

CH5021
MOLECULAR SIMULATION OF SOFT MATTER
SYSTEMS

EVAPORATION INDUCED SELF ASSEMBLY OF NANOPARTICLES

PROJECT REPORT

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I. INTRODUCTION

Fabrication of ultra-thin films of nanoparticles is of critical importance for the manufacture of sensors, optical devices and magnetic storage media. One common method to prepare thin films of nanoparticles is by suspending them in a solution and evaporating the solvent off a substrate. The factors that influence the structure formed is dependant on the evaporation dynamics of the solvent including volatility/equilibrium vapour pressure, solvent-nanoparticle interaction, nanoparticle-nanoparticle interaction, concentration of nanoparticles in the solution etc. This study tries to replicate the work done by Cheng, Grest and et.al., on the evaporation of Lennard-Jones fluids and subsequently induced nanoparticle assembly, in a model system.

II. SIMULATION METHOD

The molecular dynamics study was performed on two systems; a system with pure solvent and a system with nanoparticles dispersed in the solvent, both in contact with vacuum.

The solvent particles interact with a Lennard-Jones potential with the following interaction potential:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad r_c = 2.5\sigma$$

where, r_c is the cutoff radius for interaction.

The nanoparticle-solvent interaction is modelled using a colloid potential of the form:

$$U_{cc}(r) = U_a + U_r, \quad r < r_c$$

$$U_a = -\frac{A_{cc}}{6} \left(\frac{2a_1a_2}{r^2-(a_1+a_2)^2} + \frac{2a_1a_2}{r^2-(a_1-a_2)^2} + \ln \left(\frac{r^2-(a_1+a_2)^2}{r^2-(a_1-a_2)^2} \right) \right)$$

$$U_r = \frac{A_{cc}}{37800} \frac{\sigma^6}{r} \left(\frac{r^2-7r(a_1+a_2)+6(a_1^2+7a_1a_2+a_2^2)}{(r-a_1-a_2)^7} + \frac{r^2+7r(a_1+a_2)+6(a_1^2+7a_1a_2+a_2^2)}{(r+a_1+a_2)^7} \right)$$

$$U_{cs}(r) = \frac{2a^3\sigma^3A_{cs}}{9(a^2-r^2)^3} \left(1 - \sigma^6 \left[\frac{5a^6+45a^4r^2+63a^2r^4+15r^6}{15(a-r)^6(a+r)^6} \right] \right), \quad r < r_c$$

A_{cc} is the Hamaker's constant for colloid-colloid interaction

A_{cs} is the Hamaker's constant for colloid-solvent interaction

The nanoparticle interact with solvent particles with Hamaker's constant $5.0 \epsilon/\sigma$ and cutoff 7.5σ . The nanoparticles interact between themselves with Hamaker's constant $1.0 \epsilon/\sigma$ and cutoff 12.5σ . The solvent has a diameter σ whereas the nanoparticle has a diameter 10σ .

The simulations were carried out in a box of dimensions $40 \sigma \times 40 \sigma \times 40 \sigma$, periodic in all direction for the equilibration run and fixed only in the vertical Z direction for the evaporation run. Before the onset of evaporation, the density of solvent in both the cases were maintained at

$\sim 0.5 \text{ N}/\sigma^3$. The systems were initially relaxed with an NVT run, assigning velocities corresponding to $T \varepsilon/k_b$ and maintaining it using a Langevin thermostat with damping parameter 0.01. After relaxation, the box size was scaled to twice the height along the vertical Z direction and a liquid-vapour interface was allowed to form. Then, evaporation was initiated by defining a deletion region at the top of the simulation box and removing 100 solvent particles per 100 timestep from that region. During the evaporation run, the Langevin thermostat was limited to a small distance from the bottom, to model the heating of the substrate. All simulations were performed with a timestep of 0.005τ using Large Atomic/Molecular Massively Parallel Simulator (LAMMPS).

The simulations were performed in reduced units.

III. RESULTS

a) Evaporation of Pure Solvent

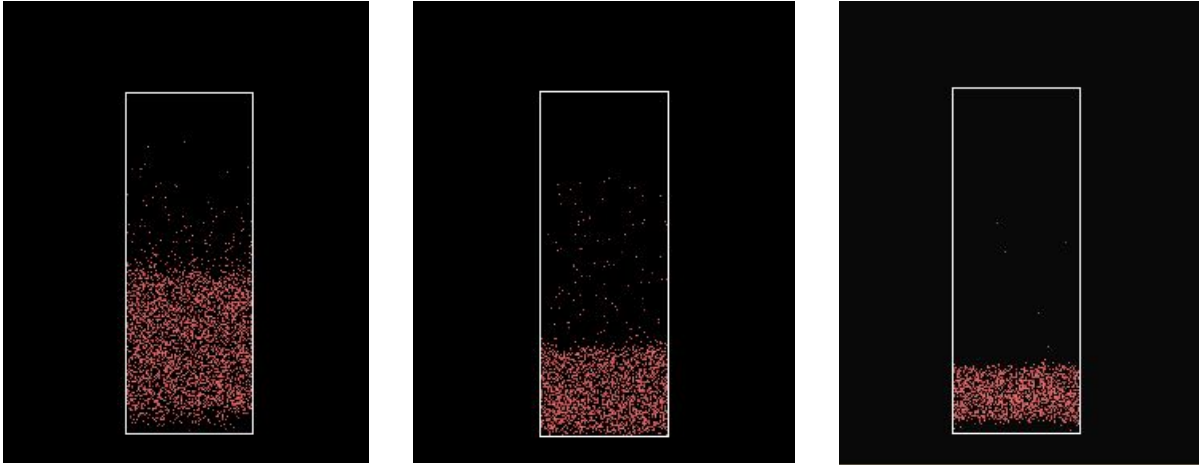


Fig 1. Screenshots of the evaporating solvent system at various timesteps

The screenshots of the evaporating system at various timesteps (Fig 1), shows the vapour region being depleted continuously, and the density of liquid and vapour differs nearly by an order of magnitude, as shown in Fig 1. This can be described by the high vapour pressure of the fluid, which is characteristic of LJ fluids, as the interaction between the individual particles is governed by a weak LJ potential, and the particles under considerations are simple monomers with no other form of interaction.

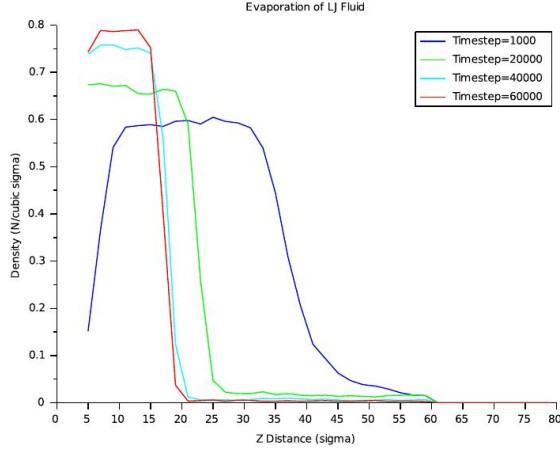


Fig 2. Density Profile along the vertical Z direction

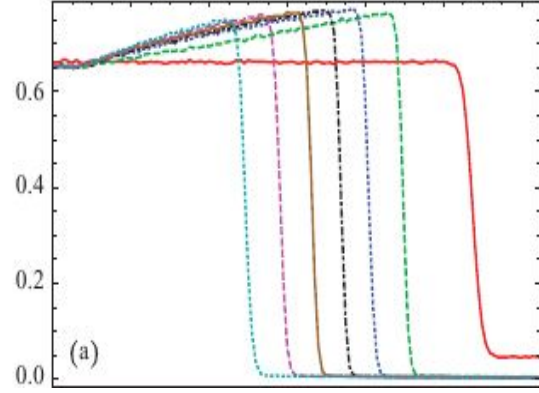


Fig 3. Density Profile along the vertical Z direction, as per Cheng, Grest et.al.[1]

The density profile averaged over volume bins that vary over the vertical Z directions resembles that obtained by Cheng, Grest et.al [1]. With increasing time, the liquid density near the interface gets enhanced as had been observed by Holyst and Litniewski [3]. This can be explained based on the Hertz-Knudsen equation, which describes the sticking of gas molecules on a surface by expressing the time rate of change of the concentration of molecules on the surface as a function of the pressure of the gas and other parameters. This is enhanced in the case of LJ fluids due to its high vapour pressure.

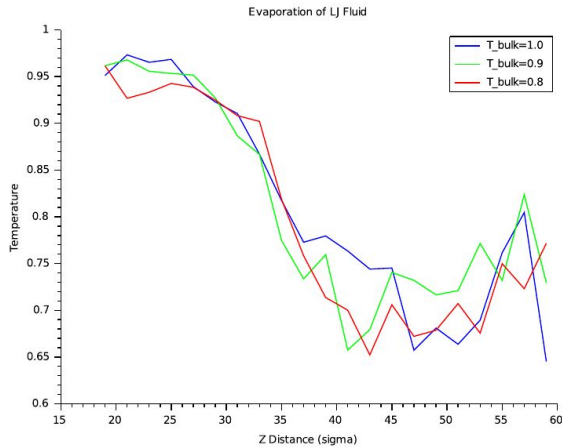


Fig 4. Temperature Profile along the vertical Z direction

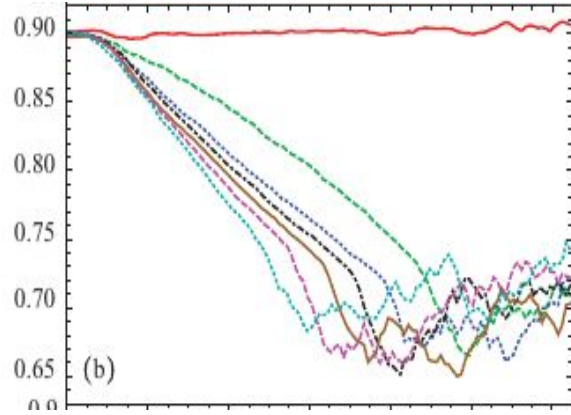


Fig 5. Temperature Profile along the vertical Z direction, as per Cheng, Grest et.al.[1]

The temperature profile obtained along the vertical Z direction also matches the results obtained by Cheng, Grest et.al [1]. While the bulk of the liquid largely maintains the initial temperature at which the liquid-vapour equilibrium was formed, at the liquid-vapour interface, the temperature drops and then rises again in the vapour region. This supports the physical observation that during evaporation, the liquid-vapour interface is always at the lowest temperature due to loss of heat as Latent Heat of Evaporation. In addition to the evaporative cooling, the temperature

profiles shown here indicate that the temperature of vapor increases with the distance from the liquid/vapor interface. This can be understood by a simple argument: molecules with higher kinetic energies evaporate faster and more energetic molecules accumulate near the depletion zone, leading to a higher temperature at this end and a temperature gradient in the vapor phase. Therefore, if the vapor temperature is measured at a certain distance away from the liquid/vapor interface, it will be higher than the actual temperature at the interface.

b) Evaporation of Solvent in Presence of Nanoparticles

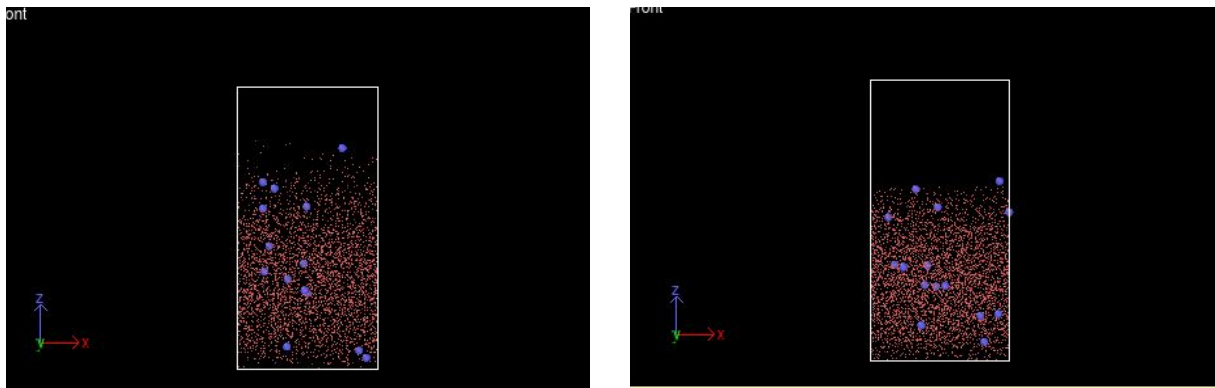


Fig 6. Screenshots of evaporating nanoparticle-solvent system at various timesteps

In the presence of nanoparticles, the formation of vapour region was found to take longer duration than in the case of pure solvent, and was depleted soon after its formation on a continuous basis. This supports the theory that evaporation rate of a solvent would be significantly affected in the presence of a strongly interacting colloid particle.

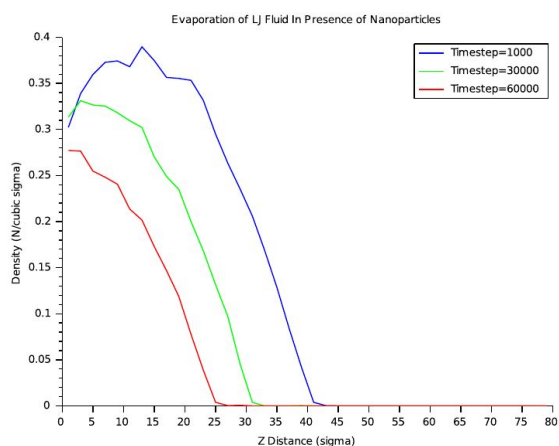


Fig 7. Density Profile for solvent along the vertical Z direction

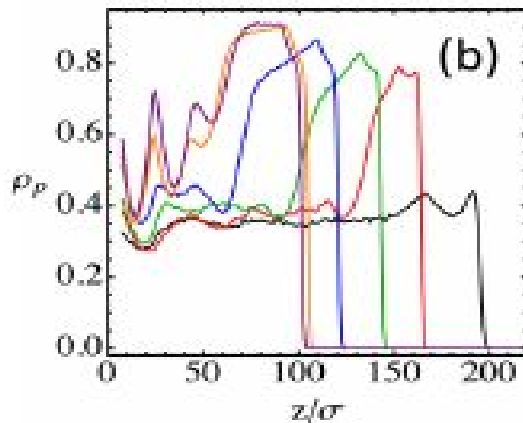


Fig 8. Density Profile for solvent along the vertical Z direction as per Cheng and Grest [4]

The density profile for solvent shows similar behaviour as per the case of evaporation of pure solvent and matches the profile obtained by the simulations of Cheng and Grest [4], as shown in Fig 7 and 8. The nanoparticles were found to achieve peak density near the liquid-vapour interface, however formation of an ordered structure was not observed (Fig 9). This could have been due to the insufficiency in the strength of interaction between the nanoparticles to order themselves during the relaxation period, insufficiency in the concentration of nanoparticles or also requirement of longer durations of time to allow relaxation. Fig 11 shows the snapshot of the ordered nanoparticle structure as obtained by Cheng and Grest [2].

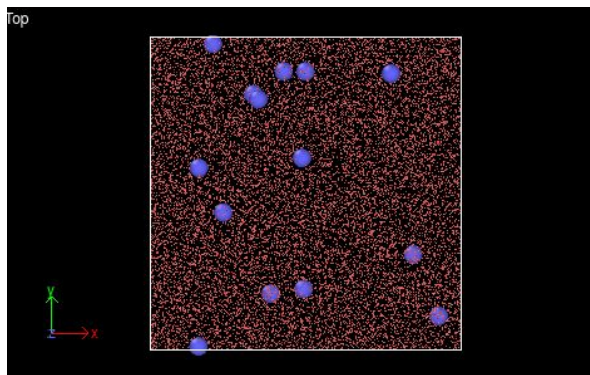


Fig 9. Horizontal cross section of arrangement of nanoparticles at the liquid-vapour interface

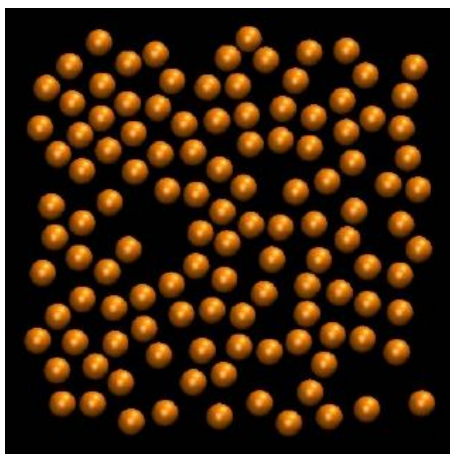


Fig 10. Horizontal cross section of arrangement of nanoparticles at the liquid-vapour interface with a nanoparticle concentration of 20 volume % [2]

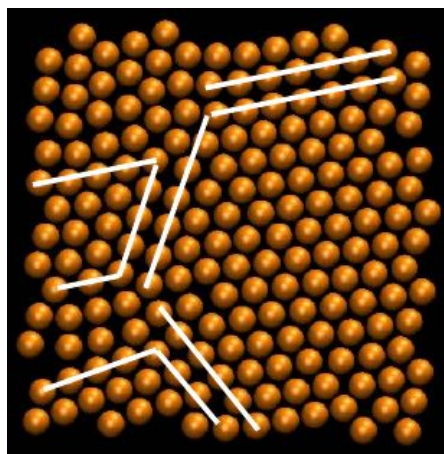


Fig 11. Horizontal cross section of arrangement of nanoparticles at the liquid-vapour interface with a nanoparticle concentration of 30 volume % [2]

IV. CONCLUSION

We have used molecular dynamics simulations to study the evaporation of pure LJ fluid systems and in the presence of nanoparticles, which influences the morphology of the final nanoparticle structure formation. The studies supports the experimental observations that the evaporation rate of solvent when in contact with a vacuum is extremely high due to a high pressure gradient

and there are strong evaporative cooling and liquid density enhancement near the liquid/vapor interface.

In the case of evaporation of solvent in presence of nanoparticles, the evaporation rate was significantly diminished. However, due to the insufficient concentration of nanoparticles or the allowed relaxation time, an ordered arrangement of nanoparticles at the liquid-vapour interface could not be observed.

The observed deviations of the results from those obtained by Cheng, Grest et.al. can be explained by the difference in the parameters chosen for the model system. Due to limited computational resources, the strength of interactions and size of the systems have had to be scaled down from those used in the reference papers. Nevertheless the trends exhibited remains the same and can very well justified to be a model system.

V. REFERENCES

1. Evaporation of Lennard-Jones fluids; Shengfeng Cheng, Jeremy B. Lechman, Steven J. Plimpton, and Gary S. Grest; The Journal of Chemical Physics 134, 224704 (2011); doi: <http://dx.doi.org/10.1063/1.3595260>
2. Molecular dynamics simulations of evaporation-induced nanoparticle assembly; Shengfeng Cheng, Gary S. Grest; The Journal of Chemical Physics 138, 064701 (2013); doi: <http://dx.doi.org/10.1063/1.4789807>
3. Evaporation into vacuum: Mass flux from momentum flux and the Hertz–Knudsen relation revisited; Robert Holyst and Marek Litniewski; The Journal of Chemical Physics 130, 074707 (2009); doi: <http://dx.doi.org/10.1063/1.3077059>
4. Dispersing Nanoparticles in a Polymer Film via Solvent Evaporation; Shengfeng Cheng and Gary S. Grest; ACS Macro Lett., 2016, 5 (6), pp 694–698; doi: 10.1021/acsmacrolett.6b00263

VI. ANNEXURE

a) Code For Equilibration of LJ Fluid

```
units      lj
atom_style sphere

lattice      sc 1.0
region      box block 0 30 0 30 0 30 units box
create_box  2 box
create_atoms 1 box

set         type 1 diameter 1.0

velocity    all create 1.0 87287 loop geom

# multi neighbor and comm for efficiency

neighbor    1 multi
neigh_modify delay 0
comm_modify mode multi

# colloid potential

pair_style  lj/cut 2.5
pair_coeff  * * 1.0 1.0 2.5

fix 1 all nvt temp 1.0 1.0 1.0
fix 2 all langevin 1.0 1.0 0.1 437624

dump        1 all atom 1000 dump.colloid

thermo_style custom step temp epair etotal press vol density
thermo      1000

timestep    0.005

run         50000

reset_timestep 0

unfix 1
```



```
change_box all z final 0.0 80.0 boundary p p f units box
fix 1 all nve
dump 2 all atom 1000 dump.equilibrium
thermo_modify lost ignore flush yes

run 200000

write_data data.equilibrium
```

b) Code for Evaporation of LJ Fluid

```
units      lj
atom_style sphere
boundary p p f

read_data data.equilibrium

velocity all create 1.0 87287 loop geom

neighbor    1 multi
neigh_modify      delay 0
comm_modify      mode multi

pair_style  lj/cut 2.5
pair_coeff   * * 1.0 1.0 2.5

region vapor block 0.0 30.0 0.0 30.0 60.0 80.0 units box
region substrate block 0.0 30.0 0.0 30.0 0.0 1.0 units box
group bottom region substrate

fix 1 all nve
fix 2 bottom langevin 1.0 1.0 0.1 437624
fix 3 all evaporate 100 100 vapor 56789

compute cc1 all chunk/atom bin/1d z center 2.0
fix 4 all ave/chunk 100 10 1000 cc1 density/number norm sample file
density.profile
fix 5 all ave/chunk 100 10 1000 cc1 temp norm sample file temp.profile

thermo_style custom step temp epair etotal press vol density
thermo 1000

dump a all atom 1000 dump.evaporate
thermo_modify lost ignore flush yes

run 100000

write_data data.evaporate
```

c) Code for Evaporation of Solvent and Self Assembly of Nanoparticles

```
units      lj
atom_style sphere
boundary p p f

read_data data-equil.npp
velocity    all create 1.0 87287 loop geom

neighbor     1 multi
neigh_modify      delay 0 one 20000 page 500000
comm_modify       mode multi vel yes

pair_style hybrid/overlay colloid 12.5 dpd/tstat 1.0 1.0 3.0 122347
pair_modify shift yes
pair_coeff * * dpd/tstat 1.0 1.0
pair_coeff  2 2  colloid 30.0 1.0 5.0 5.0 12.5
pair_coeff  1 2  colloid 70.0 1.0 5.0 0.0 7.0
pair_coeff  1 1 colloid 10.0 1.0 0.0 0.0 2.5

group solvent type 1
group np type 2

thermo_style    custom step temp epair etotal press vol density
thermo_modify lost ignore flush yes
thermo          1000

fix 1 all nve
fix 2 all langevin 1.0 1.0 0.1 437624

region vapor block 0.0 40.0 0.0 40.0 50.0 80.0 units box
region substrate block 0.0 40.0 0.0 40.0 0.0 1.0 units box
group bottom region substrate
fix 3 solvent evaporate 1000 1000 vapor 56789

compute cc1 all chunk/atom bin/1d z center 2.0
fix 4 all ave/chunk 100 10 1000 cc1 density/number norm sample file
density.profile
fix 5 all ave/chunk 100 10 1000 cc1 temp norm sample file temp.profile

thermo_style    custom step temp epair etotal press vol density
thermo_modify lost ignore flush yes
```

```
thermo          1000
minimize 1.0e-4 1.0e-6 100 100
dump 1 all atom 1000 dump.npp-rearrange

timestep        0.005
run 500000

write_data data-equil.npp-rearrange
```