\]  \hspace{1cm} (6)

In Eq. (6), \( c \to 0 \) implies that a local volume centred at \( \vec{x} \) is occupied mostly by ligand \( (A) \) molecules, and the total mechanical energy represented by the integral in Eq. (3) is transferred to ligand molecules at position \( \vec{x} \). On the other hand, the limit \( c \to 1 \) implies that the local volume is occupied mostly by gold \( (B) \) atoms, and the fraction \( m_{B(\text{gold})}/m_{A(\text{ligand})} \) of the total mechanical energy is transferred to gold atoms at \( \vec{x} \). This behaviour of \( \Pi(c) \) guarantees that the energy gained is proportional to both the mass of the local area and the type of atomic species.

### 2.3 Full form of XPFC model

Combining all the mechanisms discussed above, the complete free energy functional of the structural-phase-field-crystal (XPFC) model describing reactions in a monotectic alloy with ballistic energy input is given by

\[
\frac{\Delta F[n,c]}{k_B T \rho_0} = \int d\vec{x} \left\{ \frac{n(\vec{x})^2}{2} - \frac{\eta n(\vec{x})^3}{6} + \frac{\chi n(\vec{x})^4}{12} + \frac{\omega \epsilon(T) \cdot (c - c_0)^2}{2} + \frac{W_c}{2} |\nabla c|^2 \\
- \frac{1}{2} n(\vec{x}) \int d\vec{x}' \left[ C_{\text{eff}} (\vec{x} - \vec{x}') - \gamma \Pi(c) g (\vec{x} - \vec{x}') \right] n(\vec{x}') \\
+ \omega (n(\vec{x}) + 1) \cdot \left[ c \ln \left( \frac{c}{c_0} \right) + (1 - c) \ln \left( \frac{1 - c}{1 - c_0} \right) \right] \right\}  \hspace{1cm} (7)
\]

where \( \eta, \chi, \omega \) are constants that set the scale of the free energy in the bulk phases, \( W_c \) sets the scale of compositional fluctuations, \( \epsilon(T) \) controls the enthalpy of mixing as a function of temperature \( T \), \( C_{\text{eff}}(\vec{x} - \vec{x}') \) controls the emergence of crystal ordering from a disordered phase and \( c_0 \) is a reference concentration. Further details on these parameters is found in the supplemental information.
3 Model Outputs

3.1 Kinetics and thermodynamics outputs

From the expression of the free energy function in Eq. (7), we could extract expressions for the bulk free energy on the various phases, from which we could draw conclusions about the kinetics of NP precipitation. The derivation of bulk the free energies of bulk phases follows from a simple type of coarse graining procedure developed by us in previous work and described in the supplementary information. The explicit form of the bulk free energy of the disordered phase (denoted $\mathcal{E}_d$) and the ordered hexagonal phase (denoted $\mathcal{E}_o$) become, respectively,

\[ \mathcal{E}_d = \left(1 - \hat{C}_{eff}(0) + \gamma \hat{g}(0) \Pi(c)\right) \frac{n_0^2}{2} - \eta \frac{n_0^3}{6} + \chi \frac{n_0^4}{12} + \omega \Delta f_{mix}(n_0, c) \]  
\[ \mathcal{E}_o = \mathcal{E}_d + 3 \left(1 - \eta n_0 + \chi n_0^2 - \hat{C}_{eff}(k_a) + \gamma \hat{g}(k_a) \Pi(c)\right) \phi_0^2 - 2 \left(\eta - 2\chi n_0\right) \phi_0^3 + \frac{15}{2} \chi \phi_0^4, \]  

where here $n_0$ is the average density of a bulk phase and $c$ its average concentration, while $\Delta f_{mix}$ is a shorthand notation for the expression

\[ \Delta f_{mix} := \left[n(\bar{x}) + 1\right] \cdot \left[ c \ln \left(\frac{c}{c_0}\right) + (1 - c) \ln \left(\frac{1 - c}{1 - c_0}\right) \right] + \frac{1}{2} \epsilon (c - c_0)^2 \]  

and $\hat{C}_{eff}(k_a)$ is the Fourier transform of the effective density-density correlation function evaluated at the magnitude of reciprocal lattice vector of the lattice peak, given by $k_a = \frac{2\pi}{\xi}$. Also, $\hat{g}(k)$ is the Fourier transform of external energy interaction kernel defined above.

Phase equilibrium between $\mathcal{E}_o$ (gold) and $\mathcal{E}_d$ (gold-ligand mixture) is found from Eq. (8) and Eq. (9) following well known minimization procedures. Namely, the free energy $\mathcal{E}_o$ is minimized with respect to $\phi_0$, and the solution is substituted back into Eq. (9) yielding a free energy $\mathcal{E}_o$ that depends on the average density $n_0$ and composition $c$. Then, both $\mathcal{E}_d$ and $\mathcal{E}_o$ are compared in these variables using a common plane construction. In this work, we assumed that the average density of bulk $\mathcal{E}_0$ and $\mathcal{E}_d$ are equal, thus reducing the common
plane construction to the usual \textit{common tangent construction} in the variable \(c\).

Through their parameters, \(E_o\) and \(E_d\) (and hence the equilibrium phase properties) depend on temperature \(T\), the mass ratio between the two components, the reduced forcing frequency \(\gamma\), and force dissipation length \(R\), all of which must be approximated. Here, we adopt the same parameters for the base XPFC free energy as the monotectic system studied by Smith and Provatas in Ref. 41. Specifically, we set \(\eta = 2.0\), \(\chi = 1.0\), \(\omega = 0.3\), \(\epsilon_0 = 30\), \(T_c = 0.15\), and \(c_0 = 0.5\). The temperature is set to \(T = 0.06\). This treatment of the model thus allows us to draw the energy landscape of the system and calculate kinetic and thermodynamic parameters for the reaction \(l_1 \rightarrow \alpha + l_2\).

3.2 Microstructural outputs

It addition to thermodynamic analysis, the XPFC model also allowed us to track microstructure evolution during mechanochemical synthesis. In particular, we followed the dynamical aspects of the precipitation of Au NPs from a ligand-gold monotectic system, driven by external mechanical energy (reaction \(l_1 \rightarrow \alpha + l_2\)).

The dynamical evolution of the \(n(\vec{x},t)\) and \(c(\vec{x},t)\) fields in the structural-phase-field-crystal model is assumed to obey conserved Langevin equations for each field, which is described in detail in supplementary information.

4 Implications of the Model

The model developed for this work was used to understand two key aspects of the mechanoynthesis of Au NPs with long chain amines. The first was to test the accuracy of the ballistic term in accounting for the role of mechanic force in this reaction. The second goal was to investigate and rationalize the model’s implications on how the amine chain length controls the size of the final NPs in the reaction.
4.1 Role of ballistic term

4.1.1 How the ballistic term helps nanoparticle precipitation kinetically and thermodynamically

The role of externally induced mechanical forces on the free energy of the system was studied through Eq. 8 and Eq. 9. When there is no induced mechanical force \( \gamma = 0 \), the free energy of each phase reduces to that described by usual thermal equilibrium conditions. When there is induced mechanical force \( (\gamma > 0) \), free energy landscape of each phase is altered. Importantly, both the \( \gamma \hat{g}(0)\Pi(c) \) term and the temperature dependent correlation term \( \hat{C}_{eff}(0) \) are modulated by the square of the average density \( n_0^2 \) in the disordered phase (Eq. 8), while \( \gamma \hat{g}(k_a)\Pi(c) \) and \( \hat{C}_{eff}(k_a) \) are coupled to the square of the order parameter amplitude \( \phi_0^2 \) in the ordered phase (Eq. 9). Thus, with \( \gamma > 0 \), the symmetry breaking term \( \gamma \hat{g}(0)\Pi(c) \) increases the free energy of the disordered phase (initial stage) relative to its value with \( \gamma = 0 \) in proportion to \( \Pi(c) \). Meanwhile, in the ordered phase (formed Au NPs), the term \( \gamma \hat{g}(k_a)\Pi(c) \) decreases the free energy relative to its \( \gamma = 0 \) value in proportion to \( \Pi(c) \).

Fig. (2) shows the free energy profile of the system as a function of \( c \) and thus as it transitions from initial disordered stage to final Au NPs stage, with \( \gamma = 0 \) and \( \gamma = 0.1 \).
Figure 2: (Colour online) Dimensionless free energy landscape in $\mathcal{E} \times c \times \gamma$ space of a Au(0) - octadecylamine (C18) system. The blue curves correspond to $\gamma = 0$ and the green curves correspond to $\gamma = 0.1$. The free energy landscapes for both $\gamma$ have been subtracted by their maximum value, aligning them all at $\mathcal{E} = 0$. The black vertical dash line at $c = 0.167$ marks the reaction starting point. The difference in the green and blue vertical lines indicates $\Delta G_a$, the energy change required (relative to the maximum energy) to activate the precipitation of the ordered phase from the disordered phase.

Fig. (2) confirms visually the trends explained above. Specifically, the reaction is favoured, both kinetically and thermodynamically by the ballistic energy input ($\gamma > 0$). The time to nucleation $t_n$ can be evaluated by estimating the activation barrier $\Delta G_a$ according to

$$t_n = t_r e^{-\frac{\Delta G_a}{k_B T}}$$

(11)

where $t_r$ is a reference time which estimates the time that an atom statistically requires to hop to from the disordered phase ($l_2$) to the solid phase ($\alpha$).

Without the ballistic term, the activation barrier is $\Delta G_a = 0.0354$, while with $\gamma = 0.1$,
the activation barrier reduces to $\Delta G_a = 0.0250$, which represents a percentage reduction of $f = 29.28\%$ of the nucleation barrier compared to its value in the absence of ballistic energy. Denoting the time to nucleation with the ballistic term as $t_b$ and that without the ballistic term as $t_0$, $t_0 = \left(\frac{n}{n_b}\right)^f t_b$. Considering a typical reference time $t_r = 1$ ns and a typical mechanosynthesis reaction of $t_b = 90$ min (as described in Ref. [9]) predicts an acceleration of the reaction rate by a factor of 5346, which would take 334 days for the reaction to occur without mechanical activation. It is noteworthy that the value of $\gamma$ was chosen arbitrarily here as it is a phenomenological parameter. However, the larger $\gamma$, the more $\Delta G_a$ is reduced. This analysis thus suggests that a plausible mechanism for nanoparticle mechanosynthesis is that ballistic energy reduces the barrier to precipitation. It is also importantly to note that while these shifts in relative stability of the ordered phase relative to the disordered phase mimics an effective “temperature quench”, the induced mechanical force cannot be regarded as a higher “effective” temperature.

4.1.2 Impact of the ballistic term on nanoparticle nucleation and growth

The precipitation process was simulated with the ballistic energy term off or on, to simulate the reaction without or with the mechanical force, respectively. This group of dynamical simulations consists of three samples, where the ligand was chosen to be heptadecylamine (C17). The Au(0) : ligand ratios are all set to be 1 : 5 as in the reference experimental work[9]. The initial state of the system in each case was modelled by uniform spatial distributions for $n$ and $c$, which emulates a randomly fluctuating disordered starting phase of the system. In the Sample 1 simulation, the ballistic term was deactivated using $\gamma = 0$ and $R = 0$, and sets the noise according to Eq. [28] to simulate the reaction without mechanical force. The Sample 2 simulation is the same in every way to that in Sample 1, except the ballistic term is activated using $\gamma = 0.1$ and $R = 9.7a$. A third simulation was also performed (called Sample 3 simulation), in which the ballistic term was initially the same as that of Sample 2 simulation but was deactivated after 430 numerical time steps (model time = 66).
This was done to simulate the role of partially injecting external energy for a brief time, after which it is turned off during the remainder of an ageing process. Ageing has not been reported for Au NPs, but has been shown to be an important step in the mechanosynthesis of Bi\textsubscript{2}S\textsubscript{3} \cite{10} and Ni\textsubscript{2}P NPs \cite{12}. All microstructure simulations were performed with a numerical resolution of \( \Delta x = 0.125 \), and the numerical time steps were set to \( \Delta t = 0.00015 \). Simulations were performed using a semi-implicit Fourier method described in Ref. 45 on a uniform two-dimensional numerical mesh of 1000 \( \times \) 1000 two-dimensional grid points. The average system density was set to \( n_0 = 0.05 \), while the mobility of the density and composition fields were set to \( M_n = 1.0 \), \( M_c = 1.0 \) for simplicity. The temperature was fixed at \( T = 0.06 \).

Fig. 3 compares data from the three aforementioned simulation samples of microstructure evolution. Comparing Sample 1 with Sample 2, it is seen that no Au NPs are precipitated for a considerable period of time (Sample 1), in contrast to the rapid precipitation that occurs when the ballistic term is activated (Sample 2). An interpretation for this is that even in a well-mixed state, the precipitation will not occur because the activation energy barrier is too high in this case. As shown in the analysis of Fig. 2, turning on the ballistic energy serves to lower the activation energy barrier, which facilitates the precipitation of Au nano-particles through normal thermal fluctuations. Comparison of Sample 2 with Sample 3 was found to give different morphology for the final precipitated products. Since in Sample 3 simulations the ballistic term is deactivated at time step = 430 (time = 66), no new nuclei can form after that (and some nuclei also dissolve into the disordered matrix), leaving the nuclei remaining to continue to grow, thus attaining larger NPs sizes compared to NPs in Sample 2 where new nuclei continue to form in the matrix past = 430 time steps.
Fig. 3 shows the result of the microstructure simulations in the Sample 2 case. In the early stages of NP synthesis (figures (a) to (c)), Au is precipitated from the matrix, forming amorphous clusters and crystal seeds. However, not all of the initial clusters evolve into fully developed Au particles, as shown in frames (d) to (e). Some of these small initial clusters (and some small nuclei) are dissolved back into the disordered phase, or swallowed by other stably growing nuclei. This observation suggests the Ostwald ripening process at play, however to verify this, more statistics and larger simulation sizes are required. The final stage (f) comprises very stable Au NPs, which will continue to grow and amalgamate with each other to form large Au plates over the time scale of the simulations.
Figure 4: (Colour online) Simulated mechanosynthesis of AuNPs from a disordered heptadecylamine (C17) – Au(0) matrix, with the ballistic term continuously active (γ = 0.1 and R = 9.7a). The black / white pixels represent the dimensionless density $n$ and the colourbar readings represent the composition of Au. (a) The initial time = 0 configuration is randomly distributed with average reduced density $n_{time=0} = 0.05$ and composition $c_{time=0} = 0.167$. (b-c) show the nucleation process. (d-f) show the post-nucleation growth of NP precipitates.

Fig. 5 shows the result of the microstructure simulations in the Sample 3 case, where the mechanical forces is deactivated after 430 time steps (model time = 66). In frames (a) to (c) the initial stages of this simulation are the same as in Fig. 4. In frames (d) to (f), the mechanical force is inactive and ageing occurs. In this stage, no new nuclei are created (and some of the initial nuclei also dissolve), resulting in a smaller number of nuclei growing into larger (coarser) nano-particles that in the data of Fig. 4.
Figure 5: (Colour online) Simulated mechanosynthesis of AuNPs from a disordered heptadecylamine (C17) – Au(0) matrix, with the ballistic term active ($\gamma = 0.1$ and $R = 9.7a$) for the first 430 time steps (time = 66), and inactive for later times. The black/white pixels represent the dimensionless density $n$ and the colourbar readings represent the composition of Au. (a-c) The initial process is the same as that Fig. 4. (d-f) After 430 time steps (time = 66), the ballistic term is turned off to simulate the ageing process. Here, the rate of nucleation is nearly zero, and the initial population of nuclei undergo go growth and coarsening, expanding their size and decreasing in number compared to frames (d-f) in Fig. 4.

4.2 Effect of the amine ligand size

In the reference mechanosynthesis experiments of Au NPs, the long-chain ligand was varied along the series pentadecylamine (C15), hexadecylamine (C16), heptadecylamine (C17), and octadecylamine (C18). The resulting Au NPs featured an average diameter decreasing as a function of an increased chain length. In this series, the ligands vary both in length and mass. In our model, the size of the ligand is effectively described by the ligand mass variable $m_{\text{ligand}}$ and dissipation length variable $R$. Since we use an isotropic two-point correlation function to model inter-particle interactions in the XPFC model, we cannot presently capture anisotropic atomic-scale structures in the mass density of amines. Nevertheless, we can investigate the
role of chain length through the dependence of \( \{m_{\text{ligand}}, R\} \) in the model, which effectively captures the length scale of the ligand molecules.

4.2.1 How the ligand size affects the kinetics and thermodynamics of the reaction

Fig. 6 demonstrates the role of ligand size on the dimensionless free energy landscapes of our XPFC model, where the parameters \( \{m_{\text{ligand}}, R\} \) are set accordingly for each ligand size.

![Figure 6: (Colour online) Dimensionless free energy landscape in \( \mathcal{E} \times c \times \text{ligand-type} \) space.](image)

- (Red) pentadecylamine (C15) with \( m_{\text{ligand}} = 227.43 \text{g/mol}, R = 9.1a \), (orange) hexadecylamine (C16) with \( m_{\text{ligand}} = 241.46 \text{g/mol}, R = 9.4a \), (purple) heptadecylamine (C17) with \( m_{\text{ligand}} = 255.50 \text{g/mol}, R = 9.7a \), and (green) octadecylamine (C18) with \( m_{\text{ligand}} = 269.50 \text{g/mol}, R = 10.0a \). The free energy landscapes have been subtracted from their maximum value, aligning them all at \( \mathcal{E} = 0 \). Inset (a) shows a zoom-in of the region \( c = 0.1 \sim 0.2 \). The black vertical dash line at \( c = 0.167 \) marks the reaction starting point. Inset (b) shows the region of \( c = 0.9 \sim 1.0 \). The shift in each curve of the disordered phase relative to the maximum defines the dimensionless activation energy barrier \( \Delta G_a \) for precipitation of the ordered phase.
Fig. 6 shows that as the reactant ligand becomes longer and heavier, the free energy of the ordered phase becomes lower compared to free energy landscape’s maximum, see inset Fig. 6 (b); another effect is the activation energy barrier becomes lower as ligand weight increases, as shown in inset Fig. 6 (a). For pentadecylamine (C15) the activation barrier is $\Delta G_a = 0.0309$, while for octadecylamine (C18) it is $\Delta G_a = 0.0250$, which is a reduction of of 19.11%. Our model thus predicts a decreasing of the activation barrier $\Delta G_a$ with increasing length and mass of the ligand, which leads to a decrease in the nucleation barrier for precipitating the ordered (Au(0)) phase from the disordered ligand-rich phase. As will be shown in in section 4.2.2, since the total number of gold atoms is constant, a consequence of this trend is that the reactions with heavier ligand produce more, but smaller crystals, a trend which is consistent with the experimental observations listed in Table. 1 of Ref. 9.

4.2.2 Effect of ligand size on nanoparticle nucleation and growth morphology

A second group of simulations was conducted which consisted of four samples with different ligand types and wherein the ballistic term is active with $\gamma = 0.1$, in order to simulate the reactions using HAuCl$_4$, and different ligands from pentadecylamine (C15) to octadecylamine (C18). The Au$^{(0)}$: ligand ratio was set to be 1 : 5 as in Ref. 9. All microstructure simulations were performed with a numerical resolution of $\Delta x = 0.125$, and the numerical time steps were set to $\Delta t = 0.00225$, $\Delta t = 0.001$, $\Delta t = 0.00015$, and $\Delta t = 0.000015$ for pentadecylamine (C15), hexadecylamine (C16), heptadecylamine (C17), and octadecylamine (C18), respectively. Simulations were performed using a semi-implicit Fourier method described in Ref. 45 on a uniform two-dimensional numerical mesh of 1000 × 1000 two-dimensional grid points. The average system density was set to $n_0 = 0.05$, while the mobility of the density and composition fields were set to $M_n = 1.0$, $M_c = 1.0$ for simplicity. The temperature was fixed at $T = 0.06$. The initial configuration were once again randomly initialized for all of them. Samples 1 – 4 correspond to the ligands, pentadecylamine (C15), hexadecylamine (C16), heptadecylamine (C17), and octadecylamine (C18), respectively. AuNPs were found
to precipitate in all samples, with some typical late-time precipitate configurations for each case shown in Fig. 7.

Figure 7: (Colour online) Simulated late-stage configurations of AuNPs precipitated from a disordered ligand-Au(0) phase. The black/white pixels represent the dimensionless density $n$, and the colourbar readings represent the composition of Au. AuNPs for Four ligand types are shown: (a) pentadecylamine (C15), (b) hexadecylamine (C16), (c) heptadecylamine (C17), and (d) octadecylamine (C18).

The trend that emerges in the dynamical simulations of Fig. 7 is consistent with the predictions made in subsection 4.2.1, namely, as the ligands become longer and heavier, the average AuNP size becomes smaller. Table I summarizes the average diameters of AuNPs for each case and the results are compared to those in the reference experimental work. The trend in the average NP diameter as a function of ligand size and mass is the same as those observed experimentally. In particular, as the ligands become longer...
Table 1: Simulated and experimental data of average AuNPs diameters

| Ligand                     | Simulation (nm) | Experiment (nm) |
|----------------------------|-----------------|-----------------|
| Pentadecylamine (C15)      | 22.0 ± 0.0      | 4.2 ± 1.2       |
| Hexadecylamine (C16)       | 5.5 ± 0.7       | 1.8 ± 0.3       |
| Heptadecylamine (C17)      | 4.4 ± 0.5       | 1.5 ± 0.2       |
| Octadecylamine (C18)       | 3.6 ± 0.5       | 1.3 ± 0.2       |

and heavier, the AuNPs diameters become smaller. It is noted that the simulated AuNP diameters are quite different quantitatively from the experimental values. This is because the XPFC model employed in this work presently uses phenomenological parameters to model the parameters of the experimental situation. As a result, the simulated diameter will be linked to these phenomenological parameters and is not expected to match the experiments quantitatively. Future works will aim to map the XPFC model onto the material properties of the experimental system, at which point a quantitative comparison will be possible.

5 Summary and conclusions

We have proposed a structural-phase-field-crystal (XPFC) model with a ballistic energy term to model mechanochemical reactions. The model was applied to study a mechano synthesis experiment of ultra-small monodisperse amine-stabilized gold nanoparticles analogous to those studied experimentally in Ref. 9. An analysis of the kinetics of our model based on its thermodynamic free energy suggests a possible explanation of the mechanism of mechano synthesis, namely, that the mechanical-force induced ballistic term can reduce the activation barrier energy, making the reaction (precipitated nucleation) easier to happen. A series of Langevin-type microstructure evolution simulations demonstrated the effect of the ballistic term and its role in nucleation, growth and coarsening of NPs. Using a phenomenology for representing ligand mass an length in our model, we also qualitatively reproduce the same trends for the AuNP diameters as that observed experimentally. While our model is internally self-consistent, the parameters of the theory on which it is based yield only a phe-
nomenological reproduction of an experimental mechanochemical system at this stage. As a result, it is still too early to tell if the mechanisms for mechanochemical synthesis predicted herein are correct. However, we hope that our work will inspire further modelling work along these lines, as well as further experimental designs to alter the milling strength, frequency, and time to validate other predictions also made by our model.

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Supporting Information Available

6 Supplementary Information

6.1 XPFC Model for Mechanoassembly: detailed derivations

The detailed derivation of the new XPFC model in section 2 is shown in this supplementary information section.

We begin with a dimensionless generalized binary XPFC free energy functional

$$\frac{\Delta F[n, c]}{k_B T \rho_0} = \frac{\Delta F_{id}[n]}{k_B T \rho_0} + \frac{\Delta F_{mix}[n, c]}{k_B T \rho_0} + \frac{\Delta F_{ex}[n, c]}{k_B T \rho_0},$$

where $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $\rho_0$ is the total system reference
density. The free energy functional has been broken into the ideal $\Delta F_{id}$, mixing $\Delta F_{mix}$, and excess $\Delta F_{ex}$ parts, respectively. The field $n$, defined as $n = (\rho - \rho_0)/\rho_0$ where $\rho$ is the local mass density, plays the role of an order parameter of the model. By adopting a series of reasonable approximations for each term, the free energy form is developed in terms of $n$.

The ideal part of the free energy is defined as

$$\frac{\Delta F_{id}[n]}{\kappa B T \rho_0} = \int d\vec{x} \left\{ [n(\vec{x}) + 1] \ln [n(\vec{x}) + 1] - n(\vec{x}) \right\}$$

(13)

Following [Elder et al.], we simplify this term by expanding it about its reference density in a polynomial truncated to fourth order,

$$\frac{\Delta F_{id}[n]}{\kappa B T \rho_0} = \int d\vec{x} \left\{ \frac{n(\vec{x})^2}{2} - \frac{\eta n(\vec{x})^3}{6} + \frac{\chi n(\vec{x})^4}{12} \right\},$$

(14)

where the phenomenological parameters $\eta$ and $\chi$ are added to fit the free energy away from the reference density.

The mixing part of the free energy is taken as

$$\frac{\Delta F_{mix}[n, c]}{\kappa B T \rho_0} = \int d\vec{x} \left\{ [n(\vec{x}) + 1] \cdot \left[ c \ln \left( \frac{c}{c_0} \right) + (1 - c) \ln \left( \frac{1 - c}{1 - c_0} \right) \right] \right\},$$

(15)

where $c_0$ is the composition of the reference state. This follows the original free energy of an ideal alloy of [Ofori-Opoku et al.][42] Smith and Provatas generalized the mixing term to include enthalpy as follows,

$$\frac{\Delta F_{mix}[n, c]}{\kappa B T \rho_0} = \int d\vec{x} \omega \left\{ [n(\vec{x}) + 1] \cdot \left[ c \ln \left( \frac{c}{c_0} \right) + (1 - c) \ln \left( \frac{1 - c}{1 - c_0} \right) \right] + \frac{1}{2} \epsilon (c - c_0)^2 \right\},$$

(16)

where the phenomenological parameter $\omega$ is added to modify the mixing term away from the reference states, and the $(1/2)\epsilon (c - c_0)^2$ term is added to account for the enthalpy of mixing,
where $\epsilon$ is given by

$$
\epsilon = -4 + \epsilon_0(T - T_c)
$$

(17)

In the spirit of Landau theory, the enthalpy term has been truncated to quadratic order in $c$, with a coefficient linearly proportional to temperature $T$.

The excess part of the free energy is responsible for capturing inter-particle interactions. It is defined as

$$
\Delta F_{\text{mix}}[n, c] = \frac{1}{2k_B T \rho_0} \left\{ n(\vec{x}) * C_{nn}(\vec{x}, \vec{x}') * n(\vec{x}') + n(\vec{x}) * C_{nc}(\vec{x}, \vec{x}') * \Delta c(\vec{x}') + \Delta c(\vec{x}) * C_{cn}(\vec{x}, \vec{x}') * n(\vec{x}') + \Delta c(\vec{x}) * C_{cc}(\vec{x}, \vec{x}') * \Delta c(\vec{x}') \right\},
$$

(18)

where $\Delta c(\vec{x}) = c(\vec{x}) - c_0$ is the composition difference from the reference and $*$ is the convolution operation. Greenwood et al. further simplify this term by noting that since the microscopic density $n$ oscillates rapidly, while $c$ is a smooth field in the long wavelength limit (i.e. on scales larger than the lattice constant), the cross terms of $n$ and $c$ vanish, leaving only the quadratic terms. Approximating $C_{cc}$ by a square gradient composition contribution as in Cahn-Hilliard theory thus gives

$$
\Delta F_{\text{mix}}[n, c] = -\frac{1}{2} \int d\vec{x} \left\{ n(\vec{x}) \int d\vec{x}' C_{nn}(\vec{x}, \vec{x}') \cdot n(\vec{x}') + W_c \left| \nabla c(\vec{x}) \right|^2 \right\},
$$

(19)

where the phenomenological parameter $W_c$, is introduced to describe the energy costs associated with compositional interfaces. The form of $C_{nn}$ follows the work of Smith and Provatas who linearly interpolate $C_{nn}$ between the corresponding correlation functions of each component of the system via the local composition $c(\vec{x})$. This is done through the use of an interpolating function denoted by $\zeta(c)$, and allows the freedom of the system to select
crystal structures depending on the local solute composition. The specific form of \( C_{nn} \) in this phenomenology is given by

\[
C_{eff} := C_{nn} = \zeta_A (1 - c) \cdot C_A + \zeta_B (c) \cdot C_B,
\]

where \( \zeta_A/\zeta_B = 1 \) or 0 when \( c = 0 \) or 1. Specific forms of the \( \zeta_i \) functions \((i = A \text{ or } B)\) are discussed further below. In Eq. (20), \( C_A \) and \( C_B \) are the direct density-density correlation functions used to model interactions in the pure components \( i = A \text{ or } B \), respectively. Their form follows previous works, written in Fourier space as

\[
\hat{C}_i = e^{-T/T_i} \sum_j e^{-\frac{(k - k_i^j)^2}{2\sigma_j^2}},
\]

where \( \hat{C}_i \) denotes the Fourier transform of \( C_i \) and \( j \) indexes the primary reflection peak of the \( j^{th} \) family of lattice planes of the crystal structure adopted by component \( i \). Here, \( k_i^j \) is the lattice spacing of the \( j^{th} \) family of planes of component \( i \). The peaks of the correlation functions of each component are modulated by an exponential in temperature \((T)\), and \( T_i \) is a parameter to be set such as to activate crystallization at an appropriate temperature in each component. As shown by Smith and Provatas this system can be well approximated by choosing

\[
\zeta_A (1 - c) = 0 \quad \zeta_B (c) = e^{-\frac{(1 - c)^2}{2\alpha^2}},
\]

which yields the following effective two-point density correlation function,

\[
\hat{C}_{eff} = e^{-T/T_B} e^{-\frac{(1 - c)^2}{2\alpha^2}} e^{-\frac{(k - k_{10})^2}{2\sigma^2}}
\]

Equation (23) is used to model inter-particle interactions in the monotectic mixture studied.
in the remainder of this work. It is noted that there should strictly be a \( k = 0 \) component of \( \hat{C}_{\text{eff}} \). For simplicity, it is left out of this work.

### 6.2 Weight function \( w_R(x) \)

The weight function \( w_R(x) \) describes how the external mechanical energy dissipates across the system, which can be modulated in a variety of ways, for example, in [Enrique and Bellon](#)’s Ref. 43, Yukawa potential is used, in Ofori-Opoku et al.’s Ref. 42 Bessel function of the second kind is chosen. In this model we adopted a normalized Gaussian function,

\[
w_R(x := |\vec{x} - \vec{x}'|) = \frac{1}{R\sqrt{2\pi}} e^{-\frac{1}{2}(\frac{\vec{x}}{\pi})^2},
\]

(24)

where \( R \) is the energy dissipation length. We fixed \( R \) to a value that scaled with the ligand chain length. We do not know this scaling factor at the present time, as a result, we estimate \( R = 0.75 \times \) chain length + 4.825. In this work, we study 4 samples pentadecylamine (denoted C15), hexadecylamine (denoted C16), heptadecylamine (denoted C17), and octadecylamine (denoted C18), with chain lengths equal to 5.7a, 6.1a, 6.5a, 6.9a (a is the lattice constant of Au), respectively. For these samples, the values of \( R \) then become \( R = 9.1, 9.4, 9.7, 10.0 \), respectively.

### 6.3 Equilibrium properties: detailed derivations

The detailed derivation of the equilibrium bulk properties of this model is shown in this supplementary information section.

To investigate the equilibrium properties of the model in Eq. (7), we describe the bulk ordered states by a mode-expansion for the density around an average density,

\[
n(\vec{x}) = \rho_0(\vec{x}) + \sum_{\mathcal{G}_j} \phi_j(\vec{x}) e^{i\mathcal{G}_j \cdot \vec{x}} + \text{c.c.}
\]

(25)
where \(c.c.\) is the complex conjugate, \(n_0(\vec{x})\) is the average density of the system, \(\vec{G}_j\) represents the reciprocal basis vector of mode \(j\), and \(\phi_j\) represents the amplitude of mode \(j\). For the equilibrium analysis it is further assumed that all modes describing the crystal of interest have the same real amplitude, making \(\phi_j = \phi\) for all \(j\). It is noted that in the context of Eq. (25), disordered phases are described by \(\phi_j = 0\), and \(n_0(\vec{x})\) becomes a constant. Thus, for a crystalline phase hexagonal symmetry, such as gold nano-particles in 2D, the density expression becomes

\[
n(\vec{x}) = n_0(\vec{x}) + 2\phi \left\{ \cos \left[ \frac{2\pi}{a} \left( \frac{2y}{\sqrt{3}} \right) \right] + 4\cos \left( \frac{2\pi x}{a} \right) \cos \left[ \frac{2\pi}{a} \left( \frac{2y}{\sqrt{3}} \right) \right] \right\} \tag{26}
\]

We next proceed by substituting Eq. (26) into Eq. (7) and integrating over the area (in 2D) of a unit cell of the crystal described by the expansion in Eq. (26). In so doing, the exponential terms can be integrated exactly (with some vanishing and some giving non-zero contributions). This process is a simple form of coarse graining and is described operationally in detail in Ref. 45. The resulting coarse grained free energy is interpreted as the free energy in terms of \(\phi\) and reduces to the bulk disordered phase when \(\phi = 0\) and that of the bulk solid when \(\phi \neq 0\). In the former case it is a function of the average (bulk) density \(n_0\) and composition \(c\), while in the latter case it is a function of \(n_0\), the composition \(c\) and the order parameter \(\phi\). In scaled units \((\mathcal{E} = \Delta F / k_B T \rho_0 V)\) the explicit form of the bulk free energy of the disordered phase (denoted \(\mathcal{E}_d\)) and the ordered hexagonal phase (denoted \(\mathcal{E}_o\)) become Eq. (8) and Eq. (9) respectively.

### 6.4 Dynamics of the structural-phase-field-crystal model

We assume that in our model, total density \(n\) and total composition \(c\) are all conserved, the dynamics of the structural-phase-field-crystal model follow Langevin type conserved
equations:

\[
\begin{align*}
\frac{\partial n}{\partial t} &= M_n \nabla^2 \left( \frac{\delta F}{\delta n} \right) + \vec{\nabla} \cdot \vec{\xi}_n \\
\frac{\partial c}{\partial t} &= M_c \nabla^2 \left( \frac{\delta F}{\delta c} \right) + \vec{\nabla} \cdot \vec{\xi}_c
\end{align*}
\]  

(27)

where \( F = \Delta F[n, c]/k_B T \rho_0 \) is the reduced dimensionless free energy, while \( \vec{\xi}_n \) and \( \vec{\xi}_c \) are introduced to model the effect of thermal fluctuations on wavelengths larger than the atomic scale, which are necessary provide the fluctuations from which nucleation can arise spontaneously. From statistical thermodynamics, it can be shown that the noise sources must satisfy the fluctuation-dissipation relation:

\[
\langle \vec{\xi}_{n/c}(\vec{x}, t), \vec{\xi}_{n/c}(\vec{x}', t') \rangle = -2M_{n/c} \delta(\vec{x} - \vec{x}') \delta(t - t') \delta_{ij}
\]  

(28)

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