Diffusion of a liquid nanoparticle on a disordered substrate.

Franck Celestini*
Laboratoire de Physique de la Matière Condensée ,
UMR 6622, CNRS, Université de Nice Sophia-Antipolis,
Parc Valrose 06108, 13384 Nice Cedex 2, France
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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 ($\simeq \mu s$), 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 $N^{1/3}$.

PACS numbers:

I. INTRODUCTION

The spatial organisation of nanoparticles deposited on a substrate strongly depends on the nature and the magnitude of their mobilty during the growth process. For systems known as Volmer-Weber films [1] 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 [2, 3, 4]. This has been illustrated by Deltour *et al.* [5] 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 [6]

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 :

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

where $\mathbf{r_{cm}}(t)$ is the position of the center of mass at time t. The exponent γ is equal to one for a normal diffusion while $\gamma > 1$ and $\gamma < 1$ correspond respectively to superdiffusive and subdiffusive processes. Luedtke and Landman [7, 8] have performed simulations of gold nanocrystals adsorbed on graphite and exhibiting Lévy Flights leading to mild superdiffusion ($\gamma \simeq 1.1$). More recently and for a similar system Maruyama and Murakami [9] 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 [10].
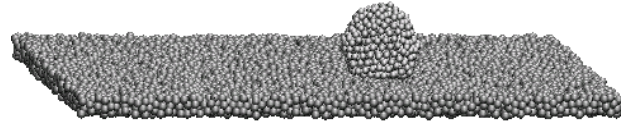
*Electronic address: Franck.Celestini@unice.fr

FIG. 1: Snapshot of a $N = 555$ gold liquid nanoparticle deposited on the disordered substrate. We measure a wetting angle $\theta \simeq 140°$

To our knowledge and in contrast to the case of solid nanoparticles, a single study [12] has been devoted to the diffusion of liquid nanoparticles. The authors have reported a discontinuity in the diffusion coefficient obtained for solid and liquid nanopaticles 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 inpection 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.
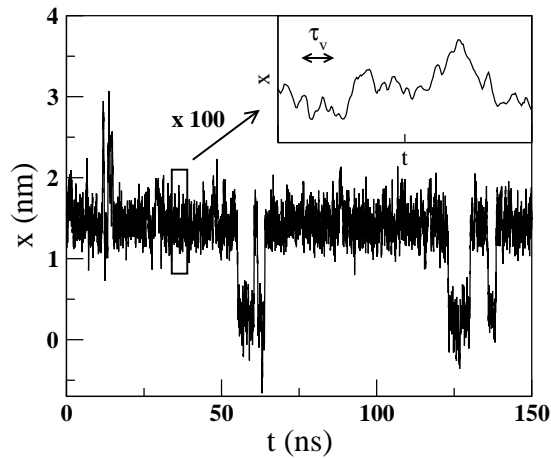
FIG. 2: Time evolution of the x coordinate of the center of mass for a particle of 555 atoms. The sticking and moving events are clearly identified. Inset : during a sticking event the CM oscillates around an equilibrium position with a characteristic vibrational period τ_v .

II. SIMULATION PROCEDURE :

The nanoparticles considered in this study have sizes ranging between $N = 87$ and $N = 555$ atoms. We use the Ercolessi glue potential [11] to describe the interactions between Au atoms with a cut-off distance of $3.9\mathring{A}$ and a time step $\delta t = 2.5\ 10^{-3} ps$. In this formalism the potential energy of the N atoms is given by :

$$U = \frac{1}{2} \sum_{i,j=1}^{N} \Phi(r_{ij}) + \sum_{i=1}^{N} U(n_i) \qquad (2)$$

The first term is a classical pair interaction. In the second term, n_i is the coordination of atom i :

$$n_i = \sum_{j=1}^{N} \rho(r_{ij}) \qquad (3)$$

where $\rho(r_{ij})$ is a function of the interatomic distance r_{ij}. The energy function U is the *glue term* associating an extra potential energy which is a function of the atom coordination.

The substrate is a slab of dimension $170 * 170 * 10 \mathring{A}^3$ made of 15562 atoms. The substrate atomic positions come from the simulation of a liquid rapidly quenched 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 [12]. Nevertheless this choice permits to reach simulation times of roughly $1\mu s$ 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 :

$$V_{ij} = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}] \qquad (4)$$

where r is the distance between the two atoms. We choose $\sigma = 2.7$ $\mathring{A}$, $\epsilon = 255$ k_b and a cut-off distance of 2.5 σ. As a consequence of this weak ϵ value, the liquid Au nanoparticles are in a weakly wetting situation with a wetting angle roughly estimated to $\theta_e \simeq 140°$. 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 [13]. We choose $T = 800K$ below the bulk melting point ($T_m \simeq 1380K$) 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 [12]. For example, for a particle of 249 atoms the diffusion coefficient is estimated to be $0.09\mathring{A}^2 ps^{-1}$. In a first run of roughly 10^7 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 $20ns$ 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 τ_v. A Fourier transform of $x_{cm}(t)$ and $y_{cm}(t)$ permits to evaluate τ_v. These results will be presented elsewhere but as a main result the vibrational period τ_v is found to scale with the square root of the particle size. Indeed because of the hysteresis contact angle [14] the liquid drop is at rest on the substrate and is exited by the thermal noise. The measured τ_v corresponds to the eigen vibrational period due to the elastic deformation of

the drop :

$$\tau_v \propto (\frac{\rho}{\gamma_{lv}})^{1/2} N^{1/2} \qquad (5)$$

where ρ is the density and γ_{lv} the liquid-vapor surface tension. This period is similar to the one found for the shape oscillations of a free liquid drop [15]. 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 separeted 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 :

$$C_{ij} = \frac{< V_i J_j > - < V_i >< J_j >}{\sigma_{V_i} \sigma_{J_j}} \qquad (6)$$

We report on Table I the different C_{ij} coefficients computed for a $N = 321$ particle during a run of $150ns$. 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

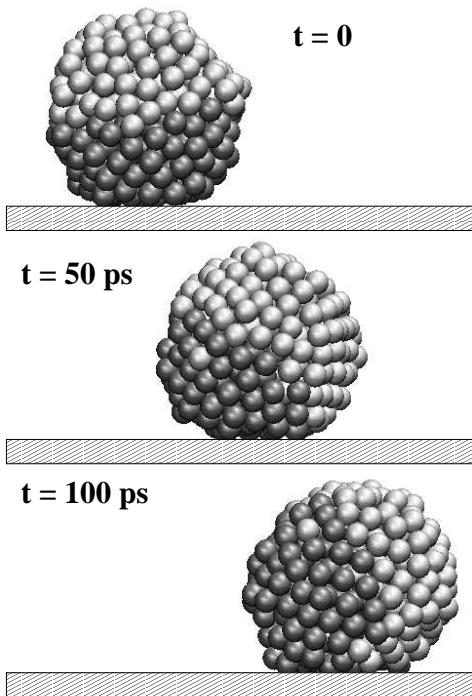
FIG. 3: Snapshots of a moving nanoparticle taken at times separeted by $50ps$. The atoms initially belonging to the lower half of the particle are grey colored to evidence the 'rolling like' move.
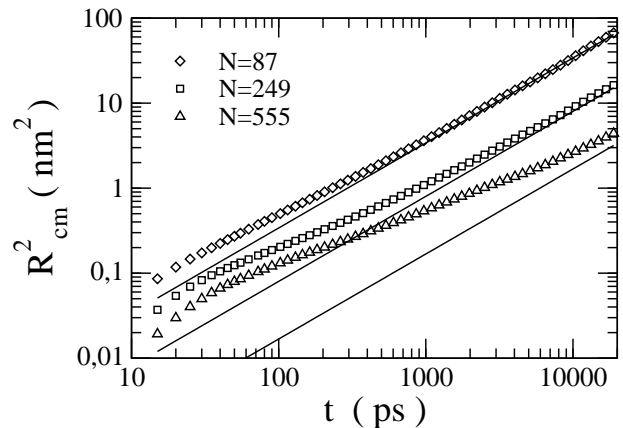

FIG. 4: Mean square displacement $R_{cm}^2(t)$ for particles with sizes $N = 87$, 249 and 555. The straigth lines correspond to the asymptotic linear regimes : $R_{cm}^2(t) \propto 4Dt$.

cross components of the velocity and the orbital moment : $C_{xy} \simeq -C_{yx} \neq 0$.

C_{ij}	x	y
x	-0.002	0.120
y	-0.137	0.007

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 subdiffusive regime with a fitted exponent $\gamma \simeq 0.72$ 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.
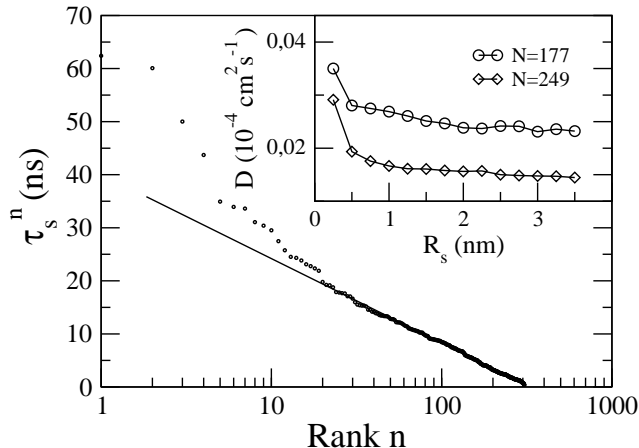
FIG. 5: Rank ordering of the sticking times for a particle of 249 atoms ($R_s = 25\mathring{A}$). The slope of the straight line corresponds to the mean sticking time of the exponential distribution. Inset : the diffusion constants $D(R_s)$ tend to a constant for sufficiently large R_s values.

Indeed we know [18] that the diffusion nature depends on the form of $\rho_R(\tau)$: 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 τ_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 [19]. For an exponential distribution we expect that the the $n-th$ largest value of τ_s, τ_s^n scale as :

$$\tau_s^n = -\bar{\tau}_s log(n/N) \tag{7}$$

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 $R_s = 25\mathring{A}$ the function τ_s^n 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 $R_{cm}^2(t)$ 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 $\bar{r}^2$ between two sticking events and finally estimate the diffusion coefficient to be $D(R_s) = \bar{r}^2/4\bar{\tau}_s$. 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 asymptotyc behavior of

$R_{cm}^2(t)$. We have demonstrate above that the diffusion remains normal whatever the particle size so that the quantity $\Phi(t) = R_{cm}^2(t)/4t$ should be of the form :

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

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 γ 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). We therefore extract the diffusion coefficients $D(N)$ through best fits of simulated $\Phi(t)$ values to equation 8 (the value of γ 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 cristalline nanoparticle on a solid substrate [5] the exponent is $\gamma = 2/3$ 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 $\simeq 1.4$ [5]. 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
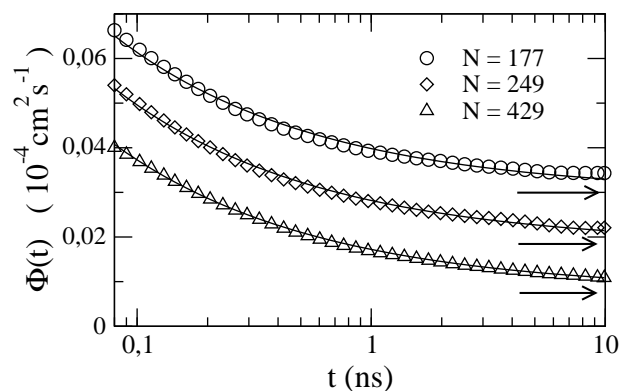

FIG. 6: Assymptotic analysis of $\Phi(t) = R_{cm}^2(t)/4t$ for nanoparticles with $N = 177, 249 and 429$. Full lines are best fits to the simulated data and the arrows indicate the extrapolated values of D.

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 $D \simeq 4 \ nm^2 s^{-1}$ for a particle of radius $\simeq 100 nm$) are definitely too large to be consistent with experimental observations [21, 22] of completely sticked liquid nanoparticles. This suggests that the power law is no longer vadid 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 differents 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 α is therefore proportional to γ_{lv}. 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 $\alpha = 0.051 eV atoms^{-1/3}$. 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 [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 :

$$D(N,T) \propto e^{-\Delta E_i/kT} f(N) e^{-\Delta E_c(N)/kT} \qquad (9)$$

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 [23].

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 $\Delta E = 0.504 eV$ (Fig. 8.). This value is greater than the one obtained from the previous analysis of the $D(N)$ data. Using the fitted α value we indeed found $\Delta E_c(N = 177) = 0.286 eV$. Equation 9. predicts that the overall activation energy ΔE should be the sum of ΔE_i and ΔE_c. 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 : $\Delta E_i = 0.196 eV$. Finally we found $\Delta E_c(N = 177) + \Delta E_i = 0.482 eV$ that compares rather well with $\Delta E = 0.504 eV$ 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-
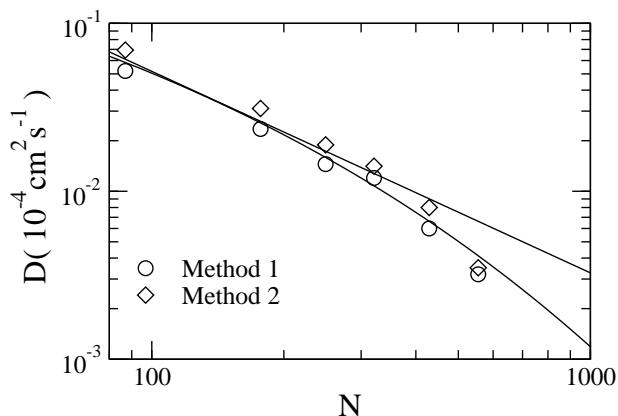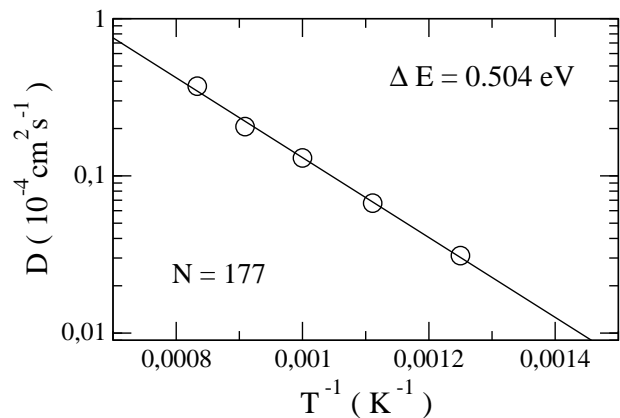
FIG. 7:   Diffusion coefficients as a function of the system size. We represent the value obtained by the two methods. The two straight lines correspond to the best fits to a power law and to a law in which the activation energy is a function of the system size.

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 $0.504 eV$.

sequence the diffusion is normal with a mean square displacement asymptotically linear in t. The diffusion coefficients are reported as a function of size and temperature. A phenomenologicalexpression 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 sticked liquid nanoparticle.

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