3. Calculation of Equilibrium Properties

3.1 Thermodynamic Properties

- Temperature, Internal Energy and Pressure
- Free Energy and Entropy

3.2 Calculation of Dynamic Properties

- Diffusion Coefficient
- Thermal Conductivity
- Shear Viscosity
- Infrared Absorption Coefficient

Temperature

$$T = \frac{1}{3Nk_B}\left\langle \sum_{i=1}^{N} m_i v_i^2 \right\rangle$$ For Monatomic Molecule

Remember Thermodynamics

$$\frac{E_k}{n_f N} = \frac{1}{2}k_B T$$ Kinetic energy for each freedom

$$n_f = \begin{cases} 3 & \textit{for monoatomic molecules} \\ 5 & \textit{for diatomic molecules} \end{cases}$$

Thermodynamics Properties

Internal Energy or Total Energy

$$U = E_k + E_p = \frac{3}{2}Nk_B T + \left\langle \sum_i \sum_{j>i} \phi(\mathbf{r}_{ij}) \right\rangle$$

Remember Thermodynamics for Ideal Gas

$$U = E_k = \frac{n_f}{2}N_A k_B T = \frac{n_f}{2}R_0 T$$ per mol

$$u = \frac{U}{m'} = \frac{n_f}{2}\frac{R_0}{m'}T = \frac{n_f}{2}RT$$ per mass

k_B : Boltzmann Constant, 1.38066×10^{-23} J/K
N_A : Avogadro Number, 6.02205×10^{23} 1/mol
R_0 : Universal Gas Constant, 8.31433 J/(mol K)
m': Molecular Weight (kg/mol)

Pressure by virial theorem

$$P = \frac{N}{V}k_B T - \frac{1}{3V}\left\langle \sum_i \sum_{j>i} \frac{\partial \phi}{\partial \mathbf{r}_{ij}} \cdot \mathbf{r}_{ij} \right\rangle$$

Thermodynamics for Ideal Gas

$$P = \frac{N}{V}k_B T$$

$$PV = nN_A k_B T = nR_0 T$$ For n mol

$$P = \frac{nN_A}{V}k_B T = \rho k_B T$$ ρ: Number density

Radial Distribution Function

Radial Distribution Function (Pair Correlation Function)

$$\rho g(r) = \frac{1}{N}\left\langle \sum_i^N \sum_{j\neq i}^N \delta[r - r_{ij}] \right\rangle$$

$$g(r) = \frac{\langle N(r,\Delta r)\rangle}{\frac{1}{2}N\rho V(r,\Delta r)}$$

Ratio of a local density ρ(r) to the system density ρ

Long-Range Corrections (1)

$$\frac{E_p}{N} = 2\pi\rho\int_0^\infty \phi(r)g(r)r^2 dr$$

$$\frac{E_p}{N} = 2\pi\rho\int_0^{r_c} \phi(r)g(r)r^2 dr + 2\pi\rho\int_{r_c}^\infty \phi(r)g(r)r^2 dr$$

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

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

$$E_{pLR}^* = \frac{8\pi\rho^*}{3(r_c^*)^3}\left(\frac{1}{3(r_c^*)^6} - 1\right) \approx -\frac{8\pi\rho^*}{3(r_c^*)^3}$$ For Lennard-Jones

Long-Range Corrections (2)

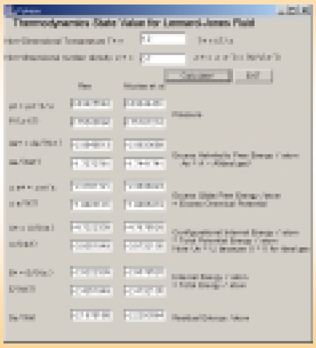
For Pressure

$$p = \tilde{p} + p_{LR}$$

$$p_{LR} = -\frac{2}{3}\pi\rho^2 \int_{r_c}^{\infty} r \frac{d\phi(r)}{dr} g(r) r^2 dr$$

$$p^*_{LR} = \frac{-16\pi\rho^{*2}}{3(r_c^*)^3}\left(1-\frac{2}{3(r_c^*)^6}\right) \approx \frac{-16\pi\rho^{*2}}{3(r_c^*)^3}$$ For Lennard-Jones

Empirical Relations(1)



Temperature
Density

Pressure
Helmholtz Free Energy
Gibbs Free Energy
Potential Energy
Internal Energy
Entropy

Ree correlation
and Nicolas et al. correlation

Empirical Relations(2)

$$P^* = \rho^* T^* + P_e^* = \rho^* T^* + f(\rho^*, T^*)$$

$$A_e^* = T^* \int_0^{\rho^*}\left(\frac{P^*}{\rho^* T^*}-1\right)\frac{1}{\rho^*}d\rho^*$$

$$U_e^* = \left.\frac{\partial(A_e/T^*)}{\partial T^*}\right|_{\rho^*} T^{*2} = \int_0^{\rho^*}\frac{1}{\rho^*}\left(P^*-T^*\left.\frac{\partial P^*}{\partial T^*}\right|_{\rho^*}\right)d\rho^*$$

$$T^* S_e^* = U^* + \left(\frac{P^*}{\rho^*} - T^*\right) - \mu_e^*$$

Test Particle Method(1)

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{EV} = -kT\left(\frac{\partial \ln\Omega}{\partial N}\right)_{EV}$$

$$\mu_e = \mu - \mu_{ig} = -kT \ln\left[\frac{1}{\langle kT\rangle^{3/2}}\left\langle (kT_{in})^{3/2}\exp\left[-\frac{U_t}{kT_{in}}\right]\right\rangle\right]$$

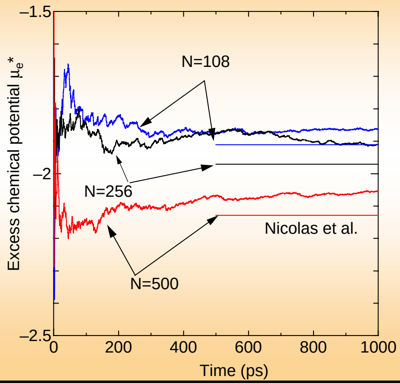
$kT_{in} = 2E_k/(3N)$ Instantaneous Temperature

$\mu_{ig} = -kT\ln[1/(\rho\Lambda^3)]$ Chemical Potential for Ideal Gas

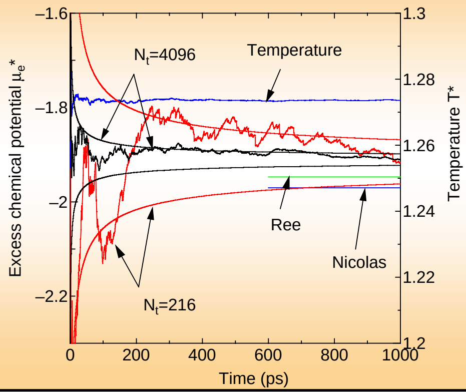
$\Lambda = \sqrt{h^2/(2\pi mkT)}$ Thermal De Broglie Wavelength

$U_t = U_{t,MD} - \frac{16\pi}{3}\frac{\rho^*}{r_{TC}^{*3}}$ Twice long-range correction

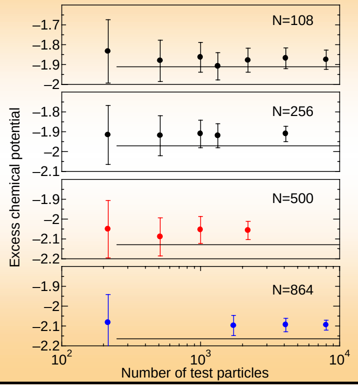
Test Particle Method (2)



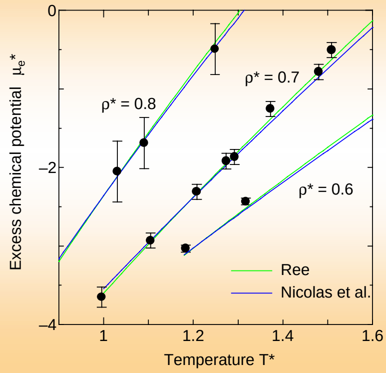
Test Particle Method (3)



Test Particle Method (4)



Test Particle Method (5)



Dynamic Properties

(Self) Diffusivity, Fick's Law

$$\dot{n} = -D\frac{\partial n}{\partial x}$$

Thermal Conductivity, Fourier's Law

$$q = -\lambda\frac{\partial T}{\partial x}$$

Viscosity, Newton Fluids

$$F = \mu\frac{\partial u}{\partial x}$$

Dynamic Properties

3 types of method:

Equilibrium Molecular Dynamics
:Correlation functions

Nonequilibrium Molecular Dynamics
:Fictious Field

Direct Molecular Dynamics
:Boundary Condition

Equilibrium Molecular Dynamics

(Self) Diffusivity

$$D = \frac{1}{3}\int_0^\infty < v_i(t)\cdot v_i(0) > dt$$

$$= \frac{1}{3}\int_0^\infty < v_x(t)\cdot v_x(0) + v_y(t)\cdot v_y(0) + v_z(t)\cdot v_z(0) > dt$$

Einstein's Equation:

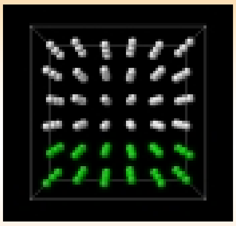
$$\gamma = \int_0^\infty < \dot{A}_i(t)\cdot \dot{A}_i(0) > dt$$

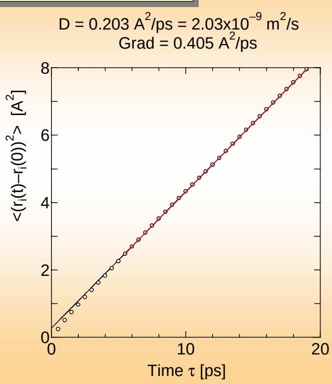
For large t

$$2t\gamma = \frac{1}{2t} < (A(t) - A(0))^2 >$$

$$D = \frac{1}{6t} < |r_i(t) - r_i(0)|^2 >$$

Diffusion Coefficient





Equilibrium Molecular Dynamics

Thermal Conductivity

$$D = \frac{V}{k_B T^2} \int_0^\infty < j_\alpha^\varepsilon(t) \cdot j_\alpha^\varepsilon(0) > dt$$

$$\lambda = \frac{V}{k_B T^2 2t} < (\delta\varepsilon_\alpha(t) - \delta\varepsilon_\alpha(0))^2 >$$

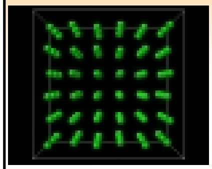
$$\delta\varepsilon_\alpha = \frac{1}{V}\sum_i r_{i\alpha}(\varepsilon_i - <\varepsilon_i>)$$

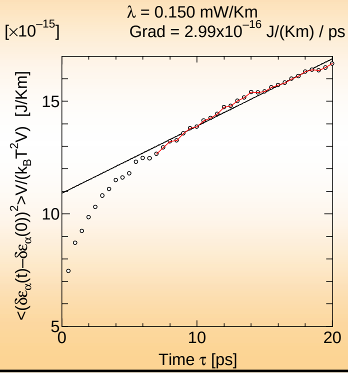
$$\delta\varepsilon_x = \frac{1}{V}\sum_i r_{ix}(\varepsilon_i - <\varepsilon_i>)$$

$$\delta\varepsilon_y = \frac{1}{V}\sum_i r_{iy}(\varepsilon_i - <\varepsilon_i>)$$

$$\varepsilon_i = p_i^2 / 2m_i + \frac{1}{2}\sum_{j \neq i} v(r_{ij})$$

Thermal Conductivity





Equilibrium Molecular Dynamics

Shear Viscosity

$$\mu = \frac{V}{k_B T} \int_0^\infty < \mathrm{P}_{\alpha\beta}(t) \cdot \mathrm{P}_{\alpha\beta}(0) > dt$$

$$= \frac{V}{k_B T 2t} < (\mathrm{D}_{\alpha\beta}(t) - \mathrm{D}_{\alpha\beta}(0))^2 >$$

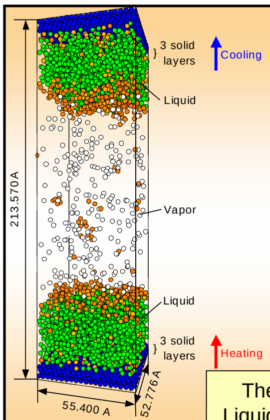
$$\mathrm{D}_{\alpha\beta} = \frac{1}{V}\sum_i r_{i\alpha} p_{i\beta}$$

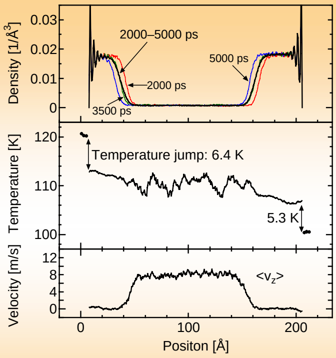
Property	Definition	Statistical Mechanical Green-Kubo Formula	With Einstein Relation For large *t*
Diffusion coefficient	$\dot{n} = -D\frac{\partial n}{\partial x}$	$\frac{1}{3}\int_0^\infty \langle \boldsymbol{v}_i(t)\cdot \boldsymbol{v}_i(0)\rangle dt$	$\frac{1}{6t}\left\langle \lvert \boldsymbol{r}_i(t) - \boldsymbol{r}_i(0)\rvert^2 \right\rangle$
Thermal conductivity[1]	$q = -\lambda\frac{\partial T}{\partial x}$	$\frac{V}{k_B T^2}\int_0^\infty \langle \tilde{q}_\alpha(t)\cdot \tilde{q}_\alpha(0)\rangle dt$	$\frac{V}{k_B T^2 2t}\left\langle (\delta\varepsilon_\alpha(t) - \delta\varepsilon_\alpha(0))^2 \right\rangle$
Shear viscosity[2]	$F = \mu\frac{\partial U}{\partial x}$	$\frac{V}{k_B T}\int_0^\infty \langle \tilde{p}_{\alpha\beta}(t)\cdot \tilde{p}_{\alpha\beta}(0)\rangle dt$	$\frac{V}{k_B T 2t}\left\langle \left(\tilde{D}_{\alpha\beta}(t) - \tilde{D}_{\alpha\beta}(0)\right)^2 \right\rangle$

$$\tilde{q}_\alpha = \frac{\mathrm{d}\delta\varepsilon_\alpha}{\mathrm{d}t},\quad \delta\varepsilon_\alpha = \frac{1}{V}\sum_i r_{i\alpha}(\varepsilon_i - \langle\varepsilon_i\rangle),\quad \varepsilon_i = \frac{m_i v_i^2}{2} + \frac{1}{2}\sum_{j\neq i}\phi(r_{ij}),\quad \alpha = x, y, z$$

NVE only. $\tilde{p}_{\alpha\beta} = \frac{1}{V}\left(\sum_i m_i v_{i\alpha} v_{i\beta} + \sum_i \sum_{j>i} r_{ij\alpha} f_{ij\beta}\right)$, $\tilde{D}_{\alpha\beta} = \frac{1}{V}\sum_i m_i r_{i\alpha} v_{i\beta}$, $\alpha\beta = xy, yz, zx$

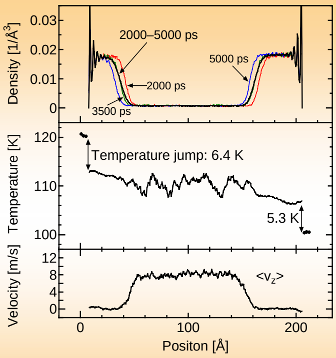
Dynamic Properties





Thermal Boundary Resistance over Liquid-Solid Interface: $10^{-7} \sim 10^{-6}$ m²K/W

Therm. Sci. Engng., 1999, vol. 7, no. 1, pp. 63-68.



Thermal Conductivity

$\lambda_L = q_W / (\partial T / \partial z)$

0.082 W/m·K

Handbook value
0.097 W/m·K
at the saturated temperature of 110 K

Thermal Resistance over Liquid-Solid Interface

Infrared Absorption Spectrum

Absorption Cross Section α(ω)

$$\alpha(\omega) = \frac{\pi\omega\{1 - \exp(-\hbar\omega / k_B T)\}}{3\varepsilon_0 \hbar n c N} I(\omega),$$

Quantum Mechanics
Perturbation Theory

Transition Rate I(ω)

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp(-i\omega t)\mathrm{d}t \langle \boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(t)\rangle_0$$

Power Spectrum
of Dipole Moment

Classical Limit

$$\hbar\omega / k_B T \to 0 \qquad \alpha(\omega) = \frac{\pi\omega^2}{3\varepsilon_0 k_B T n c N} I(\omega)$$

Monte Carlo Simulation (Metropolis Method)

Random Number

↓

Configuration of Molecules

↓

Weighted Average for Statistical Property

Random Change of Configuration
Select or not by the Probability
Distribution and Random Number

constant NVE (number, volume and energy: microcanonical)
constant NVT (number, volume and temperature: canonical)
constant NPT (number, pressure and temperature)
constant μVT (chemical potential, volume and temperature: grand-canonical)