II. Modelling MD trajectories - time series analysis

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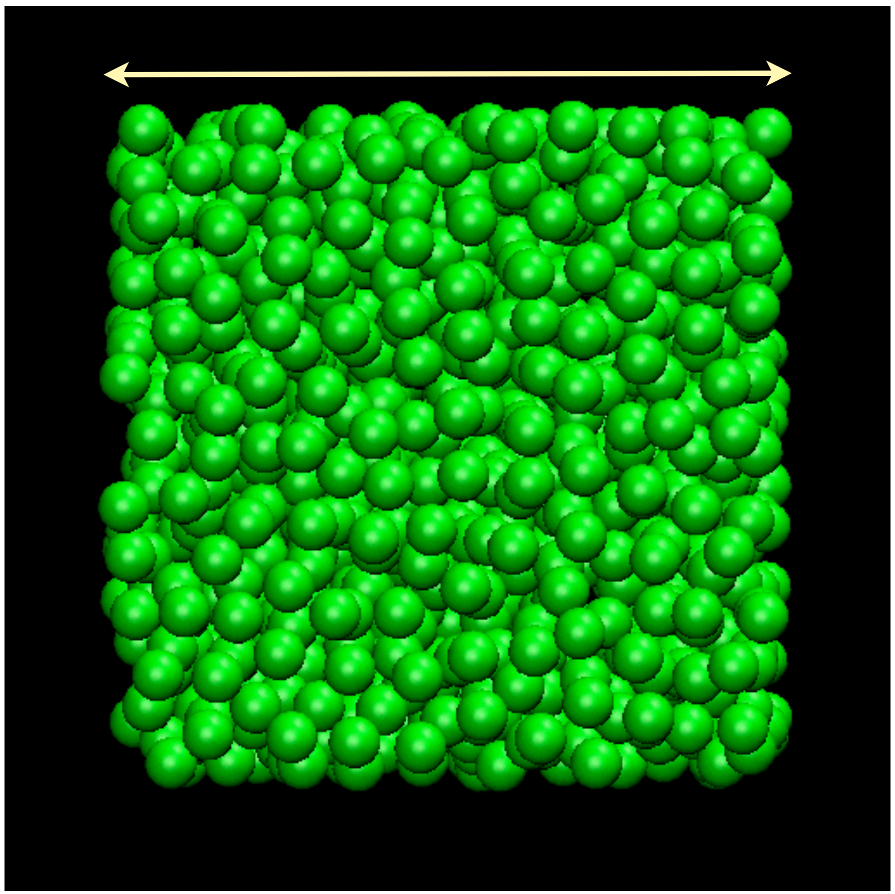
Molecular dynamics simulation

PHYSICAL REVIEW VOLUME 136, NUMBER 2A 19 OCTOBER 1964

Correlations in the Motion of Atoms in Liquid Argon*

A. RAHMAN
Argonne National Laboratory, Argonne, Illinois
(Received 6 May 1964)

~ 3.6 nm



- Solve Newton's equations of motion

$$M_i \ddot{\mathbf{r}}_i = -\frac{\partial U}{\partial \mathbf{r}_i}$$

$$U = \sum_{ij} 4\epsilon \left(\left[\frac{\sigma}{r_{ij}}\right]^{12} - \left[\frac{\sigma}{r_{ij}}\right]^{6} \right)$$

- Discretization and iterative solution yields trajectories = time series (< 100 ns)

$$\mathbf{r}_i(n+1) \leftarrow 2\mathbf{r}_i(n) - \mathbf{r}_i(n-1) + \frac{\Delta t^2}{M_i}\mathbf{F}_i(n)$$

$$\mathbf{v}_i(n) \leftarrow \frac{\mathbf{r}_i(n+1) - \mathbf{r}_i(n-1)}{2\Delta t}.$$

$$\text{Forces:} \quad \mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i}$$

PHYSICAL REVIEW VOLUME 159, NUMBER 1 5 JULY 1967

Computer "Experiments" on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules*

LOUP VERLET†
Belfer Graduate School of Science, Yeshiva University, New York, New York
(Received 30 January 1967)

The equation of motion of a system of 864 particles interacting through a Lennard-Jones potential has been integrated for various values of the temperature and density, relative, generally, to a fluid state. The equilibrium properties have been calculated and are shown to agree very well with the corresponding properties of argon. It is concluded that, to a good approximation, the equilibrium state of argon can be described through a two-body potential.

$$V(r)=4((\sigma/r)^{12}-(\sigma/r)^{6}).$$

interaction potential

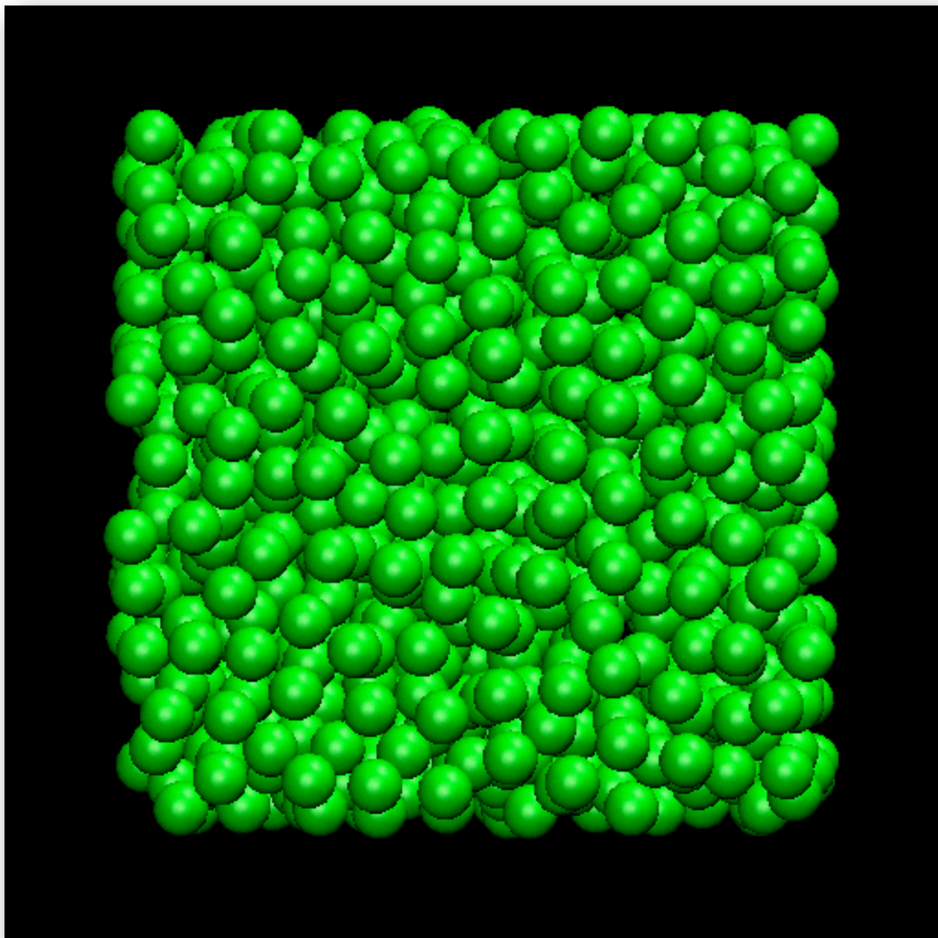
$$m\frac{d^2\mathbf{r}_i}{dt^2}=\sum_{j\neq i}\mathbf{f}(r_{ij}).$$

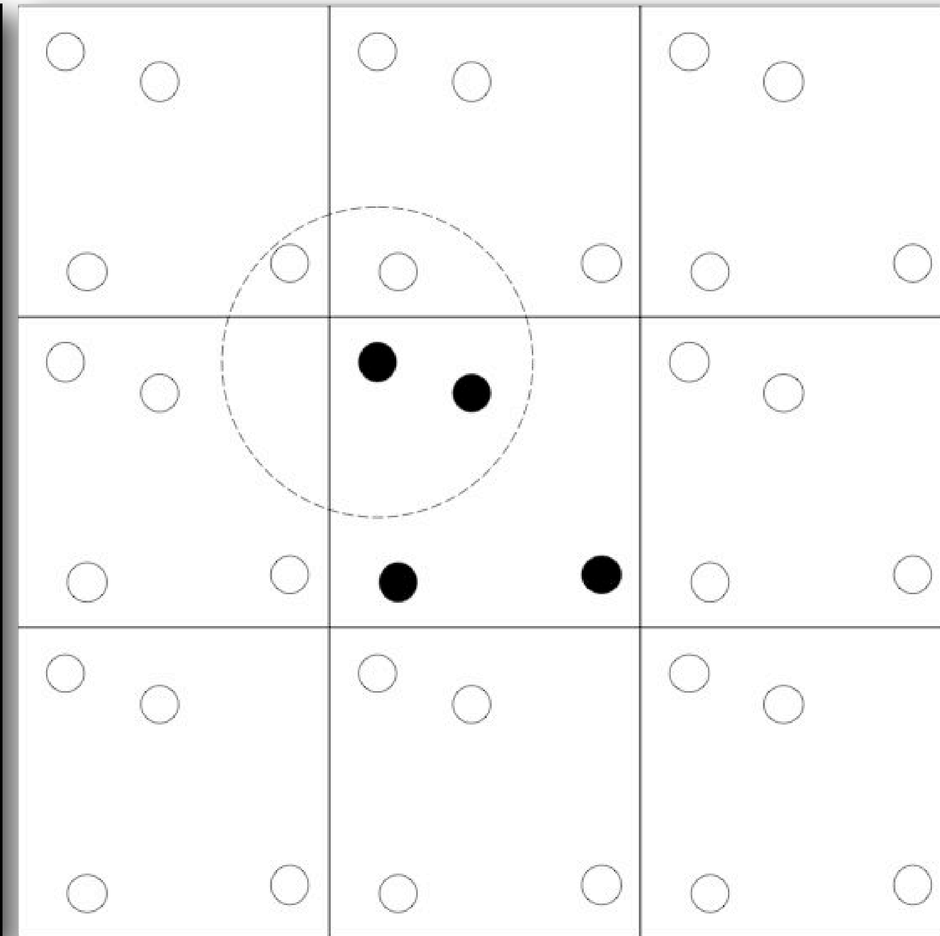
pairwise additive forces

$$\mathbf{r}_i(t+h)=-\mathbf{r}_i(t-h)+2\mathbf{r}_i(t)+\sum_{j\neq i}\mathbf{f}(r_{ij}(t))h^2,$$

Verlet algorithm

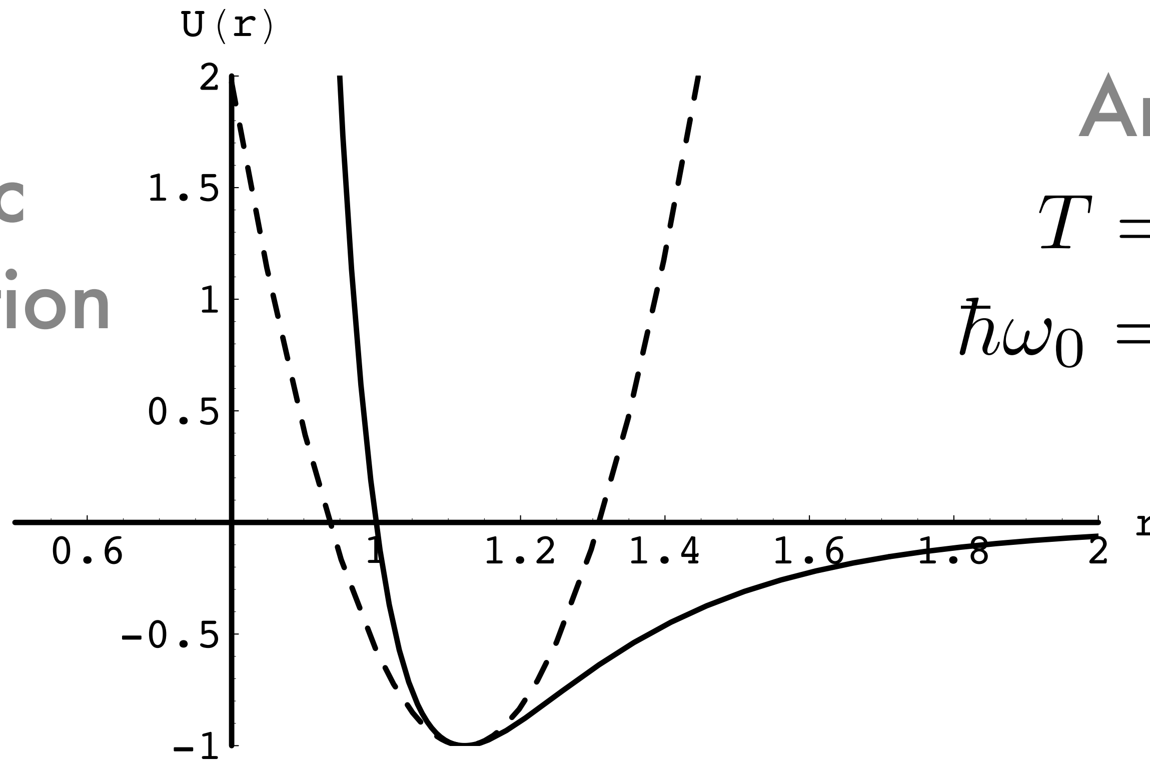
Periodic boundary conditions





The limit of classical mechanics

Harmonic approximation



Argon :

$$T = 94.4\,K$$

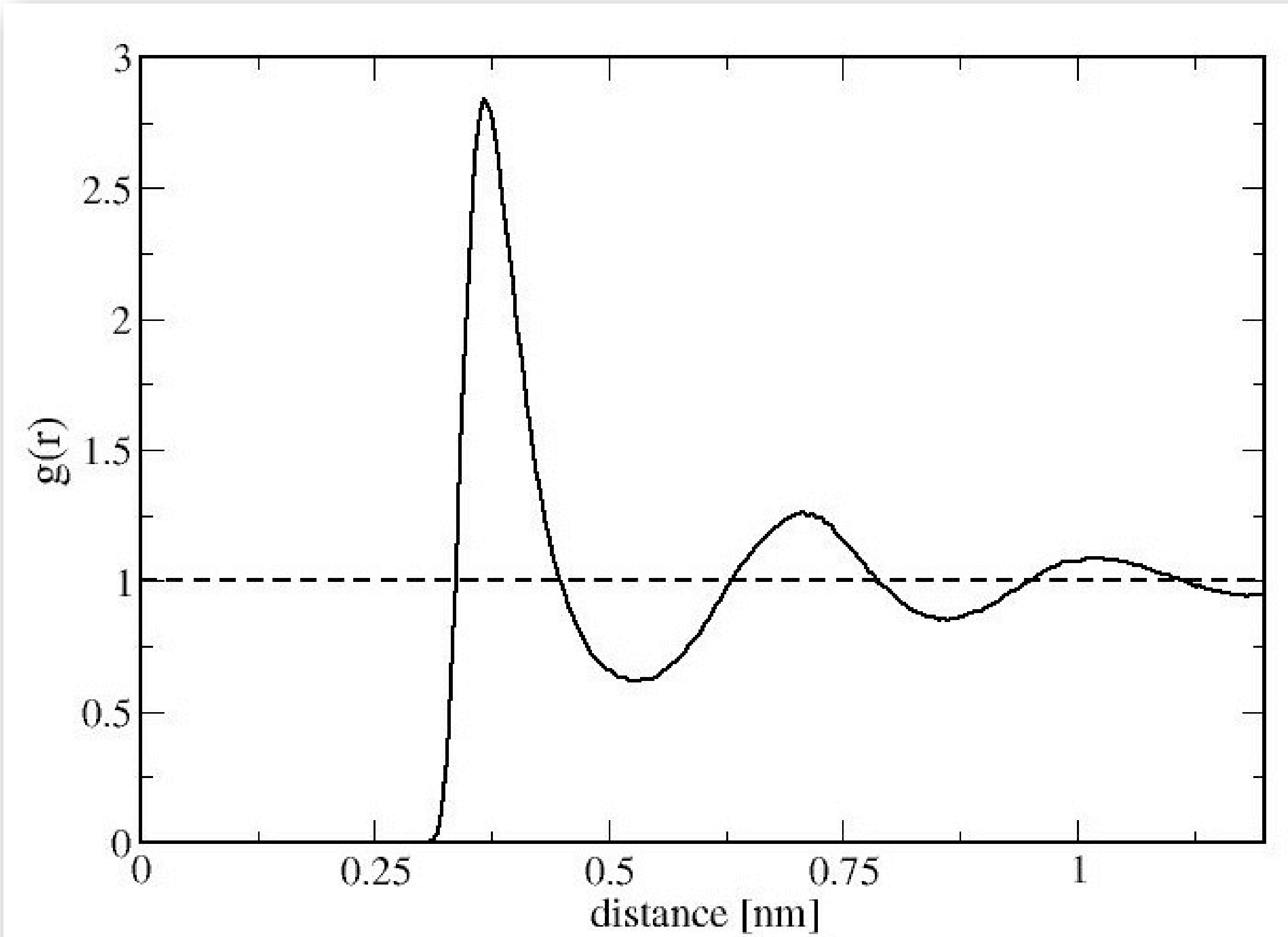
$$\hbar\omega_0 = 0.4\,k_B T$$

$$U_{LJ}(r) = 4\epsilon\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right) \approx -\epsilon + \frac{18\cdot 2^{2/3}\epsilon\left(r-r_0\right)^2}{\sigma^2}$$

$$\boxed{\hbar\omega_0 \ll k_B T}$$

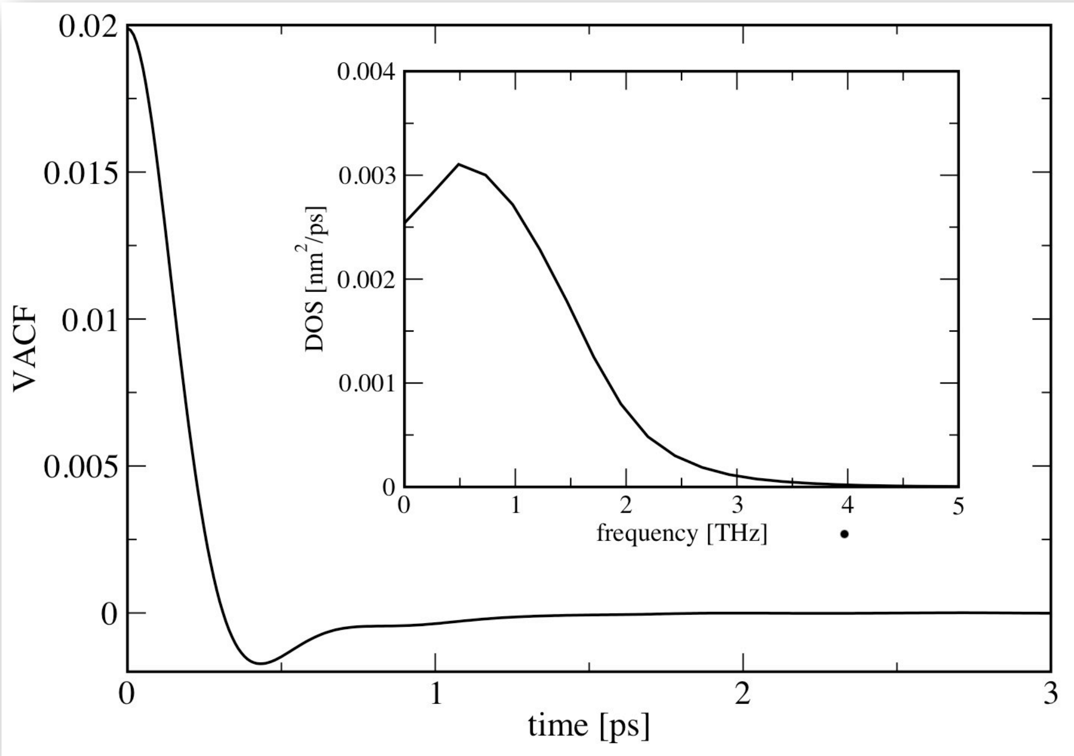
$$\omega_0 = \sqrt{\frac{18\cdot 2^{2/3}\epsilon}{\mu\sigma^2}}$$

Spatial correlations



$$g(r) = \frac{1}{4\pi r^2 \rho} \frac{1}{N} \sum_{\alpha} \sum_{\beta \neq \alpha} \langle \delta(r - |R_\alpha - R_\beta|) \rangle$$

Correlations in time



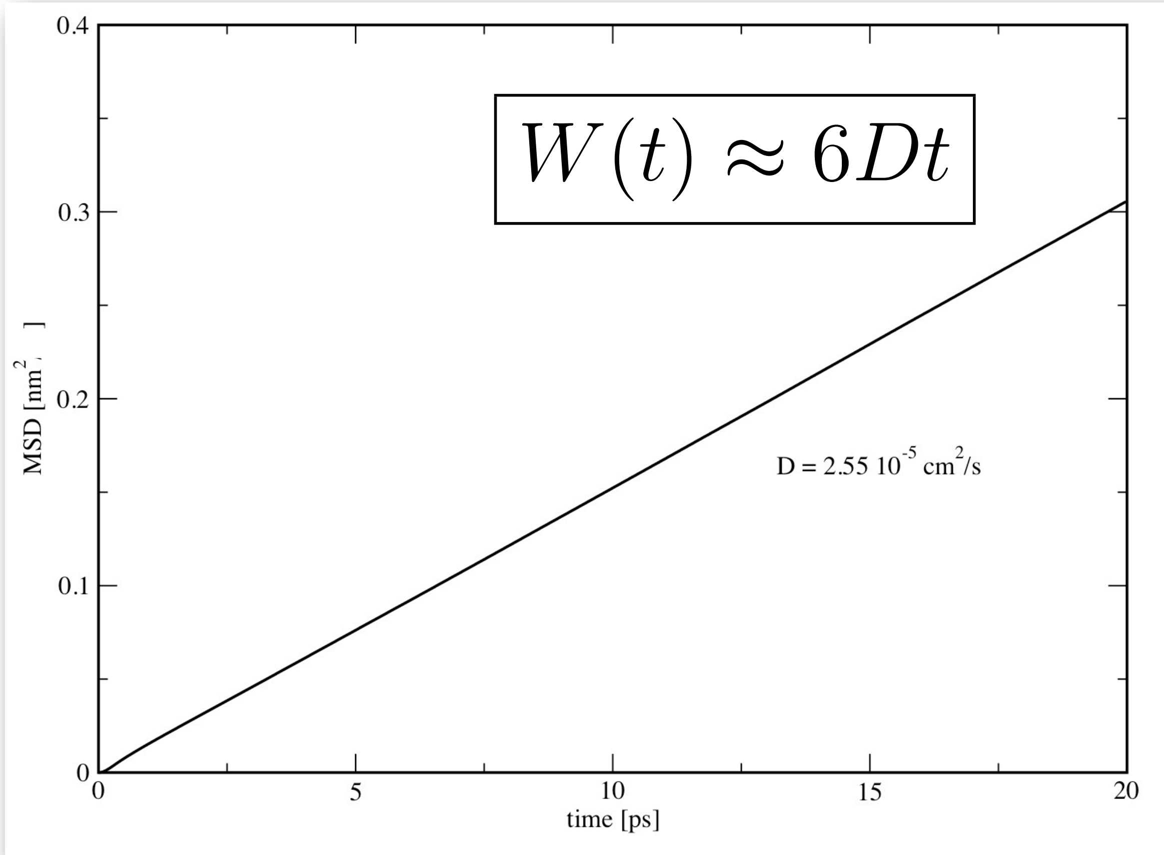
Velocity autocorrelation function and its Fourier spectrum (insert)

$$c_{vv}(n) = \frac{1}{N} \sum_{\alpha=1}^{N} w_\alpha c_{vv,\alpha}(n)$$

$$\tilde{c}_{vv}(k) = \frac{1}{2} \sum_{n=-N_t-1}^{N_t} w(n) c_{vv}(n) \exp\left(-2\pi i \frac{kn}{2N_t}\right)$$

$$c_{vv,\alpha}(n) = \frac{1}{3(N_t - n)} \sum_{k=0}^{N_t-n-1} \mathbf{v}_\alpha^T(k+n) \cdot \mathbf{v}_\alpha(k), \quad n = 0, 1, 2, \ldots$$

Mean square displacement



$$W(n) = \frac{1}{N} \sum_{\alpha=1}^{N} w_\alpha W_\alpha(n)$$

$$W_\alpha(n) = \frac{1}{N_t - n} \sum_{k=0}^{N_t-n-1} \Big(\mathbf{R}_\alpha(k+n) - \mathbf{R}_\alpha(k) \Big)^2, \quad n = 0, 1, 2, \ldots$$

Autoregressive (AR) model

$$v(n) \equiv v(n\Delta t), \quad n \in \mathbb{Z}.$$

time series

$$\boxed{v(n) = \sum_{k=1}^{P} a_k^{(P)} v(n-k) + \epsilon_P(n)}$$

AR model of order P

$$\begin{aligned} \langle \epsilon_P(n) \rangle &= 0, \\ \langle \epsilon_P(n) \epsilon_P(n') \rangle &= \sigma_P^2 \delta_{nn'}. \end{aligned}$$

"white noise"

parameters of the model: $\alpha_1^{(P)}, \ldots, \alpha_P^{(P)}, \sigma_P$

Wiener-Hopf equations

$$\langle \epsilon_P(n) v(n-k) \rangle = 0 \qquad (k = 1, \ldots, P)$$

$$\Rightarrow \boxed{\sum_{k=1}^{P} c_{vv}(|j-k|) a_k^{(P)} = c_{vv}(j), \qquad j = 1 \ldots P}$$

yields the coefficients $a_k^{(P)}$

$$\Rightarrow \boxed{\sigma_P^2 = c_{vv}(0) - \sum_{k=1}^{P} a_k^{(P)} c_{vv}(k)}$$

Wiener-Khintchine theorem

- Finite sample of a signal

$$v_M(n) = \begin{cases} v(n) & \text{si} \quad -M \leq n \leq M \\ 0 & \text{sinon} \end{cases}$$

- z-Transform

$$f(n) = \frac{1}{2\pi i} \oint_C dz\, z^{n-1} F_{(>)}(z) \quad \longleftrightarrow \quad \begin{aligned} F(z) &= \sum_{n=-\infty}^{+\infty} f(n) z^{-n}. \\ F_>(z) &= \sum_{n=0}^{\infty} f(n) z^{-n}. \end{aligned}$$

$$(f \circ g)(n) = \sum_{j=-\infty}^{+\infty} f(n+j) g^*(j) \quad \longleftrightarrow \quad F(z) G^*(1/z^*)$$

- Correlation function

$$c_{vv}(n) = \lim_{M \to \infty} \frac{1}{2M+1} \sum_{k=-M}^{M} v(n+k) v^*(k)$$

$$\Rightarrow \quad \boxed{C_{vv}(z) = \lim_{M \to \infty} \frac{1}{2M+1} V_M(z) V_M^*(1/z^*)}$$

Fluctuation & dissipation

AR model
$$V(z) = \frac{\mathcal{E}_P(z)}{1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}}$$

$$\lim_{M\to\infty} \frac{1}{2M+1} V(z) V^*(1/z^*) = \frac{\lim_{M\to\infty} \frac{1}{2M+1} \mathcal{E}_P(z)\mathcal{E}_P^*(1/z^*)}{\left(1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right)\left(1 - \sum_{l=1}^{P} a_l^{(P)} z^{l}\right)}$$

$$C_{vv}^{(AR)}(z) = \frac{C_{\epsilon\epsilon}(z)}{\left(1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right)\left(1 - \sum_{l=1}^{P} a_l^{(P)} z^{l}\right)}$$

$$C_{vv}^{(AR)}(z) = \frac{\sigma_P^2}{\left(1 - \sum_{k=1}^{P} a_k^{(P)} z^{-k}\right)\left(1 - \sum_{l=1}^{P} a_l^{(P)} z^{l}\right)}$$

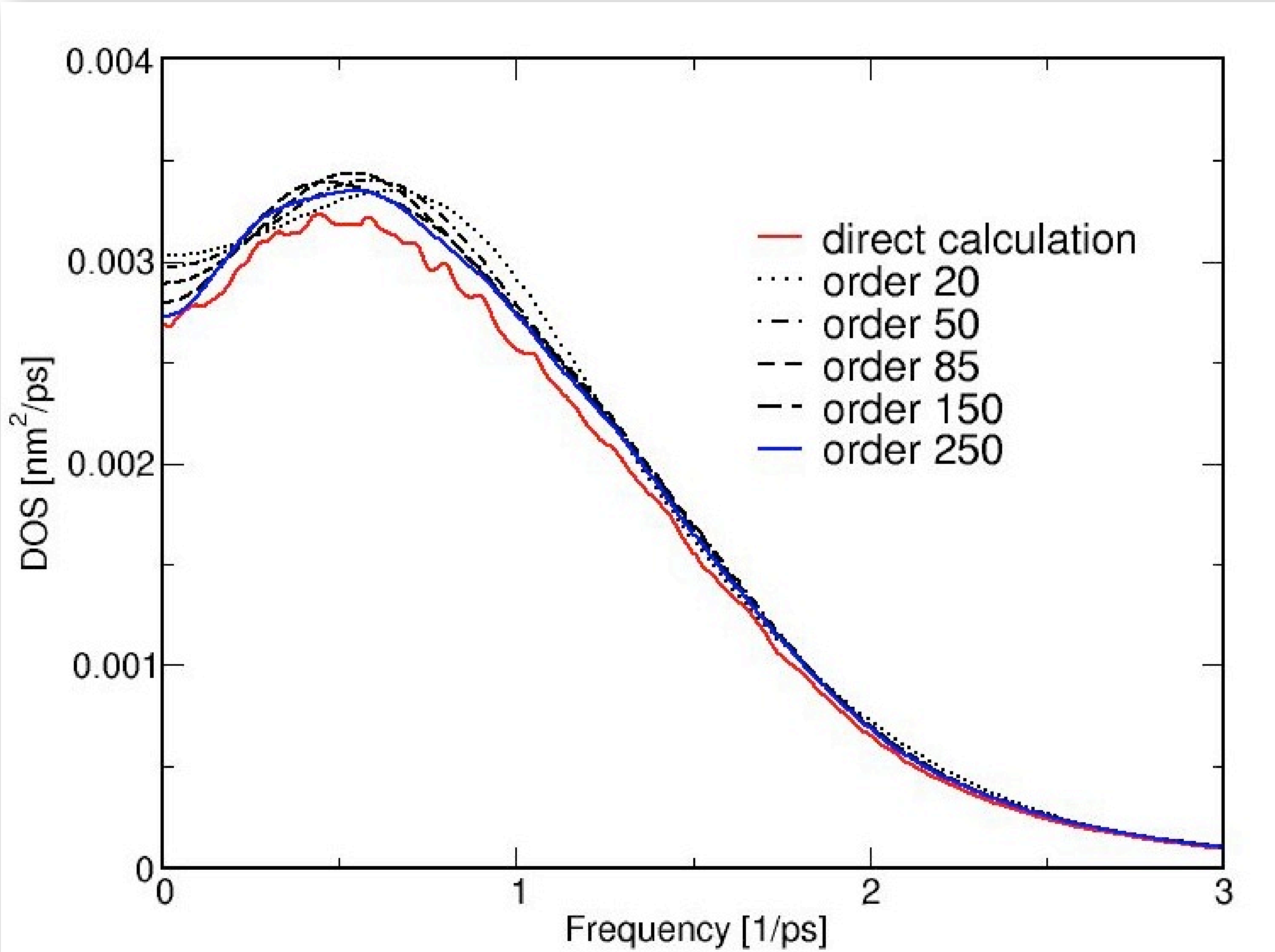
"all pole" model

Spectral analysis

$$\tilde{c}_{vv}^{(AR)}(\omega) = \Delta t \sum_{n=-\infty}^{+\infty} c_{vv}^{(AR)}(n) \exp[-in\omega\Delta t] \approx \tilde{c}_{vv}(\omega)$$

$$\boxed{\tilde{c}_{vv}^{(AR)}(\omega) = \Delta t \, C_{vv}^{(AR)}\left(\exp[i\omega\Delta t]\right)}$$

DOS for liquid argon



G.R. Kneller and K. Hinsen. *J. Chem. Phys.*, 115(24):11097–11105, 2001.

Correlation function

$$p(z) = z^P - \sum_{k=1}^{P} a_k^{(P)} z^{P-k}$$

characteristic polynomial

$$C_{vv}^{(AR)}(z) = \frac{1}{a_P^{(P)}} \frac{-z^P \sigma_P^2}{\prod_{k=1}^{P}(z - z_k) \, \prod_{l=1}^{P}(z - z_l^{-1})}$$

$$|z_k|_{max} < |z| < \frac{1}{|z_k|_{max}}$$

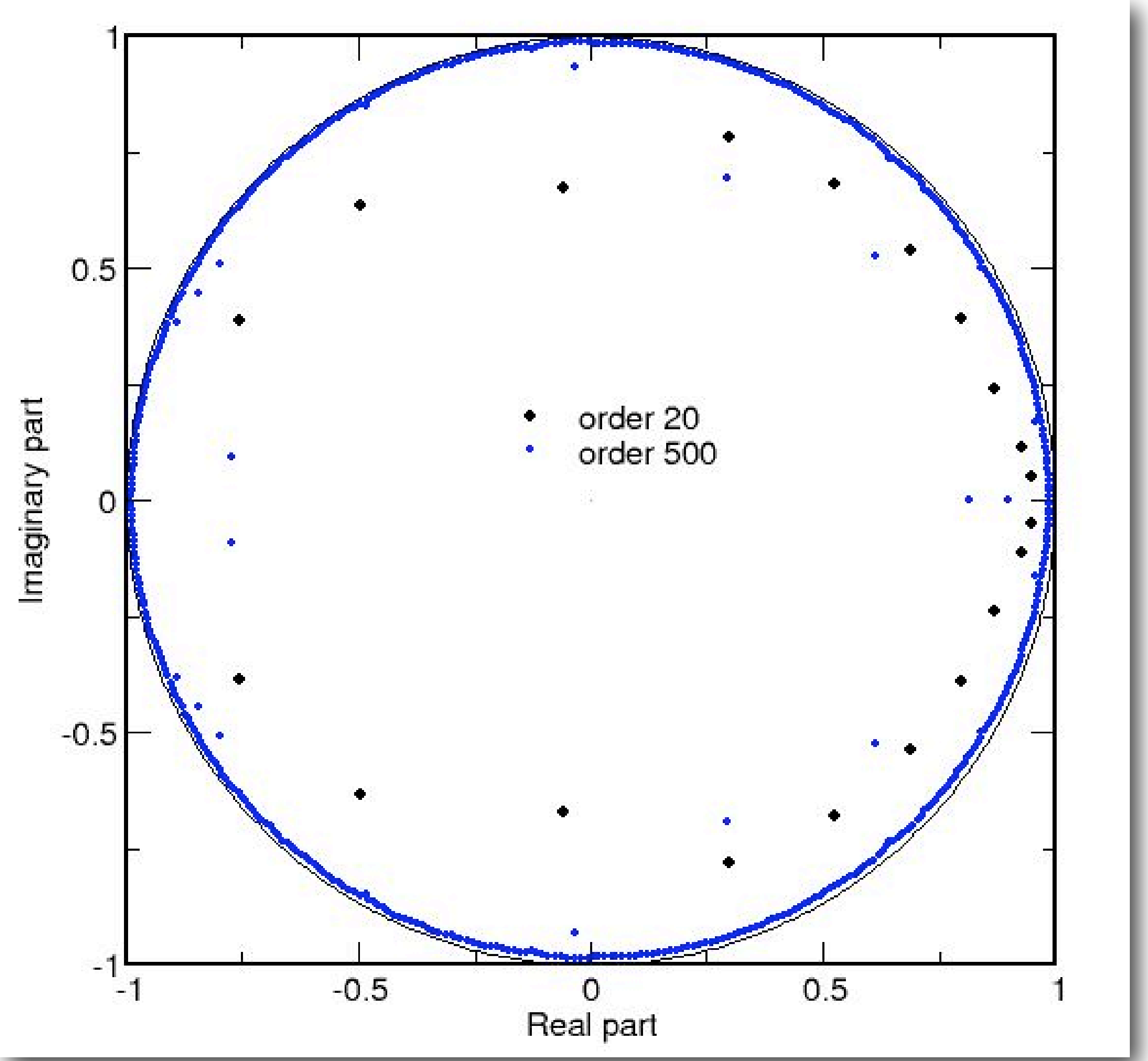
zéros de $p(z)$

$$c_{vv}^{(AR)}(n) = \sum_{j=1}^{P} \beta_j z_j^{|n|}$$

$$\beta_j = \frac{1}{a_P^{(P)}} \frac{-z_j^{P-1} \sigma_P^2}{\prod_{k=1,k\neq j}^{P}(z_j - z_k) \, \prod_{l=1}^{P}(z_j - z_l^{-1})}$$

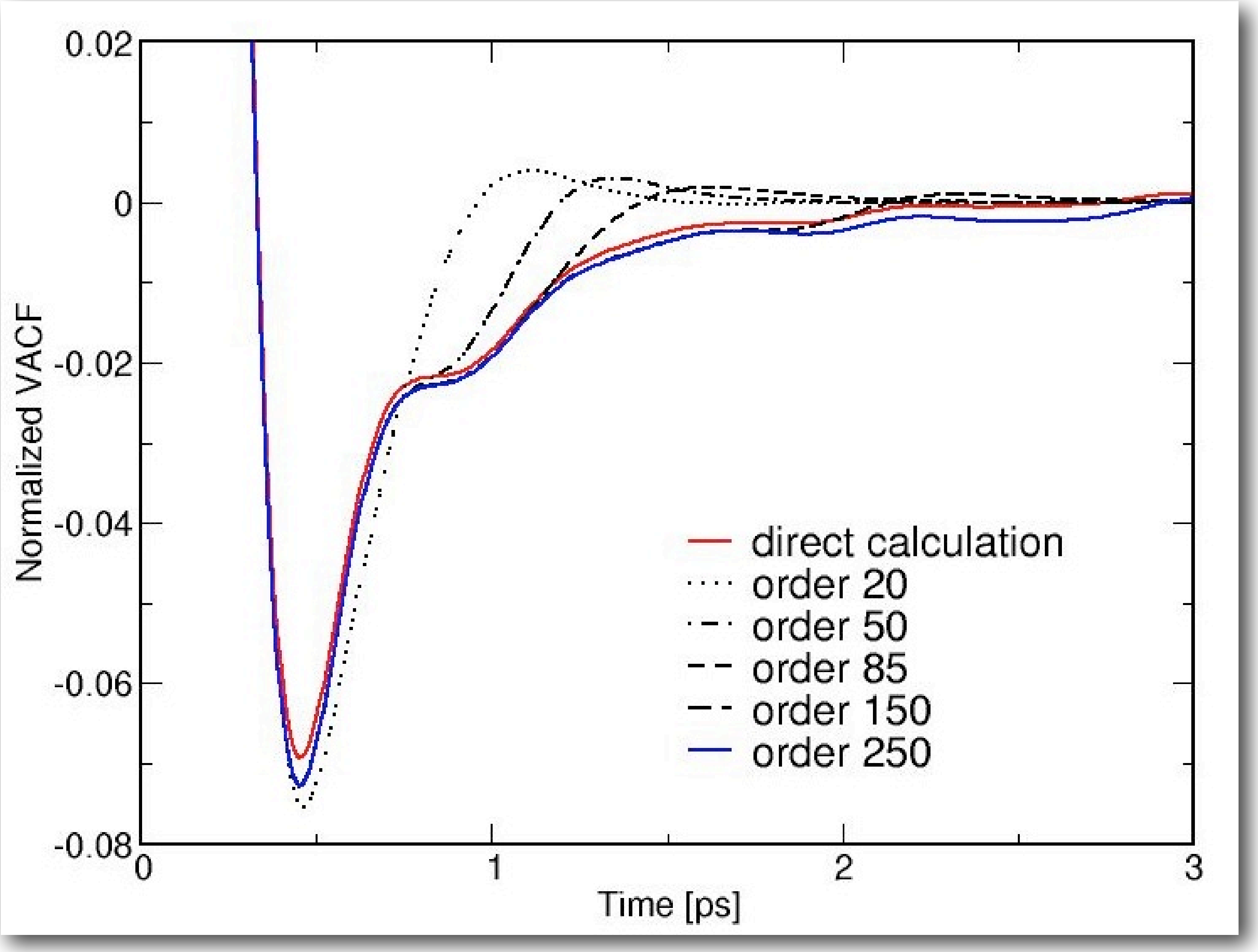
$$|z_k| < 1, \qquad k = 1, \ldots, P$$

stability



Poles in the complex plane

VACF for liquid argon



Memory function

$$\frac{c_{vv}(n+1) - c_{vv}(n)}{\Delta t} = -\sum_{k=0}^{n} \Delta t \, \kappa(n-k) c_{vv}(k)$$

$$\frac{zC_{vv,>}(z) - zc_{vv}(0) - C_{vv,>}(z)}{\Delta t} = -\Delta t K_{>}(z) C_{vv,>}(z)$$

$$K_{>}(z) = \frac{1}{\Delta t^2}\left(\frac{zc_{vv}(0)}{C_{vv,>}(z)} + 1 - z\right)$$

$$C_{vv,>}^{(AR)}(z) = \sum_{j=1}^{P} \beta_j \frac{z}{z - z_j}$$

$$\sum_{n=0}^{\infty} \kappa^{(AR)}(n) z^{-n} = \frac{1}{\Delta t^2}\left(\frac{c_{vv}(0)}{\sum_{j=1}^{P} \beta_j \frac{1}{z - z_j}} + 1 - z\right)$$

calculus of $\kappa(n)$ by polynomial division

Memory function from a given correlation function

$$\dot{c}(t) = -\int_0^t d\tau\, c(t-\tau)\kappa(\tau)$$

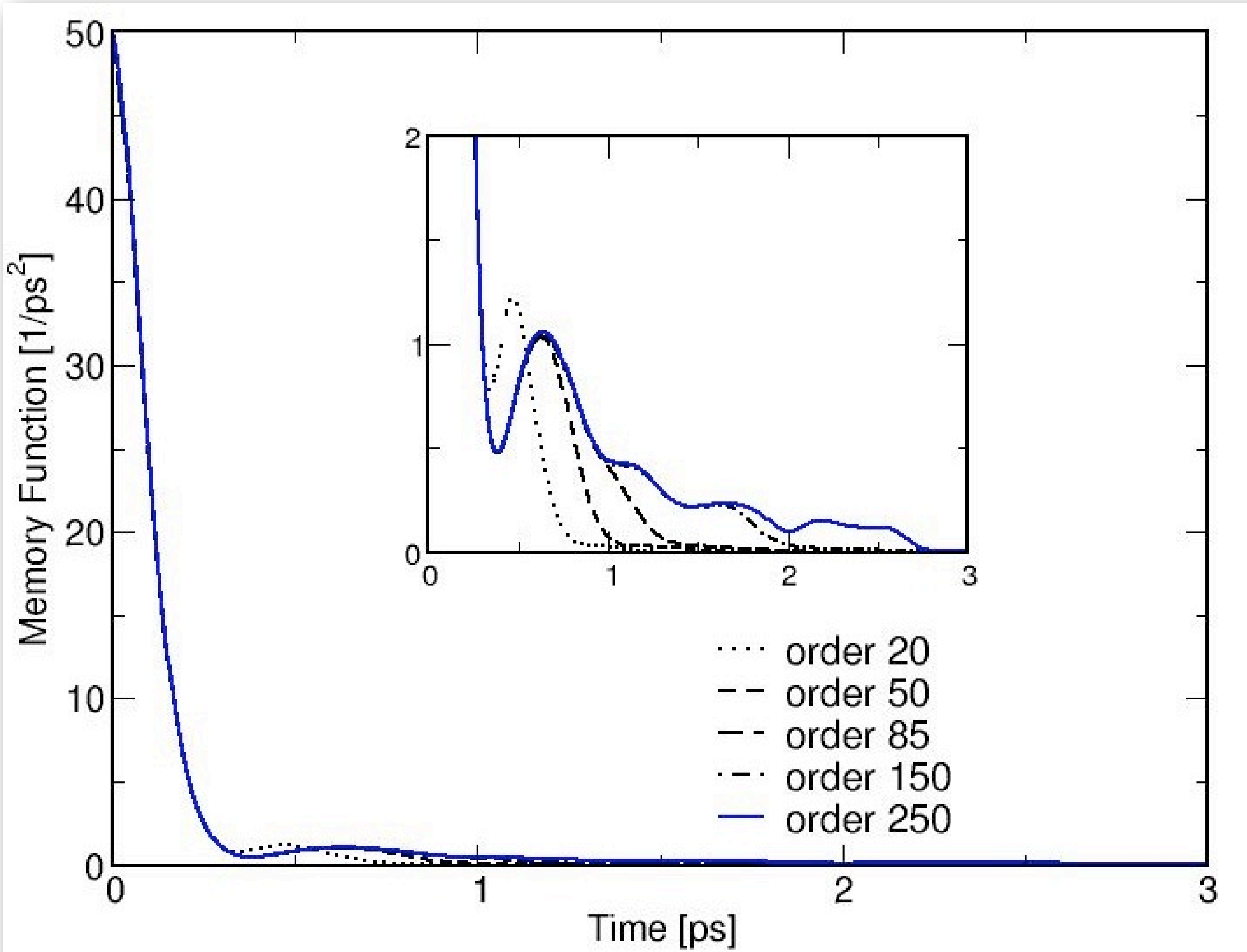
$$\dot{c}(n) = -\sum_{k=0}^{n} \Delta t\, w_k c(n-k)\kappa(k), \quad n = 0, \ldots, P.$$

$$\dot{c}(n) \approx \frac{c(n+1) - c(n)}{\Delta t}$$

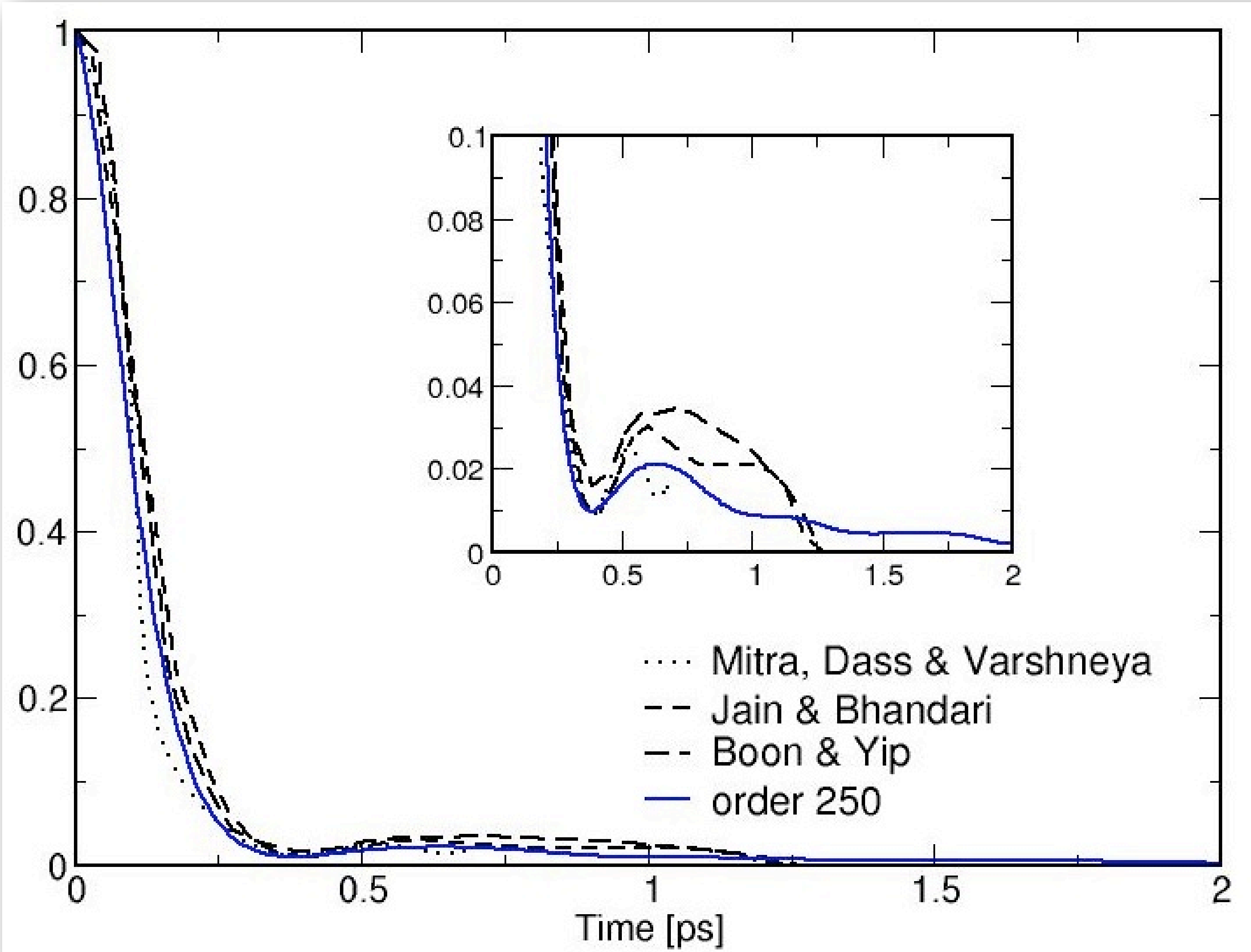
$$\begin{pmatrix} c(0) & 0 & 0 & 0 & \ldots & 0 \\ c(1) & c(0) & 0 & 0 & \ldots & 0 \\ c(2) & c(1) & c(0) & 0 & \ldots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ c(P) & c(P-1) & c(P-2) & c(P-3) & \ldots & c(0) \end{pmatrix} \begin{pmatrix} w_0\kappa(0) \\ w_1\kappa(1) \\ w_2\kappa(2) \\ \vdots \\ w_P\kappa(P) \end{pmatrix} = -\frac{1}{\Delta t} \begin{pmatrix} \dot{c}(0) \\ \dot{c}(1) \\ \dot{c}(2) \\ \vdots \\ \dot{c}(P) \end{pmatrix}$$

Recursive solution...

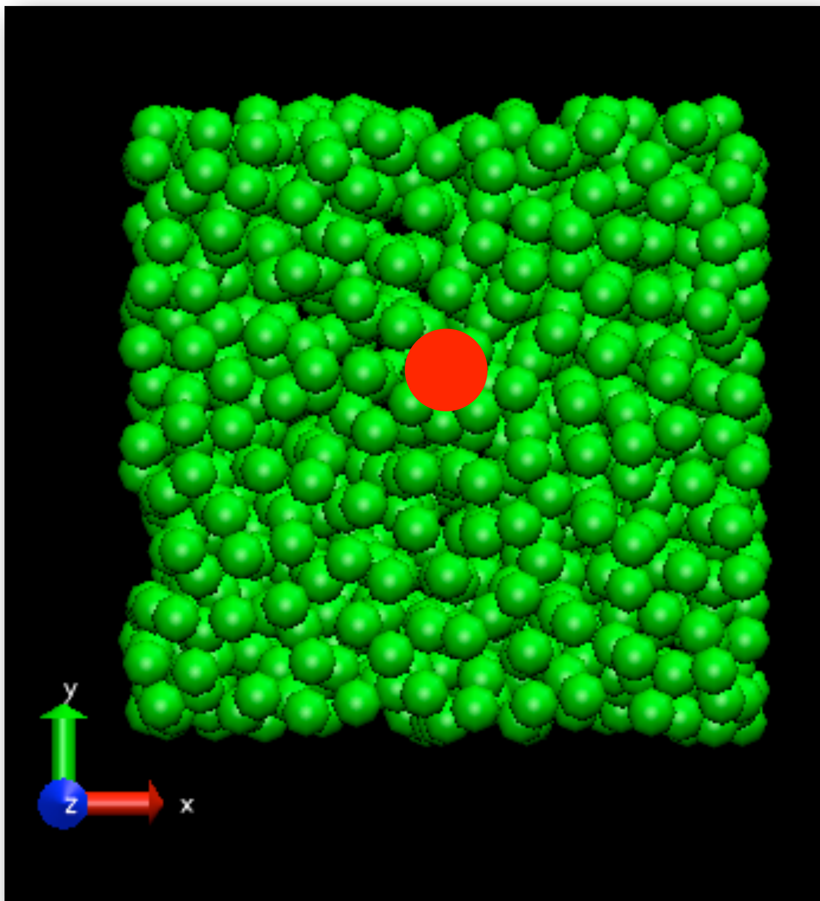
Memory function for liquid argon



Numerical results and analytical models



Brownian dynamics

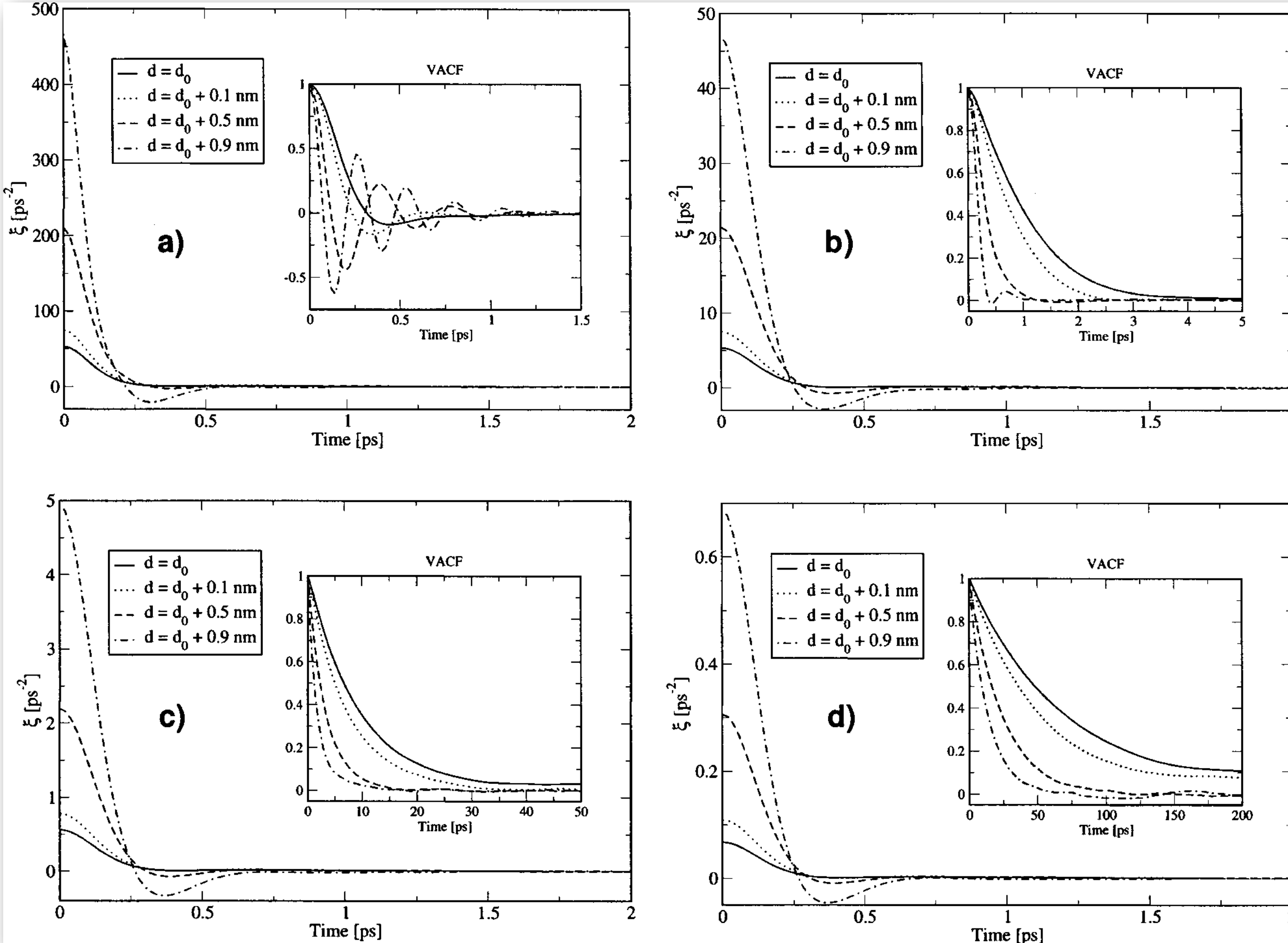


$$U_{SS} = \sum_{ij \in S} 4\epsilon \left(\left[\frac{\sigma}{r_{ij}} \right]^{12} - \left[\frac{\sigma}{r_{ij}} \right]^{6} \right),$$

$$U_{TS} = \sum_{j \in S} 4\epsilon \left(\left[\frac{\sigma}{r_{Tj} - \delta} \right]^{12} - \left[\frac{\sigma}{r_{Tj} - \delta} \right]^{6} \right)$$

S = solvant, T = traceur

Vary the mass and the size of the tracer particle independently



G.R. Kneller, K. Hinsen, and G. Sutmann. *J. Chem. Phys.*, 118(12):5283–5286, 2003.

Qualitative interpretation by a two-pole model

$$\kappa(t) = \kappa(0)\exp(-\eta t)$$

$$\kappa(0) = \frac{\langle \delta F^2 \rangle}{\mu k_B T} \equiv \omega_0^2$$

$$c_{vv}(t) = \frac{k_B T}{M}\exp\left(-\frac{\eta t}{2}\right)\left\{\cos(\tilde{\omega}_0 t) + \frac{\eta}{2\tilde{\omega}_0}\sin(\tilde{\omega}_0 t)\right\}$$

$$\tilde{\omega}_0 = \sqrt{\omega_0^2 - \frac{\eta^2}{4}}$$

a) Large and light particle: $\omega_0 \gg \eta \Rightarrow \tilde{\omega}_0 \approx \omega_0$

b) Small and heavy particle : $\omega_0 \ll \eta$

$$c_{vv}(t) \approx \frac{k_B T}{M}\exp\left(-\omega_0^2 \eta^{-1} t\right) \qquad (t \gg \eta^{-1})$$

$$\gamma = \omega_0^2 \eta^{-1} = \int_0^\infty dt\, \kappa(t)$$

$$\omega_0^2 \ll \eta^2 \Rightarrow \gamma \ll \eta$$

Separation of time scales for $c_{vv}t)$ (”slow”) and $\kappa(t)$ (”fast”)

Justification of form b)

$$\hat{c}_{vv}(s) = \frac{k_B T}{M} \frac{s+\eta}{s(s+\eta)+\omega_0^2}$$

$$c_{vv}(t) = \frac{1}{2\pi i} \oint_C ds\ \exp(st)\hat{c}_{vv}(s)$$

$$s_{1,2} = -\frac{\eta}{2}\left(1 \mp \sqrt{1 - \left[\frac{2\omega_0}{\eta}\right]^2}\right)$$

$\omega_0 \ll \eta$

$$\begin{aligned} s_1 &\approx -\omega_0^2 \eta^{-1}, \\ s_2 &\approx -\eta. \end{aligned}$$

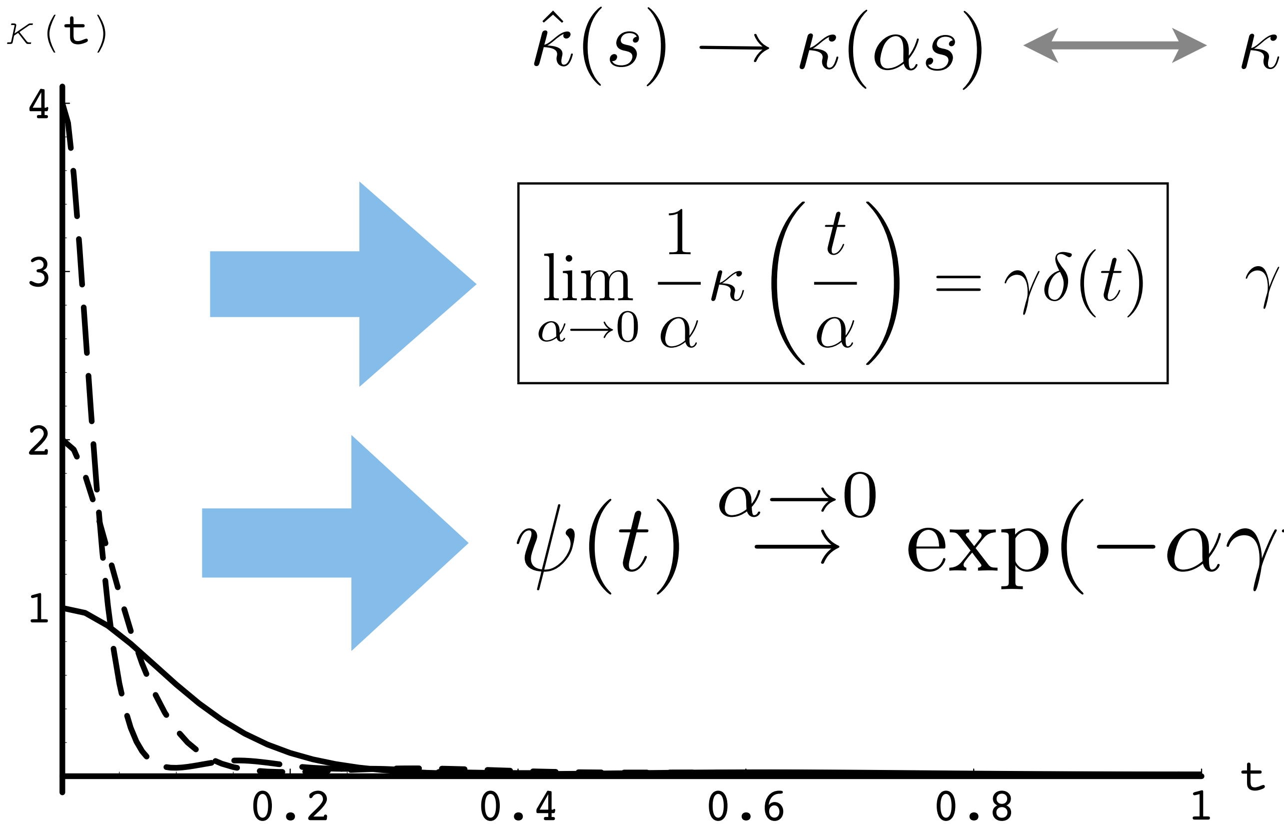
$$c_{vv}(t) = c_1 \exp(s_1 t) + \underbrace{c_2 \exp(s_2 t)}_{\approx 0 \text{ if } t \gg \eta^{-1}}$$

Scaling of the memory function

$$\psi_\alpha(t) = \frac{1}{2\pi i}\oint_C ds\, \frac{\exp(st)}{s+\alpha\hat{\kappa}(s)},$$

$$\overset{s\to s/\alpha}{=} \frac{1}{2\pi i}\oint_{C'} ds\, \frac{\exp(s\alpha t)}{s+\hat{\kappa}(\alpha s)}.$$

$$\hat{\kappa}(s) \to \kappa(\alpha s) \longleftrightarrow \kappa(t) \to \frac{1}{\alpha}\kappa\left(\frac{t}{\alpha}\right)$$



$$\boxed{\lim_{\alpha\to 0}\frac{1}{\alpha}\kappa\left(\frac{t}{\alpha}\right) = \gamma\delta(t)} \qquad \gamma \equiv \int_0^\infty dt\,\kappa(t)$$

$$\psi(t) \overset{\alpha\to 0}{\longrightarrow} \exp(-\alpha\gamma t)$$

The limit $\alpha \to 0$ has no physical meaning!

Define a coarse-grained time scale

$$\frac{\psi(t+\Delta t)-\psi(\Delta t)}{\Delta t} = -\gamma\psi(t) \quad \Rightarrow \quad \psi(n) = (1-\gamma\Delta t)^{|n|}$$

discrete analogue of
an exponential function

$$\psi(\Delta t) = 1-\gamma\Delta t \approx 1-\frac{\Delta t^2}{2}\kappa(0)$$

Hamiltonien
dynamics

$$\Rightarrow \boxed{\Delta t = 2\int_0^\infty dt\, \frac{\kappa(t)}{\kappa(0)}} \quad \text{et} \quad \boxed{\Delta t \ll \frac{1}{\sqrt{\kappa(0)}}}$$

Conditions for Brownian dynamics on the time scale $t \gg \Delta t$.

Again the two-pole model...

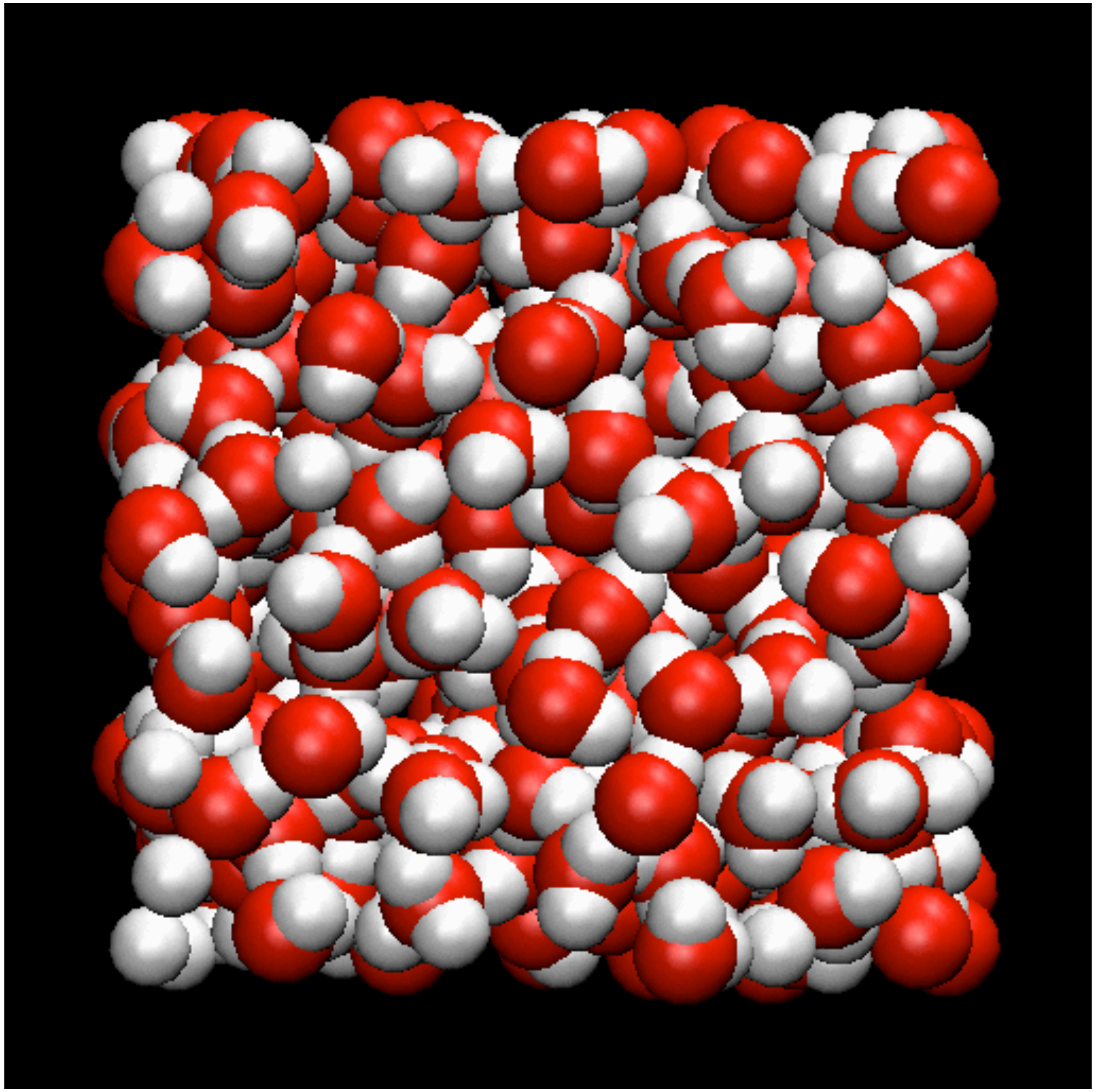
$$\kappa(t) = \kappa(0)\exp(-\eta t) \qquad \kappa(0) = \frac{\langle \delta F^2 \rangle}{\mu k_B T} \equiv \omega_0^2$$

Brownian dynamics if $\Delta t = 2\eta^{-1}$ and $\Delta t \ll \omega_0^{-1}$

This is equivalent to $\omega_0 \ll \eta$

$$c_{vv}(t) \approx \frac{k_B T}{M} \exp\left(-\omega_0^2 \eta^{-1} t\right)$$

Dynamics of water molecules



Simulation of 256 water molecules in a cubic box with periodic boundary conditions and the SPC/E potential

Analytical model [1]

$$F_s(q,t) = \langle \exp(iq[x(t) - x(0)]) \rangle$$

Intermediate scattering function for single particle motions

$$\ddot{F}_s(q,t) + \int_0^t d\tau M^{(2)}(q,\tau)\dot{F}_s(q,t-\tau) + q^2\langle v^2\rangle F_s(q,t) = 0.$$

memory function of order 2

$$M^{(2)}(q,t) = M^{(2)}(q,0)\left\{\alpha\exp(-t/\tau_1) + (1-\alpha)\exp(-t/\tau_2)\right\}$$

fast relaxation by collisions

structural relaxation

[1] V. Calandrini, *et al.*, *J. Chem. Phys*, 120:4759–4767, 2004.

Which mass for the scattering atom ?

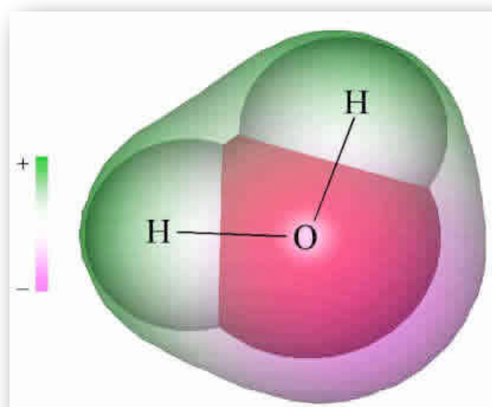
$$\hat{F}_s(q,s) = \cfrac{1}{s + \cfrac{\langle v^2 \rangle q^2}{s + (2\langle v^2 \rangle q^2 + \omega_0^2 \left\{ \frac{\alpha}{s+\tau_1^{-1}} + \frac{1-\alpha}{s+\tau_2^{-1}} \right\}}}$$

4 pole model

$$\langle v^2 \rangle = \frac{k_B T}{m_{\text{eff}}}$$

$$\omega_0^2 = \frac{\langle \dot{v}^2 \rangle}{\langle v^2 \rangle}$$ *par MD*

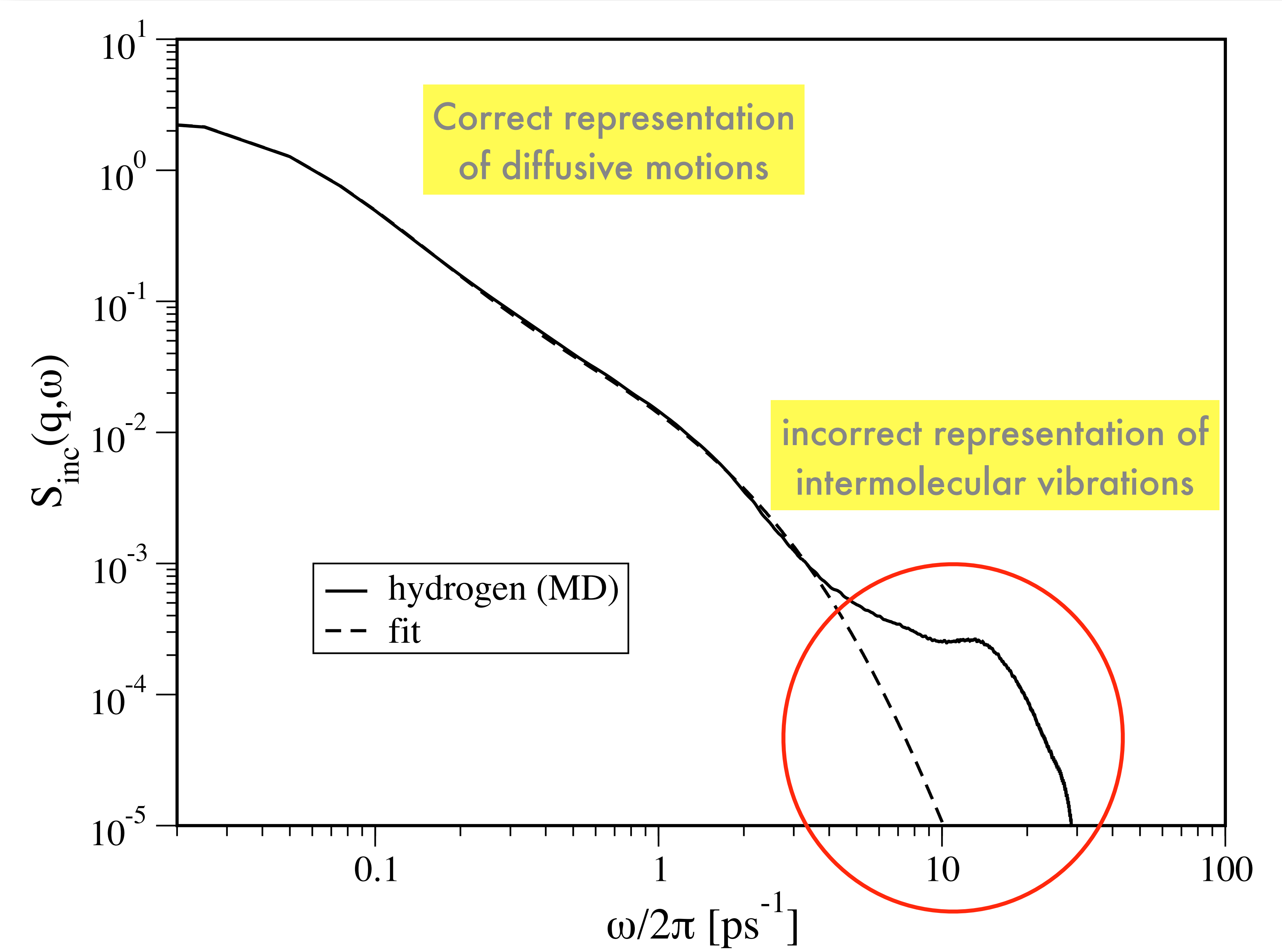
In a rigid molecule this is the ***Sachs-Teller mass**[1]* *of the scattering atom (here a hydrogen atom)*



$$\begin{aligned} m_{H_1} &= m_{H_2} = 1.896, \\ m_O &= 17.08, \\ \Omega_H^2 &= 11881\, ps^{-2}, \\ \Omega_O^2 &= 1941\, ps^{-2}. \end{aligned}$$

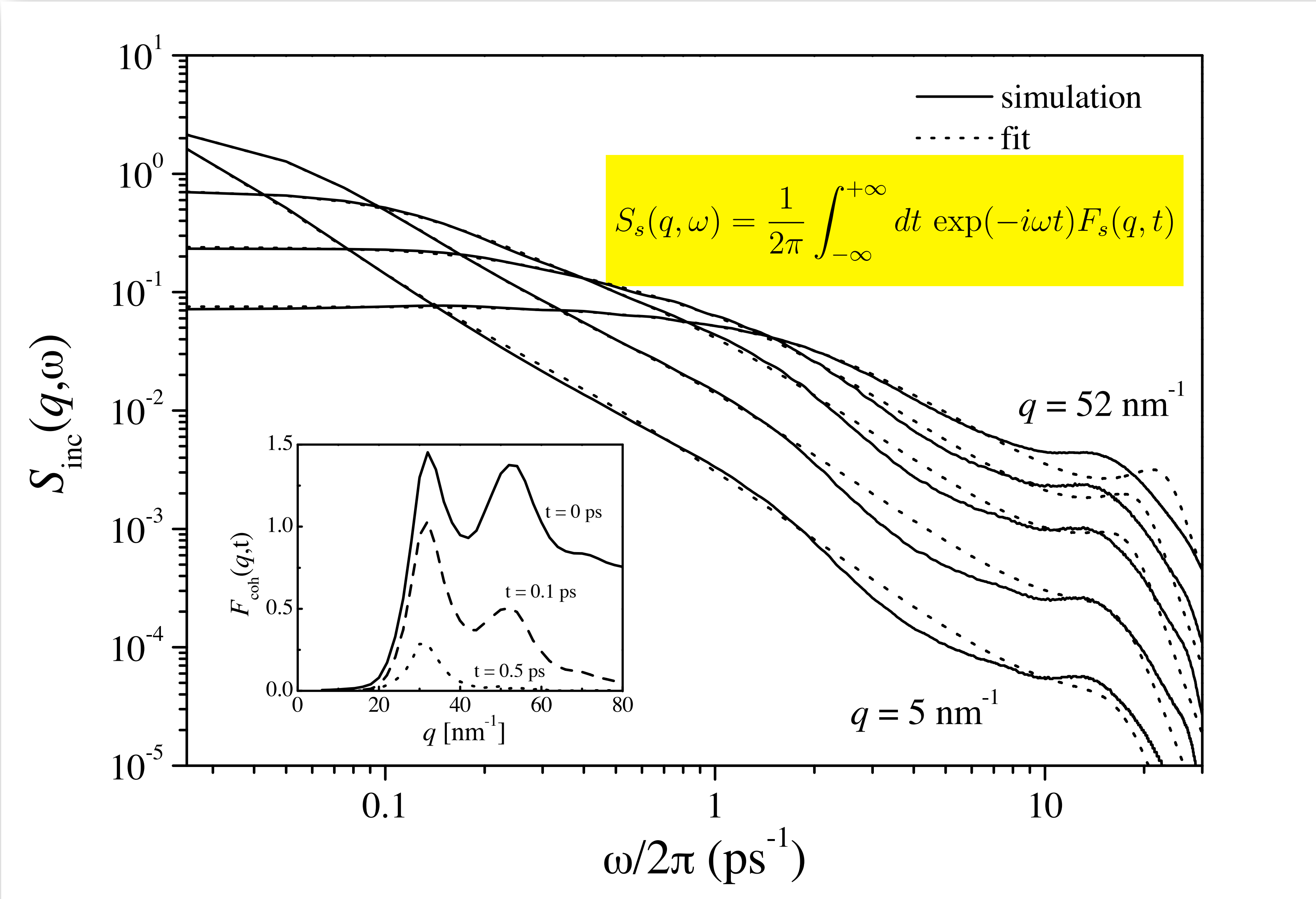
[1] G.R. Kneller. *J. Chem. Phys.*, 125:114107, 2006.

Using the molecular mass in the model... [1]



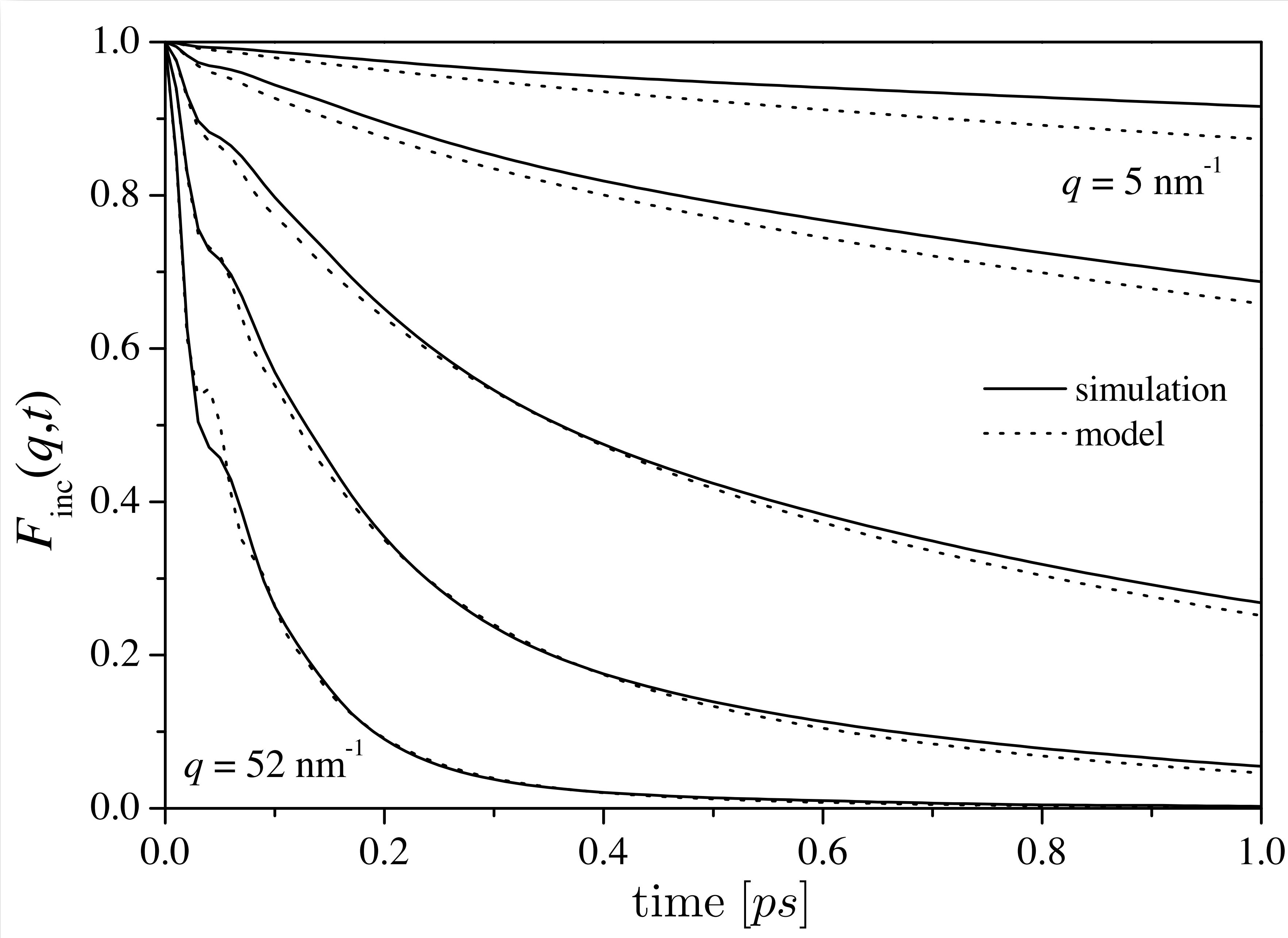
[1] V. Calandrini, *et al.*, *J. Chem. Phys*, 120:4759–4767, 2004.

Using the Sachs-Teller mass instead... [1]

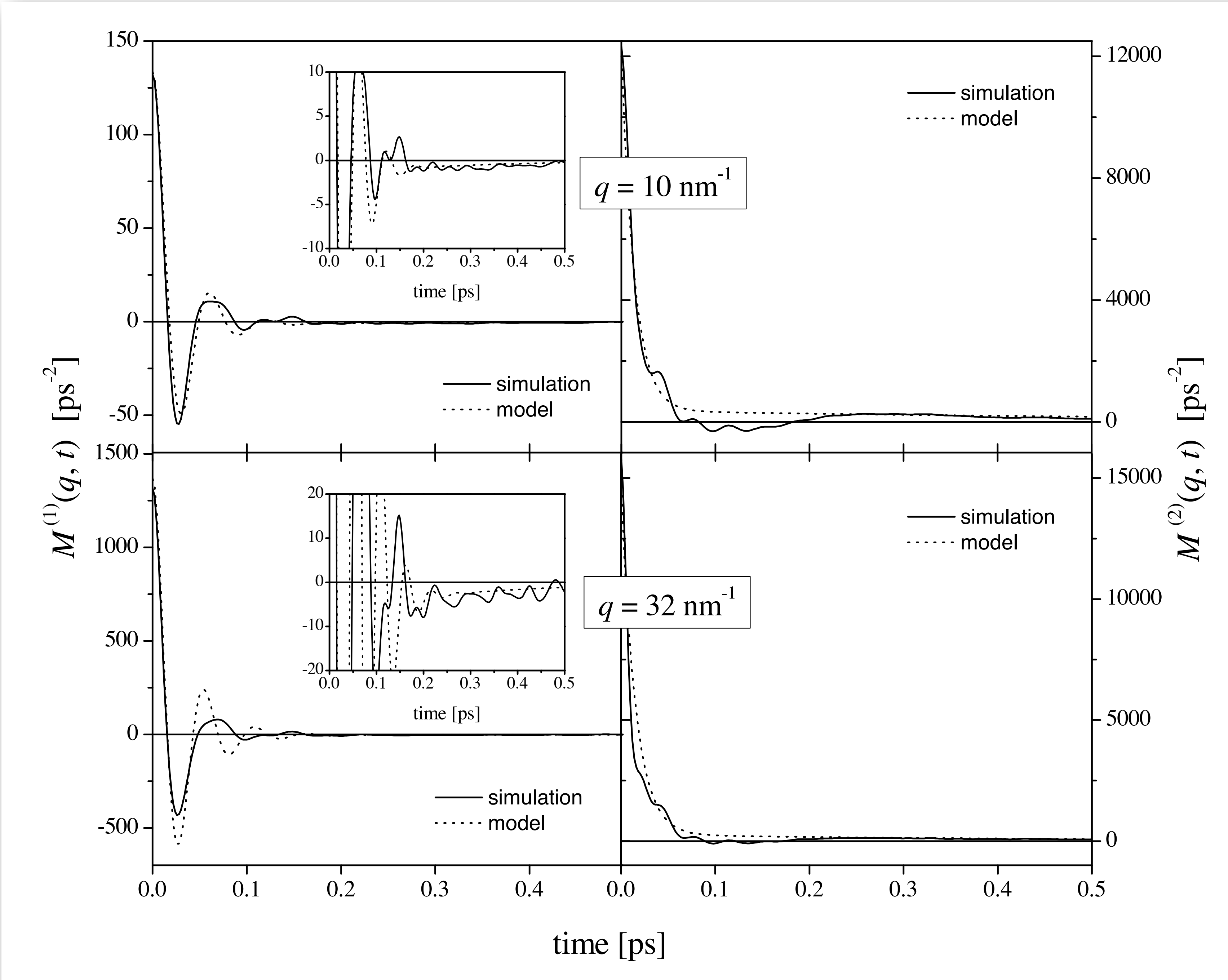


[1] V. Calandrini, G. Sutmann, A. Deriu, and G.R. Kneller, *J. Chem. Phys.*, 125:236102, 2006.

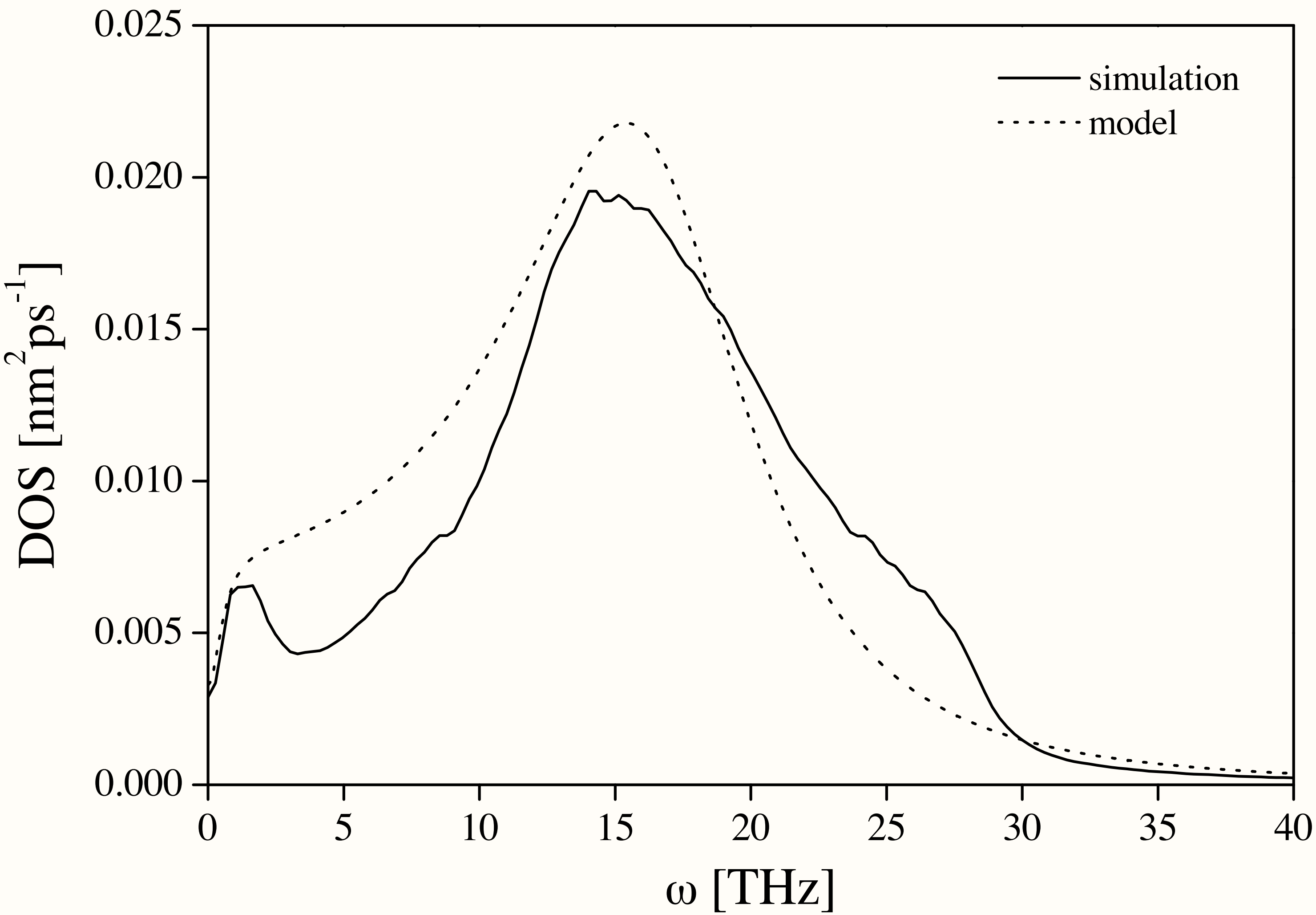
Resulting intermediate scattering function



Associated memory functions of prder 1 and 2



Density of states



References

[1] M.P. Allen and D.J. Tildesley. *Computer Simulation of Liquids*. Oxford University Press, Oxford, 1987.

[2] D. Frenkel and B. Smit. *Understanding Molecular Simulation*. Academic Press, London, San Diego, 1996.

[3] A. Papoulis. *Signal Analysis*. McGraw Hill, 1984.

[4] A. Papoulis. *Probablity, Random Variables, and Stochastic Processes*. McGraw Hill, 3rd edition, 1991.

[5] S. Haykin. *Adaptive Filter Theory*. Prentice Hall, 1996.