Droplet Propulsion by Thermal Modulation of the Liquid-Solid Interfacial Energy

Nikolai V. Priezjev

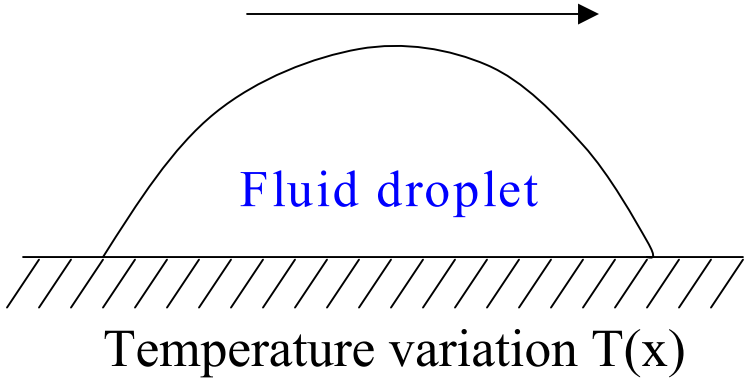
http://www.princeton.edu/~priezjev

Prof. Sandra M. Troian
Microfluidic Research & Engineering Laboratory
Dept. of Chemical Engineering
Princeton University

Priezjev and Troian, preprint (2004)

Outline

- Details of molecular dynamics model
- Isothermal wall conditions:
  free diffusion of droplet center mass



- Droplet motion in presence of temperature gradient

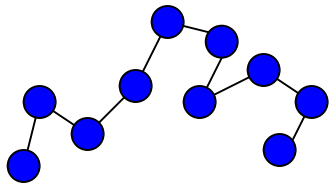
Why is the droplet moving?

Estimation of thermocapillary force at liquid vapor interface

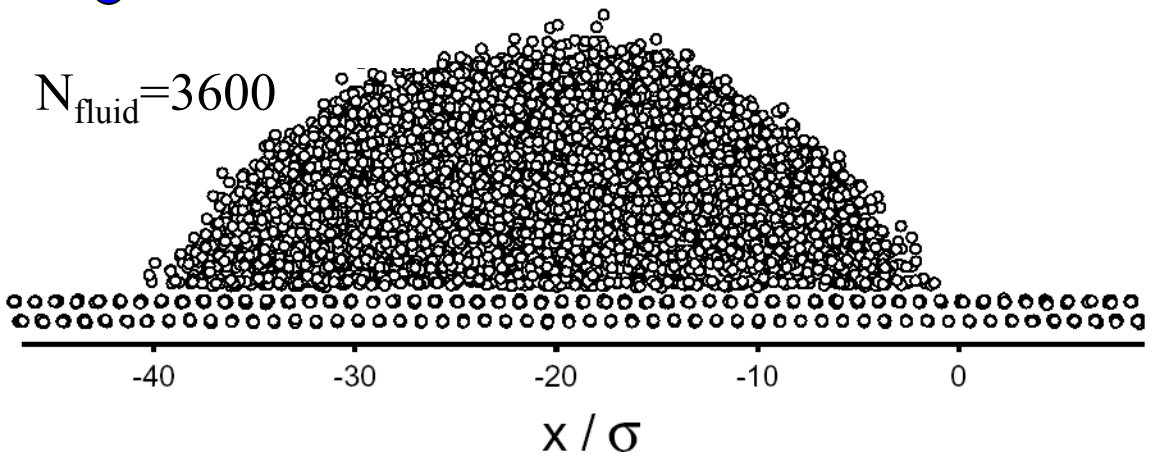
Variation in the effective surface adhesive energy

- Conclusions

Molecular Dynamics Simulation Model



Bead-spring model: 10-mers



Modified Langevin thermostat for wall atoms:

$$T(x)=T_0(1-\alpha x) \quad \text{where } T_0=1.0\,\varepsilon/k_B$$

Temperature gradient

$$m\ddot{y}_i + m\Gamma\dot{y}_i = -\sum_{i\neq j}\frac{\partial V_{ij}}{\partial y_i} + f_i$$

Interaction potentials:

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

$$V_{FENE}(r) = \frac{1}{2}kr_o^2 \ln\left(1-\frac{r^2}{r_o^2}\right)$$

$r_{cut\text{-}off} = 2.5\sigma$

$\varepsilon_{wf} = 0.9\varepsilon$ wall-fluid interaction

$\rho_w = 0.8\ \sigma^{-3}$ wall density

$\Gamma = \tau^{-1}$ friction coefficient

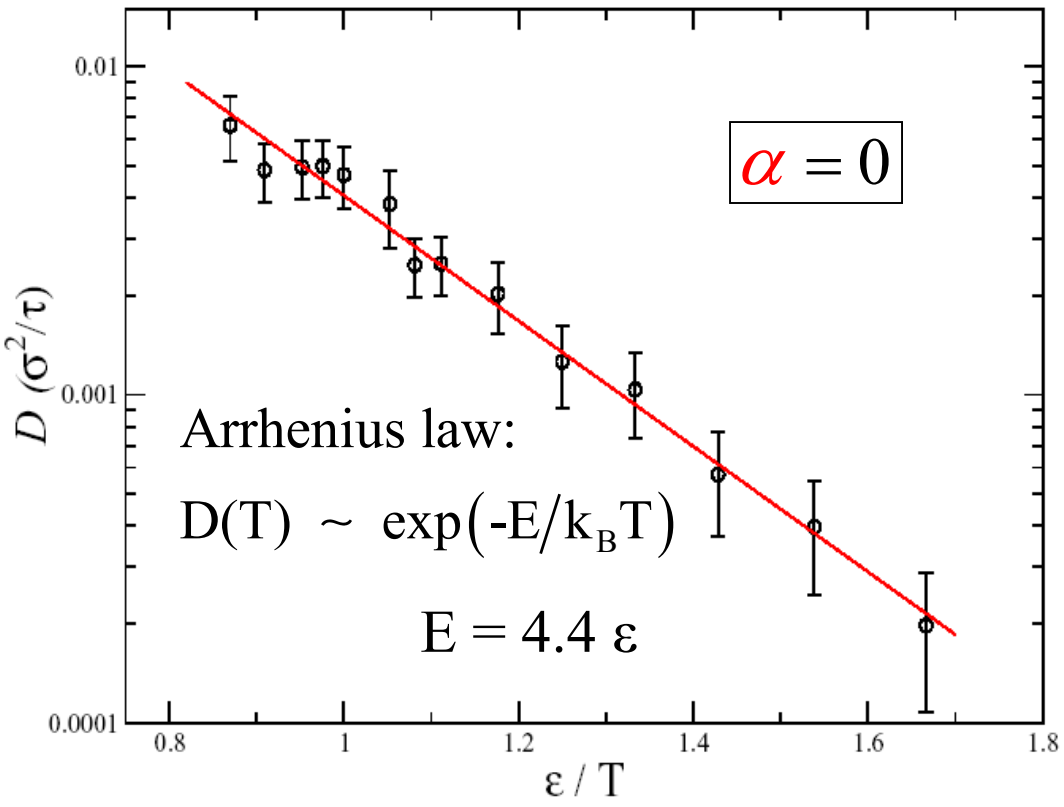
f_i = Gaussian random force

$T_{max} \sim 1.4\,\varepsilon/k_B$

$T_{min} \sim 0.6\,\varepsilon/k_B$

Isothermal wall conditions

Applied T_0: 0.6 – 1.3 ε/k_B



$$x_{CM} = \frac{1}{N_{fluid}} \sum_{i=1}^{N_{fluid}} x_i$$

Diffusion coefficient:

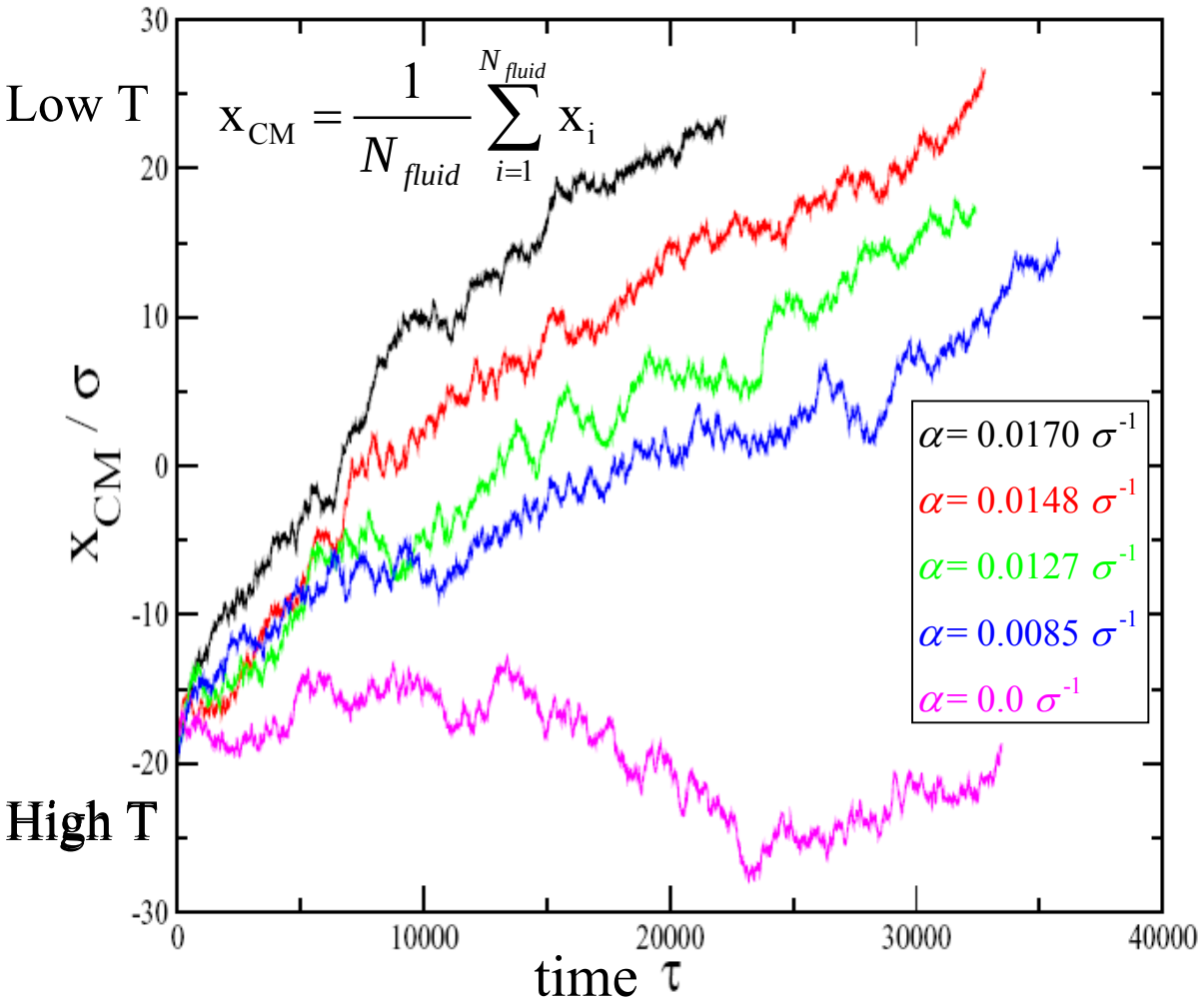
$$D = \frac{1}{2t} \left\langle \left| x_{CM}(t) - x_{CM}(t') \right|^2 \right\rangle$$

for $t - t' \gg \tau$

- Diffusion follows Arrhenius dependence
- For typical duration of simulation $10^4\tau$ droplet center mass diffuses about 10σ for T=1.0 ε/k_B

$\alpha \neq 0$?

Droplet Motion in Presence of Temperature Gradient



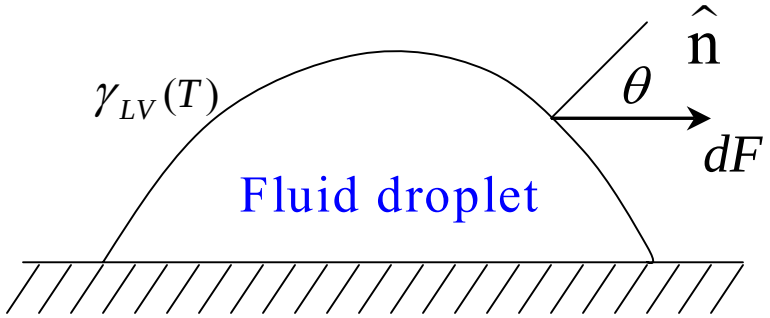
$$T(x) = T_0(1 - \alpha x)$$

$$T_0 = 1.0\,\varepsilon/k_B$$

- Faster motion for higher gradient α
- Small gradient α: trajectory is liner with superimposed fluctuations
- Large gradient α: trajectory becomes curved (slow motion at right cold end)

Why is the Droplet Moving?

Estimation of thermocapillary force:

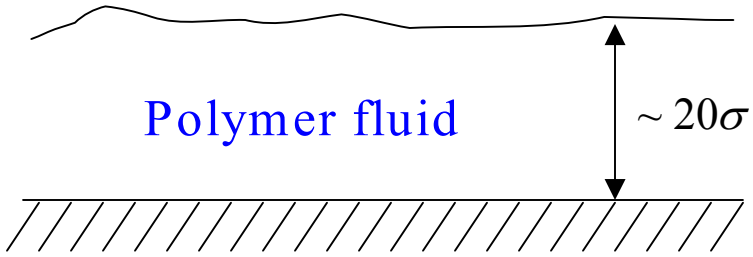


$$F = \int \frac{d\gamma_{LV}}{dT}\frac{dT}{dx} Sin\theta \; dS$$

pulling stress — interface

Typical force $F = O(1)\varepsilon/\sigma$ is small

Estimation of surface tension γ_{LV}



γ_{LV} = surface tension decreases monotonically

from $\gamma_{LV}(T=0.6)=1.28\ \varepsilon\sigma^{-2}$

to $\gamma_{LV}(T=1.3)=0.54\ \varepsilon\sigma^{-2}$

for the thin polymer vapor interface

Broska et al., Langmuir, `93

Ford and Nadim, Phys. Fluids, `94

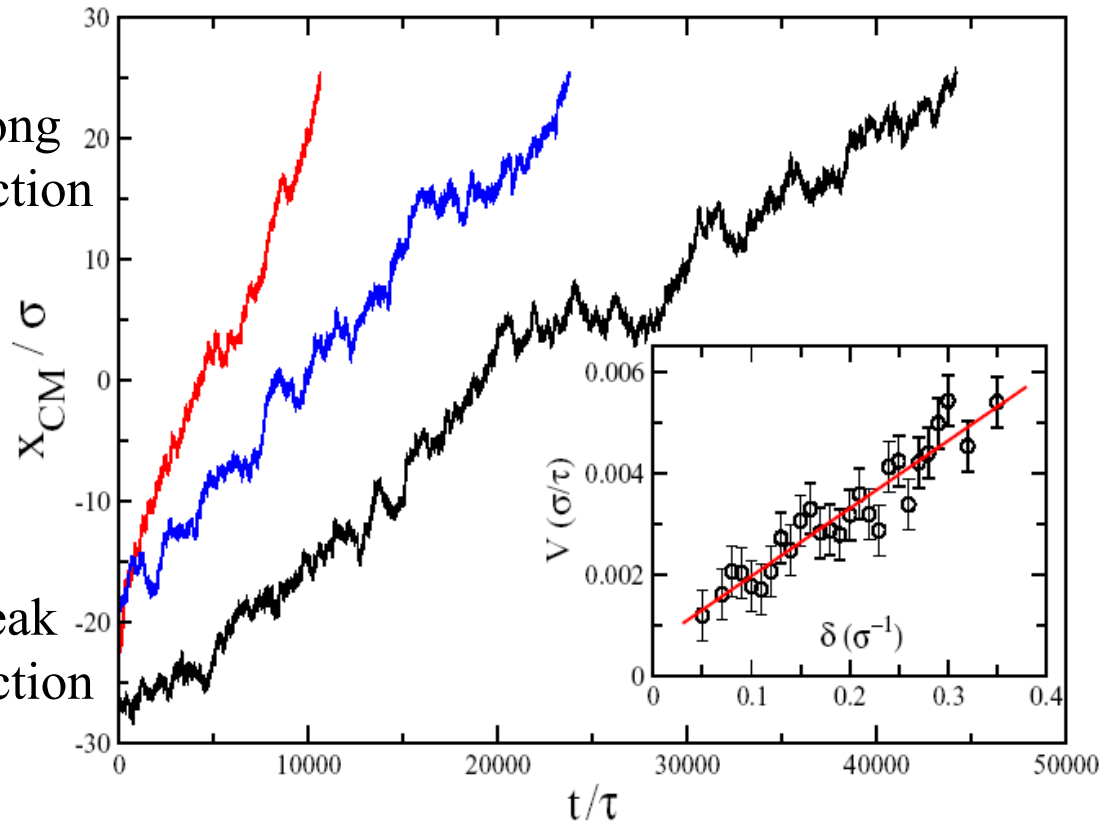
TEST:

F/N_{fluid} = free diffusion

$10^3 \cdot F/N_{fluid}$ = recover $\alpha \neq 0$

Droplet Diffusion Influenced by Adhesion Energy Variation

Isothermal wall conditions:



$$\varepsilon_{wf}(x) = \varepsilon_{wf}(1 + \delta x)$$

δ = surface energy gradient

$T_0 = 1.0\,\varepsilon/k_B$ is constant

- Faster motion for higher gradient δ
- Trajectory for $\delta = 0.1\ \sigma^{-1}$ is similar to motion at temperature gradient $\alpha = 0.0127\sigma^{-1}$

$$x_{CM} = \frac{1}{N_{fluid}} \sum_{i=1}^{N_{fluid}} x_i$$

Brochard, Langmuir **5**, 432 (1989)

Chaudhury and Whitesides, Science **256**, 1539 (1992)

Conclusions:

Using molecular dynamics simulations, we have investigated the behavior of polymeric droplet under imposed temperature gradient.

- Diffusion of the droplet's center of mass follows Arrhenius law.
- Faster CM droplet motion for higher temperature gradient.
- Thermocapillary effects at the liquid/vapor interface play a minor role.
- The motion of the droplet is dominated by the variable liquid-surface interaction energy. Drift velocity of the center of mass grows linearly with surface energy gradient.