Sub-Arrhenius diffusion in a binary colloidal system

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The dynamics of binary colloidal mixture subjected to an external potential barrier is investigated using molecular dynamics simulations. The depletion interactions between the potential barrier and larger components of the mixture alters the dynamics of the system significantly. The larger particles undergo sub-Arrhenius diffusion while smaller particles obey normal Arrhenius diffusion. These results show that quantum phenomena such as tunneling is not required to have sub-Arrhenius diffusion, in contrast to the general agreement in the literature. The depletion interactions between the external potential barrier and larger component increases with decreasing temperature which makes the effective activation energy for barrier crossing temperature dependent leading to sub-Arrhenius diffusion.

I. Introduction

Understanding thermally activated escape over a barrier is at the heart of many important phenomena such as transport processes in living cells, polymeric solutions, colloidal systems, conformational diffusion in proteins, chemical reactions etc. to name a few. Since the seminal work of Hendrik A. Kramers in 1940 [1], this problem attracted lot of attention in different fields of science [2]. Kramers treated this problem as the escape of a Brownian particle from a metastable state and obtained the escape rate over a potential barrier subjected to Gaussian white noise. Temperature dependence of this escape rate or diffusion coefficient is given by Van’t Hoff - Arrhenius - Kramers formula [3, 4],

\[ D(T) = D_0 e^{(-E_a/k_BT)} \]  

This equation was first proposed by Van’t Hoff and Arrhenius and later derived by Kramers by solving the Fokker-Plank equation for Brownian motion in phase space in the presence of a nonlinear potential function. The Van’t Hoff-Arrhenius law is found to be robust in the description of diffusion coefficient or rate constant in many processes such as particle diffusion in solids and liquids [3, 6], diffusion in microporous materials [7, 8], elementary chemical reactions [4, 10], enzymatic catalysis [11, 12], electrical conductivity in ionic liquids and super ionic conductors [13, 14] etc. However, deviations from Van’t Hoff - Arrhenius equation are observed in many systems especially at low temperatures. In general, these deviations are attributed to a temperature-dependent activation energy in contrast to the energy barrier independent of temperature in the Arrhenius picture. These deviations are generally classified into two: super-Arrhenius and sub-Arrhenius diffusion depending the convex or concave nature of the log(D) versus 1/T curves. They correspond to an increase or decrease in the activation energy as temperature decreases.

Recently a simple formalism was proposed [15-19], inspired by Tsallis nonextensive statistical mechanics [20] to describe the deviations from Arrhenius behaviour in diffusivities or rate constants in terms of a single parameter. Exploiting Euler’s expansion for exponential function as the limit of a succession, this formalism proposes a deformed-Arrhenius equation for the temperature dependence of diffusion coefficient,

\[ D(T) = A \left[ 1 - d \frac{E_0}{k_B T} \right]^{1/d} \]  

This formula represents both Arrhenius and non-Arrhenius behaviour of diffusion. Here \( E_0 \) is the height of the potential barrier and \( d \) is known as the deformation parameter, the sign of which will determine the nature of deviations from Arrhenius behaviour. Then the activation energy for diffusion is defined as

\[ E_a = -\frac{d \ln D}{d(1/k_BT)} = E_0 \left( 1 - \frac{E_0 d}{k_B T} \right)^{-1} \]

\[ \cong E_0 + d \frac{E_0^2}{k_B T} \quad \text{(for small } d \text{)} \]  

For positive values of \( d \), super-Arrhenius behaviour is observed and sub-Arrhenius behaviour is observed for negative values of \( d \). For \( d = 0 \) equations (2) and (3) tend to the form of Arrhenius equation. Super-Arrhenius behaviour of diffusion is mainly found in systems where collective or cooperative dynamics is predominant such as dynamics of supercooled liquids [21, 22], diffusion through membranes [23, 24], macroscopic sliding of bacteria [25] etc. Meanwhile, sub-Arrhenius behaviour is mainly seen in chemical reactions [26, 28] and quantum tunneling was proposed to be responsible for such behaviour. In fact, Bell model for incorporate tunneling in chemical kinetics was extended to correlate the deformation parameter \( d \) with the parameters of the energy barrier [29, 30]. Therefore in the literature, there is a consensus that super-Arrhenius behaviour occurs in classical systems, while sub-Arrhenius behaviour occurs at processes where quantum tunneling plays a significant role. To the best of our knowledge, there has been no

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investigations reported in the literature of a classical system exhibiting sub-Arrhenius diffusion. However, sub-Arrhenius behaviour has been observed in the sedimentation of weekly-aggregated colloidal gels \cite{31}. In this article, we report a purely classical system of binary colloidal mixtures, subjected to an external potential energy barrier, undergoing sub-Arrhenius diffusion. We show that one of the components in the binary mixture undergoes sub-Arrhenius diffusion, while the other component exhibits normal Arrhenius diffusion. This contrasting behaviour of different components in the mixture can be attributed to the attractive depletion interaction between the potential energy barrier and the larger component in the mixture.

II. Model and simulation details

We have carried out canonical ensemble molecular dynamics simulations of a binary mixture of colloidal particles, the two components of the mixture differ in their sizes, subjected to an external potential barrier. The interaction potential, $V_{ab}(r_{ij})$, between these particles is soft-sphere repulsion, given by

$$V_{ab}(r_{ij}) = \epsilon_{ab} \left( \frac{\sigma_{ab}}{r_{ij}} \right)^{12}$$  \hspace{1cm} (4)

where $r_{ij}$ is the distance between two particles $i$ and $j$ and $a, b = l, s$, where $l$ stand for the the larger particles and $s$ for the smaller particles. In our simulations, $\sigma_{ss} = 1.0, \sigma_{ll} = 2.0, \epsilon_{ss} = 1.0$ and $\epsilon_{ll} = 4.0$ all being expressed in reduced units. The parameters for interaction between the unlike species is determined by the Lorenz-Berthelot mixing rules; i.e., $\sigma_{sl} = (\sigma_{ss} + \sigma_{ll})/2.0$ and $\epsilon_{sl} = \sqrt{\epsilon_{ss}\epsilon_{ll}}$.

The system is subjected to an external potential which is in the form of gaussian barrier at the center of the simulation box along the z-axis \cite{32, 33}.

$$V_{ext}(z) = \epsilon_{ext} e^{-\left( \frac{z-w}{w} \right)^2}$$ \hspace{1cm} (5)

We chose the width of the external potential to be $w = 3.0$ and the height of the barrier to be $\epsilon_{ext} = 3.0$. Recent experimental advance make it possible to realise such external potentials in colloidal systems \cite{34}. As in ref. \cite{33}, we use an equivolume mixture with a total volume fraction of $\phi = 0.20$. We kept the masses of both the species same since we are interested to see only the effect of depletion interactions in the dynamics. The dynamics of this system has been investigated using canonical ensemble molecular dynamics simulations. The equations of motion are solved simultaneously using a fifth order Gear predictor-corrector method \cite{33}, applying periodic boundary conditions along all the three directions. We have repeated the simulations for three different simulation boxlengths, i.e., $L = 13.0, 15.0$ and $17.0$ to study the finite size effects on the dynamics, keeping the total volume fraction to be 0.20. Because of the periodic boundary conditions, different boxlengths essentially mean different periodicity for the external potential barrier. Each simulation runs for a total of $5 \times 10^6$ timesteps with each timestep being $dt = 0.001$ in reduced units, in which first $1 \times 10^6$ are not used in calculating the equilibrium and dynamic properties. The simulations are repeated three times for each set of parameters and the dynamical properties are averaged over.

This model system has been investigated before to establish that the presence of smaller particles invoke depletion interactions between the larger particles as well as between the larger particles and the potential barrier \cite{32, 33}. It has been shown that this attractive depletion interaction significantly alter the structural and dynamical behaviour of the particles. At low enough temperatures, the smaller particles get localised between the potential barriers (multiple barriers occur because of the periodic boundary conditions) and undergo a slowing down of dynamics, while the larger particles diffuse normally without acknowledging the presence of the repulsive barrier \cite{33}. It may also be noted that the single component systems undergo a slowing down in their dynamics in both the case of larger and smaller particles (see additional information). This striking dynamical behaviour has been attributed to the changes in the effective potential barrier due to the depletion interaction between the larger particles and the potential barrier. We attempt to further understand the nature of depletion interaction and its effect on the dynamics of the system, especially at low temperatures where changes in dynamical properties are significant.

III. Results and discussion

As we decrease the temperature of this system, the self-diffusion coefficient of different species shows markedly different behaviour. While the diffusion coefficient ($D_s^z$) of smallar particles along the $z$-direction decreases rapidly as temperature decreases, the larger particles diffusivity ($D_l^z$) decrease rather very slowly (see figure 3(a) in the additional information). This slow change in the self-diffusion coefficient of larger particles suggests that the activation energy for their dynamics is temperature-dependent and the diffusion can be non-Arrhenius. In order to verify this, we calculated the activation energy of diffusion for both the species of particles. We have also carried out two additional simulations - one with larger particles only and another with smaller particles only. From these simulations we calculated the activation energy for each of the components in the absence of depletion interactions. This will enable us to calculate the change in activation energy due to the depletion interaction between the potential barrier and the larger particles. The diffusion is found to be Arrhenius
FIG. 1: Arrhenius plot for (a) small particles and (b) large particles. Small particles follow Arrhenius law, while larger particles follow sub-Arrhenius behaviour. The points are from simulation data and the lines are fits to Arrhenius or d-Arrhenius law. The data points for $L = 15$ and $L = 17$ shifted by 1 and 2 orders of magnitude.

FIG. 2: Activation energy versus temperature for larger particles.

The Arrhenius plot of diffusion of larger particles is found to obey the $d$-Arrhenius equation as revealed by the nonlinear fits to the diffusivity data shown in Figure 1. The temperature dependent activation energy can be calculated from the $d$-parameter using equation 3. This has been plotted at Figure 2 for different boxlengths. The activation energy is less than the activation energy for diffusion when only large particles are present at all temperatures. This is in agreement with the suggestion that the attractive depletion interaction between the potential barrier and larger particles effectively lowers the barrier for the larger particles to cross. The reduction in the activation energy is larger as the temperature is lowered. This essentially means the depletion interaction is temperature dependent and become more and more prominent as temperature decreases. This also explains why the diffusion coefficient remains same or changes very slowly as temperature is lowered. The diffusivity depends on two factors here; namely activation energy and temperature or more precisely the ratio of activation energy to temperature. In case of smaller particles the activation energy remains constant; so the ratio of activation energy to temperature becomes larger as temperature decreases. This reduces the diffusivity rapidly. In case of larger particles, the activation energy decreases as temperature lowers so that the ratio changes very little at different temperature. This in turn ensures that the diffusivity of larger particles remains more or less same irrespective of the changes in temperature.

In order to gain further insight into the mechanism of this interesting behaviour in the dynamics of the particles in the binary mixture, we calculated the free energy of interaction along the $z$-direction. This is obtained from the density profile of each of the components along the $z$-direction, using

$$G(z) = -k_B T \ln n_i(z)$$

where $n_i(z)$ is the density profile for each of the species along the $z$-direction normalised with respect to the bulk density. Figure 3 shows the free energy of interaction for smaller particles in two different systems; namely only smaller particles with the external potential barrier (dashed line) and the binary mixture with external
FIG. 3: Free energy of interaction for the small particles along the $z$-direction when the system has only small particles (dashed lines) and when both large and small particles present (solid lines).

potential barrier (solid lines) at four different temperatures. When only small particles are present, there is no depletion interaction and barrier does not get modified. However, the binary mixture invokes depletion interaction between the barrier and the larger particles. So the density of larger particles near the barrier increases and because of this crowding, the smaller particles will move away further from the barrier. This increases the effective free energy for smaller particles, which is evident in Figure 3. However, since the volume fraction is small, this decline in the density of smaller particles from the region of external potential barrier does not depend on temperature and hence the free energy of interaction remains unchanged with respect to temperature. So the effective potential barrier is temperature independent and the diffusion process remain Arrhenius. However at higher volume fractions, the effective barrier become temperature dependent and the diffusion becomes super-Arrhenius. Figure 4 shows the free energy profile of larger particles for two different systems: (1) only larger particles with external potential barrier and (2) the binary mixture with external potential barrier at four different temperatures. There are few points to be noted here. Firstly, for larger particles in the binary mixture, there is a minimum for free energy of interaction at the spatial position of the external potential barrier rather than a maximum, which is observed in the case of single component system or in the case of smaller particles in the binary mixture. Here the free energy barrier particles have to face in their dynamics is the difference in free energy between the minimum and bulk (free energy value away from the external potential barrier). This barrier height is much smaller compared to the barrier height particles have to cross in single component system. Secondly, for the single component system the barrier height does not change significantly with respect to temperature while the barrier height decreases with decreasing temperature in case of binary mixture. These observations are consistent with the conclusions made based on the activation energy calculations outlined above. The fact that the free energy barrier is temperature dependent for the binary mixture and that the barrier height decreases with decreasing temperature provides an explanation for the sub-Arrhenius diffusion observed in the case of larger particles.

From the density profile, we can also calculate the
mean force as \[ F(z) = k_B T \frac{d \ln n_i(z)}{dz} \tag{7} \]
along the direction of the potential barrier. Here \( F(z) = F_+(z) - F_-(z) \), where \( F_+(z) \) is the mean force of interaction along positive \( z \) direction and \( F_-(z) \) is the mean force along negative \( z \) direction. These are plotted in Figure 5 and 6 for smaller particles and larger particles respectively. From figure 5 it is clear that the force on smaller particles near the potential barrier is repulsive (negative on the left side of the barrier and positive on the right side) both in the single component system and in the binary mixture. Also it is clear that the magnitude of the force does not change significantly with respect to temperature and hence the dynamics remains Arrhenius. However, the effective force in the larger particles shows a very contrasting behaviour. The force is mainly attractive towards the barrier (positive on the left of the barrier and negative on the right). And the magnitude of the force changes as the temperature changes. This confirms the sub-Arrhenius behaviour observed in the diffusivity of larger particles. It should be noted that the fluctuation in the mean force in the region of potential barrier at low temperatures arises due to the splitting of the peak in density profile at lower temperatures.

Waiting time distributions measure the delay times between successive hops of particles in a dynamics process. We have also calculated the waiting time distributions for both large and small particles from the molecular dynamics trajectories by calculating the delay time between successive jumps of the particles over the barrier. A log-log representation of these waiting time distributions for both the particles has been plotted in Figure 7. As temperature decreases, the waiting time distribution for both type of particles flattens out. This is expected as particles will spend more time between two potential barriers before crossing over and their dynamics become more and more localized as the temperature decreases. However, the decay of waiting time distribution of smaller particles is much slower compared to that of larger particles. These distributions can be very well fitted to a sum of two exponentials. This essentially tells us that there are two time scales associated with the barrier crossing of particles. We have plotted the two relaxation times(\( \tau_1 \) and \( \tau_2 \)) for smaller particles and the two relaxation times(\( \tau_3 \) and \( \tau_4 \)) for larger particles against temperature in the inset of Figure 7(a) and 7(b) respectively. One of the relaxation times(\( \tau_1 \) or \( \tau_3 \)) in each case remains mostly unaffected as temperature decreases; while the other (\( \tau_2 \) or \( \tau_4 \)) increases as the temperature decreases. \( \tau_1 \) (or \( \tau_3 \)) corresponds to the recrossing occurs near the potential
barriers, which explains the weak dependence on temperature. The larger relaxation time, \( \tau_2 \) (or \( \tau_4 \)) can be attributed to the long time diffusion due to barrier crossing. As evident in the figure, \( \tau_2 \) increases rapidly with decreasing temperature and \( \tau_4 \) increases more slowly as temperature decreases. This indicates increasing localization of smaller particles between the repulsive barriers compared to that of larger particles and support the sub-Arrhenius diffusion observed in the dynamics of larger particles.

It will be interesting to note that the two components of the binary mixture follow different dynamics altogether. The dynamics of the larger particles is mainly determined by the depletion interactions between the larger particles and the potential barrier. This depletion interaction is temperature dependent and changes the effective barrier accordingly. Thus, we observe a sub-Arrhenius diffusive behavior for larger particles. The effective barrier of the smaller particles increases because larger particles get crowded in the region of external potential barrier and smaller particles gets depleted away from that region. This crowding of larger particles and hence the depletion of smaller particles from the region of potential barrier does not depend on temperature, especially since the volume fraction of the particles is small. So the effective potential barrier for smaller particles remain unchanged with respect to temperature and they follow Arrhenius diffusion. For such system slowing down of dynamics has been reported earlier [38]. However, a temperature dependent activation energy can be expected at higher density (or volume fraction) and smaller particles may undergo a super-Arrhenius diffusion. Work in this direction is in progress and will be reported elsewhere [37]. It should also be mentioned that the results are more general over a wide range of parameters than the set we used in these simulations [37].

IV. Conclusions

We have studied the dynamics of binary colloidal mixtures, different species in the mixture differ in their sizes, subjected to an external Gaussian potential by using canonical molecular dynamics simulations. We have shown that, contrary to the agreement in literature that sub-Arrhenius diffusion is related to quantum phenomena, a classical system can show a sub-Arrhenius temperature dependence of diffusivity. An increase in the probability of crossing the barrier can lead to sub-Arrhenius behaviour irrespective of the nature of the process involved. In this sense, the depletion interactions in the present investigation or quantum tunneling in the earlier reported investigations have similar effects on the barrier crossing. Eventhough the results we obtained are for a binary mixture of colloids, we believe our findings are applicable to many other systems which involve barrier crossing. Many of the biological transport process which involve more than one components, differing in their dimensions, shows faster diffusivity for bigger components [33, 40]. Similarly, anomalous changes in diffusivity with respect to particle dimensions are reported for particles diffusion in porous materials such as zeolites [41, 42] and metal oxide frameworks [43, 44]. The pathways of transport in these systems involve many bottlenecks, which can be similar to the external potential used in our investigations. Therefore, our results contribute to the understanding of such processes.

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