Diffusion of a liquid nanoparticle on a disordered substrate.

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We perform molecular dynamic simulations of liquid nanoparticles deposited on a disordered substrate. The motion of the nanoparticle is characterised by a 'stick and roll' diffusive process. Long simulation times (≃ µs), analysis of mean square displacements and stacking time distribution functions demonstrate that the nanoparticle undergoes a normal diffusion in spite of long sticking times. We propose a phenomenological model for the size and temperature dependence of the diffusion coefficient in which the activation energy scales as $N^{1/3}$.

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I. INTRODUCTION

The spatial organisation of nanoparticles deposited on a substrate strongly depends on the nature and the magnitude of their mobility during the growth process. For systems known as Volmer-Weber films for which nanoparticles are isolated from each other, it is of importance to understand their diffusion on the substrate. This diffusion is directly related to the interaction between the substrate and the nanoparticle so that depending on the system studied one can found slow or fast diffusing nanoparticles. This has been illustrated by Deltour et al. who demonstrated that a small change in the mismatch between the lattice parameters of a Lennard-Jones cluster and the substrate induces an important variation of the diffusion coefficient. More recently, a surprising increasing mobility with increasing size of the nanoparticle has also been reported.

From a more fundamental point of view it is important to determine the nature of the nanoparticle diffusion. The simplest method is to look at the time dependence of the mean square displacement of the center of mass:

$$< R_{cm}^2(t) >= < (r_{cm}(t) - r_{cm}(0))^2 > \propto t^\gamma$$  \hspace{1cm} (1)

where $r_{cm}(t)$ is the position of the center of mass at time $t$. The exponent $\gamma$ is equal to one for a normal diffusion while $\gamma > 1$ and $\gamma < 1$ correspond respectively to superdiffusive and subdiffusive processes. Luedtke and Landman have performed simulations of gold nanocrystals adsorbed on graphite and exhibiting Lévy Flights leading to mild superdiffusion ($\gamma \approx 1.1$). More recently and for a similar system Maruyama and Murakami found a crossover between superdiffusion and normal diffusion. These different diffusion regimes are influenced by the way the nanoparticle moves on the surface. Sliding of the whole nanoparticle seems the most probable scenario but a rolling mechanism has also been observed for small clusters.

To our knowledge and in contrast to the case of solid nanoparticles, a single study has been devoted to the diffusion of liquid nanoparticles. The authors have reported a discontinuity in the diffusion coefficient obtained for solid and liquid nanoparticles near the melting point. In this paper we perform molecular dynamics simulations of gold liquid nanoparticles deposited on a weakly disordered substrate. The first section of this paper presents the simulation details and in the second one we characterize the motion of the nanoparticle on the substrate. We show that it is made of sticking and moving events. The existence of a contact angle hysteresis is at the origin of the oscillations around an equilibrium position. A visual inspection and the measure of the correlation between the velocity and the angular momentum evidence the tendency of the nanoparticle to experience a 'rolling like' motion to reach another equilibrium position. In the third section we examine the nature of the diffusion. Long simulation times are necessary to compute reliable mean squared displacements and sticking time distribution functions. We show that the diffusion remains normal even for the largest nanoparticles having large sticking characteristic times. A phenomenological model is finally presented to account for the size and temperature dependence of the diffusion coefficient. The main hypothesis of a size dependent activation energy is necessary to recover the simulation results.

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FIG. 1: Snapshot of a $N = 555$ gold liquid nanoparticle deposited on the disordered substrate. We measure a wetting angle $\theta \approx 140^\circ$
necessary to clearly identify the diffusion regime. The times of roughly 1 µs. Nevertheless this choice permits to reach simulation time. We therefore expect a quantitative change atoms are chosen to be frozen in order to increase the simulation in which the substrate atoms can move realistic simulation in which the substrate atoms can move below its melting temperature. We obtain a substrate with a glass structure and periodically boundary conditions applied in the x and y directions. The substrate atoms are chosen to be frozen in order to increase the simulation time. We therefore expect a quantitative change of the diffusion coefficient as compared to a more realistic simulation in which the substrate atoms can move. Nevertheless this choice permits to reach simulation times of roughly 1 µs that, as will be discussed below, are necessary to clearly identify the diffusion regime. The interaction between substrate and Au atoms are chosen to be of the Lennard Jones type:

\[ V_{ij} = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \]  

where \( r \) is the distance between the two atoms. We choose \( \sigma = 2.7 \, \text{Å}, \, \varepsilon = 255 \, k_B \) and a cut-off distance of 2.5 \( \sigma \). As a consequence of this weak \( \varepsilon \) value, the liquid Au nanoparticles are in a weakly wetting situation with a wetting angle roughly estimated to \( \theta_e \approx 140^\circ \). A snapshot of the simulated system is given in Figure 1, where we can see a \( N = 555 \) liquid nanoparticle deposited on the disordered substrate. The equations of motion are integrated using the Verlet algorithm and the temperature of the nanoparticle is fixed using the classical velocities rescaling procedure. We choose \( T = 800 \, \text{K} \) below the bulk melting point \( (T_m \approx 1380 \, \text{K}) \) but still above the solidification temperature. The liquid state of the nanoparticles is evidenced by the atomic mean squared displacements calculated in the frame of the center of mass. The values obtained for the atomic diffusion are in good agreement with previous ones. For example, for a particle of 249 atoms the diffusion coefficient is estimated to be 0.09 Å²ps⁻¹. In a first run of roughly \( 10^6 \) MD steps the liquid nanoparticle is deposited on the substrate and reach its equilibrium shape. A second long run of \( 10^9 \) MD steps is then performed. It permits to record the position of the center of mass and to compute different quantities like the probability density function of the sticking events. We checked that the same results are obtained if the second run is performed under microcanonical conditions. The velocity rescaling procedure has therefore no influence on the nanoparticle motion.

**III. ANALYSIS OF THE LIQUID DROP MOTION**

The trajectories of the center of mass (CM) show that the diffusion process is composed of two distincts events: sticking events in which the CM oscillates around an equilibrium position and moving events in which the CM reaches another equilibrium position. This is illustrated in fig. 2. where we plot the time evolution of the CM x coordinates \( x_{cm}(t) \) recorded during 20 ns for a particle of 555 atoms. For this large particle, the sticking and moving events are clearly identified. In inset we represent an hundredfold time expansion of \( x_{cm}(t) \) for the same system. During a sticking event the CM oscillates around an equilibrium position with a characteristic vibrational period \( \tau_v \). A Fourier transform of \( x_{cm}(t) \) and \( y_{cm}(t) \) permits to evaluate \( \tau_v \). These results will be presented elsewhere but as a main result the vibrational period \( \tau_v \) is found to scale with the square root of the particle size. Indeed because of the hysteresis contact angle \( \theta_e \), the liquid drop is at rest on the substrate and is exited by the thermal noise. The measured \( \tau_v \) corresponds to the eigen vibrational period due to the elastic deformation of
where \( \rho \) is the density and \( \gamma_{lv} \) the liquid-vapor surface tension. This period is similar to the one found for the shape oscillations of a free liquid drop [14]. When the particle leaves its equilibrium position, we observe a 'rolling like' move (note that the liquid drop is also changing its shape during the move) of the liquid drop on the substrate. In fig. 3 we represent three snapshots of a moving particle at times separated by 50 ps. The atoms initially belonging to the lower half of the particle are grey colored to evidence the 'rolling like' motion. To quantify this visual inspection we calculate the correlation between the components of the CM velocity (\( V_x \) and \( V_y \)) and the orbital moments (\( J_x \) and \( J_y \)). As usually the correlation coefficient \( C_{ij} \) between the components \( i \) and \( j \) are defined as:

\[
C_{ij} = \frac{< V_i J_j > - < V_i > < J_j >}{\sigma_{V_i} \sigma_{J_j}}
\]

We report on Table I the different \( C_{ij} \) coefficients computed for a \( N = 321 \) particle during a run of 150 ns. The correlation is not significative between \( V_x \) and \( J_x \) and between \( V_y \) and \( J_y \). Conversely and as expected for a 'rolling like' move, a correlation is found for the cross components of the velocity and the orbital moment:

\[
C_{xy} \approx -C_{yx} \neq 0.
\]

Note finally that these correlations coefficients are surestimated because they also characterize the vibrations around the equilibrium position. Therefore and since the radius of our particles should be of the same order than the slipping length [16, 17], we cannot rule out possible sliding moves of the nanoparticle.

**IV. SIZE AND TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENT**

We now present the results obtained for the mean square displacement \( R_{cm}^2(t) \) of particles with sizes ranging from \( N = 87 \) to \( N = 555 \) atoms. We plot in figure 4. the statistically reliable values of \( R_{cm}^2(t) \) (\( t < 20 \) ns) computed for a run length of roughly \( 1 \mu s \). For the smallest particle (\( N = 87 \)) the regime of normal diffusion is clearly indentifiable with \( R^2(t) \propto t \). As the particle size increases the time to reach a linear regime increases. For the largest particle considered in this study (\( N = 555 \)) the linear regime is not reached and the conclusion from the \( R^2(t) \) curve is not clear : one could think at a sub-diffusive regime with a fitted exponent \( \gamma \approx 0.72 \) or alternatively that the simulation time is not long enough to evidence a normal diffusion regime.

In order to reach a conclusion about the nature of the diffusion for the largest particles, we look at the probability density function (PDF) \( \rho_R(\tau) \) of the sticking events.
Events and finally estimate the diffusion coefficient to be $D$ that the mean square displacement $\bar{\rho}$ as compared to the simulation time. We also compute the sticking time $\bar{s}$ that the model of continuous time random walk \[18\] with a sticking time distributed according to a power law $\rho(\tau) \propto \tau^{-(1+\mu)}$ with $\mu < 3$ (normal diffusion regime). We therefore extract the diffusion coefficients $D(N)$ through best fits of simulated $\Phi(t)$ values to equation 8 (the value of $\gamma$ is fixed to 0.5 for the fitting procedure). We represent in figure 6. the simulated and fitted $\Phi(t)$ values for systems with $N = 177, 249$ and 429 atoms. The arrows indicate the values of the diffusion coefficient extracted from this asymptotic analysis.

We represent in figure 7. the diffusion coefficients obtained by the analysis of the sticking times PDF and by the second method described just above as a function of the system size. A first fit of these data to a power law $D(N) \propto N^\gamma$ leads to a value $\gamma = -1.3 \pm 0.1$. The agreement is satisfactory for the smallest particles but we observe a deviation for the largest $N$ values. The power law apparently tends to overestimate the value of $D$. For a LJ crystalline nanoparticle on a solid substrate \[5\] the exponent is $\gamma = 3/2$ for a large mismatch parameter. This exponent has been recently confirmed for gold supported nanoparticles \[20\]. In the case of quasi epitaxy the exponent increases apparently up to $\simeq 1.4$. This latter value is close to the one found in the present study for a liquid nanoparticle. In both cases, a critical applied force exists, below which the system cannot move. In

\[
\Phi(t) = D + \alpha t^\gamma
\]  

for large $t$ values with an exponent $\gamma < 0$ to ensure the asymptotic normal diffusion regime. Best fits of our data to this form of $\Phi(t)$ give values of $\gamma$ close to $-0.5$ with a small dispersion around this mean value ($\sigma_\gamma \simeq 0.05$). This exponent is the same than the one predicted for the model of continuous time random walk \[18\] with a sticking time distributed according to a power law $\rho(\tau) \propto \tau^{-(1+\mu)}$ with $\mu < 3$ (normal diffusion regime).

\[
\Phi(t) = D + \alpha t^\gamma \tag{8}
\]

where $N$ is the total number of observed sticking events and $\bar{\tau}_s$ the mean sticking time. As can be seen in figure 5. for a particle of 249 atoms and $R_s = 25\,\text{A}$ the function $\tau^n_s$ is clearly logarithmic in $n$. Whatever the particle size considered, for sufficiently large $R_s$ values the associated PDF is exponential and we can measure a mean sticking time $\bar{\tau}_s$. This analysis demonstrates that the diffusion remains normal even for the largest particles. The apparent subdiffusive behavior observed in the $R_s^2(t)$ curves is due to the large value of the mean sticking time as compared to the simulation time. We also compute the mean square displacement $\bar{\rho}^2$ between two sticking events and finally estimate the diffusion coefficient to be $D(R_s) = \bar{\rho}^2/4\bar{\tau}_s$. We can see on the inset of figure 5. that $D(R_s)$ tends to a constant for sufficiently large $R_s$ values. We establish here a first method to measure the diffusion coefficient.

Another possible way to extract $D(N)$ from the simulation data is to look at the asymptotic behavior of $R_s^2(t)$. We have demonstrate above that the diffusion remains normal whatever the particle size so that the quantity $\Phi(t) = R_s^2(t)/4t$ should be of the form:

\[
\Phi(t) = D + \alpha t^\gamma
\]  

FIG. 6: Asymptotic analysis of $\Phi(t) = R_s^2(t)/4t$ for nanoparticles with $N = 177, 249$ and 429. Full lines are best fits to the simulated data and the arrows indicate the extrapolated values of $D$.

FIG. 5: Rank ordering of the sticking times for a particle of 249 atoms ($R_s = 25\,\text{A}$). The slope of the straight line corresponds to the mean sticking time of the exponential distribution. Inset: the diffusion constants $D(R_s)$ tend to a constant for sufficiently large $R_s$ values.

Indeed we know \[13\] that the diffusion nature depends on the form of $\rho_B(\tau)$ : for a PDF that has a mean value (like an exponential one) the diffusion is known to be normal while for a power law PDF ($\propto \tau^{-(1+\mu)}$ with $0 < \mu < 2$ ) we expect a subdiffusive behavior. The time $\tau_s$ of a sticking event is defined as the necessary time for the CM to cross a circle of radius $R_s$ centered on its initial position. We compute the PDF for different particle sizes and different values of $R_s$. Since the statistic on sticking times is rather poor especially for the largest systems, the nature of the PDF is determined using the rank ordering method \[13\]. For an exponential distribution we expect that the the $n-th$ largest value of $\tau_s$, $\tau^n_s$ scale as:

\[
\tau^n_s = -\bar{\tau}_s\log(n/N) \tag{7}
\]
our case this force is related to the wetting contact angle hysteresis. To our knowledge no theoretical prediction of this large exponent value exists. Note finally that the diffusion coefficients calculated with the fitted power law for large particle sizes (for example $D \approx 4 \text{nm}^2 \text{s}^{-1}$ for a particle of radius $\approx 100 \text{nm}$) are definitely too large to be consistent with experimental observations \cite{21,22} of completely sticked liquid nanoparticles. This suggests that the power law is no longer valid for large particles.

We therefore propose a second phenomenological scaling law of the form: $D(N) \propto \exp(-\alpha N^{1/3}/kT)$. In this expression the activation energy of the diffusive process is a function of $N$. To escape from its equilibrium position the liquid drop is elastically deformed with advancing and receding wetting angles different of the equilibrium one. The exponent 1/3 in the proposed scaling law relates the elastic deformation caused by the wetting angle hysteresis and the parameter $\alpha$ is therefore proportional to $\gamma_{\alpha}$. We can see on fig. 7, that this scaling law reasonably fit our data on the whole range of particle sizes with a free parameter $\alpha = 0.051 \text{eV} \text{atom}^{-1/3}$. As done just above we can estimate the value of $D$ for large particles. This time the result found is in agreement with the experimental observation \cite{21,22}. Note that we have made the hypothesis that the main $N$ dependence is in the exponential. Nevertheless a size and temperature dependent prefactor should also exists so that a more general expression should be of the form:

$$D(N,T) \propto e^{-\Delta E_i/kT} f(N)e^{-\Delta E_e(N)/kT}$$

(9)

The first exponential term contains the activation energy of individual atoms. In the present case of a liquid nanoparticle this activation energy is related to the atomic diffusion within the liquid. The two other terms have been discussed above, they are reflecting the collective diffusion of the nanoparticle. The form of the function $f(N)$ depends on the nature of the dissipation and could be evaluated in the same way than for a millimetric drop \cite{22}.

To confirm this exponential relation between the diffusion coefficient and the particle size we finally look at the temperature dependence of $D$ for a particle of 177 atoms. The diffusion coefficients are computed for temperatures between 700 and 1200K. Data are well fitted by an arhenius law $D \propto \exp(-\Delta E/kT)$ and give an activation energy $\Delta E = 0.504 \text{eV}$ (Fig. 8.). This value is greater than the one obtained from the previous analysis of the $D(N)$ data. Using the fitted $\alpha$ value we indeed found $\Delta E_i(N = 177) = 0.286 \text{eV}$. Equation 9, predicts that the overall activation energy $\Delta E$ should be the sum of $\Delta E_i$ and $\Delta E_e$. We then perform simulation to measure the atomic diffusion $D_i$ within the liquid. The values $D_i(T)$ are extracted from mean square displacement calculated in the frame of the CM for different temperatures. An arhenius law fits the data and gives the value of the individual activation energy : $\Delta E_i = 0.196 \text{eV}$. Finally we found $\Delta E_e(N = 177) + \Delta E_i = 0.482 \text{eV}$ that compares rather well with $\Delta E = 0.504 \text{eV}$ and seems to confirm the phenomenological form proposed for $D(N,T)$ in Equ. 9.

V. CONCLUSIONS AND PERSPECTIVES

To summarize, we have performed molecular dynamic simulations of a liquid nanoparticle diffusing on a weakly disordered substrate. For the weakly wetting condition considered here, the nanoparticle experiences a 'rolling like' motion from an equilibrium position to another one. The sticking time distribution function is shown to be exponential even for the largest nanoparticles. As a con-

![FIG. 7: Diffusion coefficients as a function of the system size. We represent the value obtained by the two methods. The two straight lines correspond to the best fits to a power law and to a law in which the activation energy is a function of the system size.](image)

![FIG. 8: Diffusion coefficients as a function of temperature for a $N = 177$ particle. The best fit to an arhenius law gives an activation energy of 0.504eV.](image)
sequence the diffusion is normal with a mean square dis-
placement asymptotically linear in $t$. The diffusion coeffi-
cients are reported as a function of size and temperature.
A phenomenological expression for $D(N, T)$ is proposed.
The main hypothesis of an activation energy scaling with
$N^{1/3}$ is necessary to fit the simulation results.

In spite of the difficulty of a direct observation of the
nanoparticle diffusion, we hope this paper will motivate
further experimental studies. Finally, a work is currently
in progress to fully characterize the vibrational modes of
the stucked liquid nanoparticle.

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