Stable Nanocolloidal Structures in Metallic Systems

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Molecular dynamics simulations with a semiempirical interatomic potential predict the existence of a thermodynamically stable colloidal structure with nanometer-size Ta particles suspended in liquid Cu. The thermodynamic stability of this structure against coarsening, coalescence or transformation to a homogeneous solution is explained by a negative and strongly curvature-dependent tension of the Cu-Ta interfaces. Simulations with this potential provide a simple computational model for studies of generic thermodynamic properties of nanodisperse systems with a negative interface free energy.

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As was shown by Gibbs [1], thermodynamic stability of fluid-fluid interfaces requires that their interfacial free energy $\gamma$ (also called tension) be positive. This stability condition was later extended to solid-fluid interfaces and is now considered textbook knowledge. It is commonly assumed that a negative $\gamma$ would cause the interfacial area to increase indefinitely until the phases mix into a homogeneous solution. There is growing evidence, however, suggesting that, on the submicrometer and especially the nanometer scales and in the presence of surface-active agents, some interfaces can attain a negative tension and give rise to metastable or even stable disperse structures. For example, most of the liquid-liquid colloids (emulsions), such as oil in water, are thermodynamically unstable and tend to coarsen or even stable disperse structures. For example, most of the liquid-liquid colloids (emulsions), such as oil in water, are thermodynamically unstable and tend to coarsen or even stable disperse structures.

We found that an initially homogeneous Cu-Ta liquid solution is unstable and quickly transforms into a nanocolloidal structure as illustrated in Fig. 1. The Ta particles suspended in the Cu-based liquid solution have a near spherical shape (with some irregularities) and a relatively narrow distribution of sizes. The Ta concentration in the continuous liquid phase and the Cu concentration in the narrow distribution of sizes. The Ta concentration in the continuous liquid phase and the Cu concentration in the particles are very small.

To quantify the particle size distribution, we developed a numerical algorithm for automated identification of particles in saved MD snapshots. The algorithm simulates a random walk of a chosen Ta atom along nearest-neighbor Ta-Ta bonds until all atoms connected by such bonds (and thus forming an individual particle) are identified. The process continues by choosing another Ta atom outside the particle and starting a new walk. Nearest neighbors are identified using a search radius slightly larger than the position of the first peak in the Ta-Ta pair distribution function, $R_1 = 0.28$ nm. The effective diameter $D$ of a particle containing $n$ atoms is defined by $D = 1.24(n\Omega)^{1/3}$, where the numerical coefficient assumes the spherical shape of the particle and $\Omega$ is atomic volume of liquid Ta. The relatively sharp peak [12] in the size distribution (Fig. 2) corresponds to the typical particle size of around
1 to 1.5 nm ($n = 30$ to 60 atoms). This size varies with temperature and the average chemical composition but remains on the order of 1 nm.

This colloidal structure was clearly observed at temperatures 2000–3500 K and compositions of 20–50 at. % Ta. Some of these temperatures and compositions are above the liquidus line on the phase diagram, some below [13]. The colloid thus presents the nanoscale structure of what would appear to be a “homogeneous” liquid if viewed on greater length scales. At higher temperatures the particles become more diffuse and have a more irregular shape but remain visible even at 4000–5000 K. A more detailed study of the domain of existence of the nanocolloid is left for future work. Cooling the colloid down produces a nano-composite material with Ta grains embedded in crystalline Cu.

The atomic motion in the colloid was examined by analyzing atomic trajectories and tracing the motion of groups of labeled atoms. Even at the lowest temperatures studied here, both Cu and Ta atoms diffused over distances exceeding the block size, showing that the particles were given enough time to coalesce, coarsen or dissolve if these processes were favored thermodynamically. No signs of such processes were found. The analysis confirms that the colloidal structure exists in thermodynamic equilibrium and is not caused by slow kinetics. Individual particles move extensively by a Brownian motion. They occasionally collide with one another, sometimes briefly merge and break apart, while constantly exchanging atoms by diffusion through liquid Cu. The structure is fully stable against permanent aggregation.

To further verify the stability of the colloidal structure against coarsening, we performed simulations in which an additional particle with $n = 4$–5 times the average $n$ was introduced in an equilibrium colloid by switching the chemical species of Cu atoms to Ta in a spherical region. The oversized particle quickly (~100 ps) breaks into smaller ones until a uniform colloidal structure is restored with an equilibrium size distribution. Figure 3 shows another test, in which an MD run started with layers of liquid Ta and Cu separated by initially flat interfaces. The interfaces quickly (~40 ps) lose the plane morphology and become extremely rugged, with Ta particles chipping away from the interface and drifting into the liquid Cu. Depending on the average composition, this process eventually results in either a uniform colloidal or a system with leftover liquid Ta and a colloid separated by rugged interfaces. Such tests were performed at several temperatures and compositions, with results invariably confirming the stability of the colloidal structure and instability of plane interfaces.
It was found that the pressure $p$ in central regions of the Ta particles was negative, confirming that the Ta/Cu interfaces have a negative tension. The value of $p$ was computed by choosing an atom closest to the center of mass of the particle and averaging $p$ over a spherical area containing the first peak of the pair distribution function. Estimates from the Laplace equation $p = 2 \gamma/R$ give the physically reasonable value $\gamma = -0.5 \pm 0.1$ J/m$^2$. This estimate relies on several approximations and should be considered as preliminary. For example, the radius of the surface of tension $R$ is not known exactly and was approximated by $D/2$.

We now present a simple phenomenological model of stable nanocolloidal systems. Consider a process in which a large spherical particle immersed in a continuous phase breaks into $N_p$ smaller noninteracting particles with equal radii. Assuming that the particles are incompressible and their total volume is conserved, the total interfacial area $A$ increases with $N_p$ as $A_1 N_p^{1/3}$, where subscript 1 refers to the initial large particle. The particle curvature $k$ also increases with $N_p$ as $k_1 N_p^{1/3}$, resulting in $A = (A_1/k_1) k \propto |k|$. The total interfacial free energy is $G = \gamma A$, where the interface tension $\gamma$ depends on $k$. We postulate that $\gamma(k)$ is an analytic function at $k \to 0$ and represent it by the Taylor expansion [14,15]

$$\gamma(k) = \gamma_0 + ak + bk^2 + ck^3 + \ldots,$$

where $\gamma_0$ is tension of a plane interface ($k \to 0$). Note that the linear coefficient does not have to be zero since the positive and negative curvatures (Ta particles in Cu or Cu particles in Ta, respectively) can have different effects on $\gamma$; thus $\gamma(k)$ need not be an even function. The linear coefficient is known as the Tolman correction introduced for the size dependence of surface tension of droplets [15]. The expansion of $G$ in $k$ becomes

$$G(k) = \frac{A_1}{k_1} (\gamma_0 k + ak^2 + bk^3 + ck^4 + \ldots).$$

Three different cases are possible in which $G$ reaches a minimum that stabilizes the system at a finite particle size (Fig. 4). In all cases the coefficient $a$ is negative, $b$ is positive, and higher-order terms can be neglected. In cases I and II $\gamma_0$ is positive. Both $\gamma$ and $G$ reach minima at positive $k$, with the minimum value of $G$ being either positive (I) or negative (II). In case I, the colloid is metastable with respect to a plane interface, whereas in case II the colloid is more stable than a plane interface. In both cases, however, the plane interface is at least metastable and is separated from the colloidal state by a thermodynamic barrier. No stable colloid exists with the inverse structure ($k < 0$). In case III, $\gamma_0$ is negative and $G$ reaches two negative minima: one at a positive $k$ and the other (more shallow) at a negative $k$. Thus, two stable colloids are possible and the plane interface is unstable against transformation into one of them.

Our simulation results for the Cu-Ta system are compatible with both cases II and III. The instability of a plane interface points to case III, but we cannot exclude the existence of a barrier between the plane interface and the colloid that is easily overcome at the high temperatures of the simulations. Also, the existence of an inverse colloid remains an open question and should be investigated. Thus case II cannot be ruled out at this point. In both cases, however, the stability of the colloidal structure is due to a combination of two factors: the negative interface tension and its increase with interface curvature when the latter becomes large.

The system studied here is fundamentally different from traditional colloids, in that the negative interface tension is not caused by surfactants or surface chemical reactions but reflects an intrinsic physical effect associated with specific features of Cu-Ta interactions. Similar effects might exist in other systems, Cu-Nb and Cu-V being two potential candidates. Although the interatomic potential employed here may or may not represent the real Cu-Ta system accurately, it is suitable for at least generic studies of

FIG. 3 (color online). Interaction of Cu (yellow [light gray]) and Ta (blue [dark gray]) liquids during MD simulations at 2500 K. (a) after 20 ps; the liquid-liquid interfaces are relatively sharp, (b) after 680 ps; the interface is already rugged and Ta atoms diffusing into Cu begin to form colloidal particles, (c) after 2 ns; a nanocolloid has formed between the Ta liquid layers. The average chemical composition of the $12 \times 16 \times 9$ nm$^3$ simulation block is 50 at. % Ta.

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systems with negative $\gamma$. Such systems represent an intriguing and poorly understood state of condensed matter, which deserves attention. We emphasize that interfaces with a negative tension may exist in very diverse physical systems, ranging from emulsions to biological cells (vesicles) [9], to superconductor-normal interfaces showing negative $\gamma$ values (type-II superconductors) [16]. Many open questions remain in this field. For example, the atomistic origin of the strong curvature effect on tension, which we consider responsible for the stabilization of the colloidal particles against further shrinkage and dissolution, remains unclear. The well-known Tolman correction represents the linear approximation to the curvature effect (1), but even for this linear term, its thermodynamic nature and even the sign remain the subject of active research [17,18]. An understanding of this effect is essential in the general context of the size dependence of $\gamma$ in materials, which can affect many phenomena on the nanoscale [19]. The nature of the interactions between the disperse particles is not clear either. Besides the entropic forces and volume exclusion, there may be stronger interactions responsible for the high stability of the disperse structure. The domain of existence of the nanocolloid on the phase diagram should be determined and the transitions occurring on its boundaries characterized. Further, at high temperatures the Ta particles are similar to droplets of overcooled liquid, making the colloid essentially a nanoemulsion. It is possible that at lower temperatures the particles can become amorphous or crystalline. If $\gamma$ remains negative and curvature dependent, this could create yet another thermodynamic state of the system, which would now be a sol. By contrast to other known sols such as ink and blood, this one could be thermodynamically stable. Finally, the nanocomposite material produced by rapid solidification of the nanocolloid may present technological interest.

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[12] Much of the tail of the size distribution is caused by occasional encounters between the particles. Our numerical algorithm identifies touching particles as one particle with a large size.
[13] The colloids existing below the liquidus line are metastable with respect to decomposition into solid Ta and a new colloid with a lower average Ta concentration.