Answer   MD Simulation for Microscale Heat Transfer

2000/8/10

For a substance expressed with Lennard-Jones (12-6) potential

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad (1)$$

answer the following questions.

(a) Derive the non-dimensional forms for following variables.

- Temperature T $\quad T^* = \dfrac{k_B T}{\varepsilon}$
- Force F $\quad F^* = \dfrac{F\sigma}{\varepsilon}$
- Pressure P $\quad P^* = \dfrac{P\sigma^3}{\varepsilon}$
- Surface tension γ $\quad \gamma^* = \dfrac{\gamma\sigma^2}{\varepsilon}$
- Thermal conductivity λ $\quad \lambda^* = \dfrac{\lambda\sigma^2\sqrt{m/\varepsilon}}{k_B}$

(b) Calculate the pair separation at which the Lennard-Jones potential is a minimum.

$$\frac{d\phi(r)}{dr} = -24\varepsilon\left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\frac{1}{r}$$

$$\frac{d\phi(r)}{dr} = 0 \rightarrow 2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} = 0$$

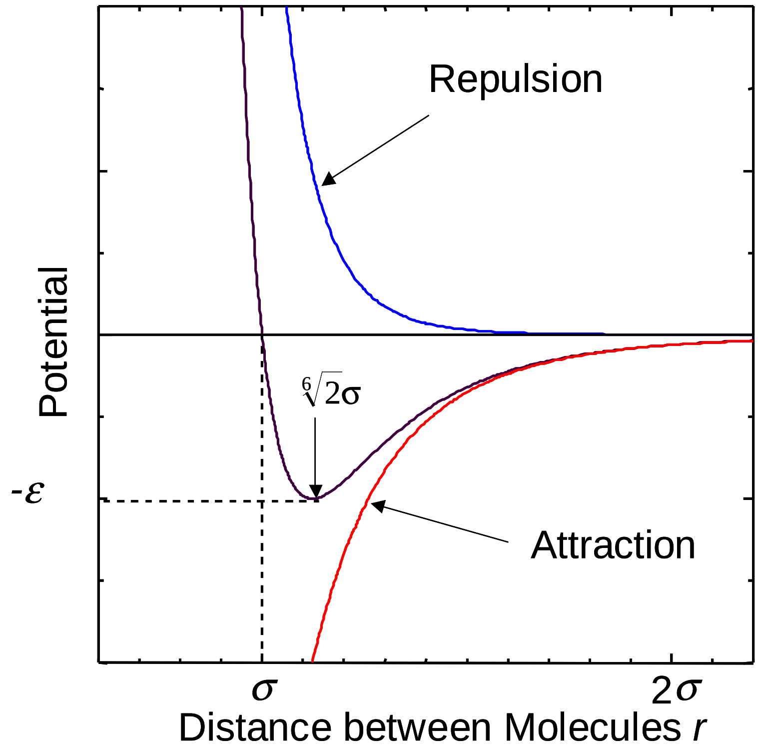
Then, $2\left(\dfrac{\sigma}{r}\right)^{6} - 1 = 0 \rightarrow \left(\dfrac{\sigma}{r}\right) = \sqrt[6]{\dfrac{1}{2}} \rightarrow r = \sqrt[6]{2}\sigma$

(c) Guess why “4” is used in equation (1). Isn’t is simpler to define the potential as

$$\phi(r) = \varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right].$$

With normal L-J the minimum energy is just -ε as following.

$$
\begin{aligned}
\phi\left(\sqrt[6]{2}\sigma\right) &= 4\varepsilon\left[\left(\frac{\sigma}{\sqrt[6]{2}\sigma}\right)^{12} - \left(\frac{\sigma}{\sqrt[6]{2}\sigma}\right)^{6}\right] \\
&= 4\varepsilon\left[\frac{1}{4} - \frac{1}{2}\right] \\
&= -\varepsilon
\end{aligned}
$$



(d) Use the Newton's second law to show that in terms of the potential parameters ε and σ, the unit of time is $\sigma\sqrt{m/\varepsilon}$, where m is the mass of one atom.

The Newton's second law in 1 dimension is

$$m\frac{d^2r}{dt^2} = -\frac{d\phi}{dr}$$

Setting that $r* = r/\sigma$, *and* $\phi* = \phi/\varepsilon$

$$m\frac{d^2(r*\sigma)}{dt^2} = -\frac{d(\phi*\varepsilon)}{d(r*\sigma)}$$

$$\frac{\sigma^2 m}{\varepsilon}\frac{d^2(r*)}{dt^2} = -\frac{d(\phi*)}{d(r*)}$$

$$\frac{d^2(r*)}{d\left(\frac{t}{\sigma\sqrt{m/\varepsilon}}\right)^2} = -\frac{d(\phi*)}{d(r*)}$$

So, $\tau = \sigma\sqrt{m/\varepsilon}$ is the natural choice.

(e) The long-range correction for potential energy E_p is expressed as

$$\frac{E_p}{N} = \frac{\tilde{E}_p}{N} + E_{pLR}$$

$$E_{pLR} \approx 2\pi\rho \int_{r_c}^{\infty} \phi(r) r^2 dr$$

Derive the following expression for Lennard-Jones potential.

$$E^*_{pLR} = \frac{8\pi\rho^*}{3(r_c^*)^3}\left(\frac{1}{3(r_c^*)^6} - 1\right)$$

$$E_{pLR} \approx 2\pi\rho \int_{r_c}^{\infty} \phi(r) r^2 dr$$

$$= 2\pi\rho \int_{r_c}^{\infty} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] r^2 dr$$

$$= 8\pi\rho\varepsilon\left[-\frac{1}{9}\sigma^{12} r^{-9} + \frac{1}{3}\sigma^6 r^{-3}\right]_{r_c}^{\infty}$$

$$= 8\pi\rho\varepsilon\left[\frac{1}{9}\sigma^{12} r_c^{-9} - \frac{1}{3}\sigma^6 r_c^{-3}\right]$$

$$= \frac{8\pi\rho\varepsilon\sigma^6}{3r_c^3}\left[\frac{\sigma^6}{3r_c^6} - 1\right]$$

Then $E_{pLR}* = \dfrac{E_{pLR}}{\varepsilon} = \dfrac{8\pi\rho *}{3r_c *^3}\left[\dfrac{1}{3r_c *^6} - 1\right]$

(f) Consider two molecules at $\boldsymbol{r}_i$ and $\boldsymbol{r}_j$. Probe that the force $\mathbf{F}_i = -\nabla_i \phi$ acting on molecule *i* is expressed as

$$\mathbf{F}_i = 24\varepsilon\left[2\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\frac{\mathbf{r}_{ij}}{r_{ij}^2}$$ where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $r_{ij} = |\mathbf{r}_{ij}|$.

$$
\begin{aligned}
\vec{F}_i &= -\nabla_i \phi(r_{ij}) \\
&= -\frac{\partial}{\partial x_i}\phi(r_{ij})\vec{i} - \frac{\partial}{\partial y_i}\phi(r_{ij})\vec{j} - \frac{\partial}{\partial z_i}\phi(r_{ij})\vec{k} \\
&= -\left\{\frac{\partial}{\partial r_{ij}}\phi(r_{ij})\right\}\frac{\partial r_{ij}}{\partial x_i}\vec{i} - \left\{\frac{\partial}{\partial r_{ij}}\phi(r_{ij})\right\}\frac{\partial r_{ij}}{\partial y_i}\vec{j} - \left\{\frac{\partial}{\partial r_{ij}}\phi(r_{ij})\right\}\frac{\partial r_{ij}}{\partial z_i}\vec{k} \\
&= 24\varepsilon\left[2\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\frac{1}{r_{ij}}\left[\frac{\partial r_{ij}}{\partial x_i}\vec{i} + \frac{\partial r_{ij}}{\partial y_i}\vec{j} + \frac{\partial r_{ij}}{\partial z_i}\vec{k}\right] \\
&= 24\varepsilon\left[2\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]\frac{\vec{r}_{ij}}{r_{ij}^{\ 2}}
\end{aligned}
$$

where,

$$
\begin{aligned}
\frac{\partial r_{ij}}{\partial x_i} &= \frac{\partial}{\partial x_i}\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \\
&= \frac{1}{2}\frac{2(x_i - x_j)}{\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}} \\
&= \frac{(x_i - x_j)}{r_{ij}}
\end{aligned}
$$

So,

$$
\begin{aligned}
\left[\frac{\partial r_{ij}}{\partial x_i}\vec{i} + \frac{\partial r_{ij}}{\partial y_i}\vec{j} + \frac{\partial r_{ij}}{\partial z_i}\vec{k}\right] &= \frac{1}{r_{ij}}\left[(x_i - x_j)\vec{i} + (y_i - y_j)\vec{j} + (z_i - z_j)\vec{k}\right] \\
&= \frac{\vec{r}_i - \vec{r}_j}{r_{ij}} \\
&= \frac{\vec{r}_{ij}}{r_{ij}}
\end{aligned}
$$