Course 05/2

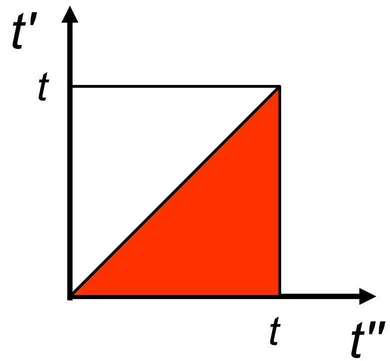
Velocity-velocity autocorrelation function

- Green-Kubo formula for diffusion coefficient
- Velocity-velocity autocorrelation function

Green-Kubo formula for diffusion coefficient

We express $\Delta r_x(t)$ in terms of the velocity:

$$\Delta r_x(t) = \int_0^t dt' \; v_x(t')$$



Then $\langle \, |\Delta r_x(t)|^2 \rangle = \langle \left(\int_0^t dt' \; v_x(t') \right)^2 \rangle$

$$= \langle \int_0^t dt' \int_0^t dt'' \;\; v_x(t') \; v_x(t'') \rangle$$

$$= 2 \langle \int_0^t dt' \int_0^{t'} dt'' \;\; v_x(t') \; v_x(t'') \rangle$$

From Einstein's relation:

$$D = \lim_{t \to \infty} \frac{1}{6} \frac{\partial}{\partial t} \langle \, \| \Delta \vec{r}(t) \|^2 \rangle \quad = \lim_{t \to \infty} \frac{1}{2} \frac{\partial}{\partial t} \langle \, |\Delta r_x(t)|^2 \rangle$$

$$= \lim_{t \to \infty} \frac{\partial}{\partial t} \langle \int_0^t dt' \int_0^{t'} dt'' \;\; v_x(t') \; v_x(t'') \rangle$$

Green-Kubo formula for diffusion coefficient

$$D = \lim_{t \to \infty} \frac{\partial}{\partial t} \left\langle \int_0^t dt' \int_0^{t'} dt'' \;\; v_x(t')\; v_x(t'') \right\rangle$$

We use $\langle v_x(t')\; v_x(t'') \rangle = \langle v_x(t'-t'')\; v_x(0) \rangle$ which is valid because equilibrium properties depend only on Δt.

$$D = \lim_{t \to \infty} \frac{\partial}{\partial t} \int_0^t dt' \int_0^{t'} dt'' \langle v_x(t'-t'')\; v_x(0) \rangle$$

$$= \lim_{t \to \infty} \int_0^t dt'' \langle v_x(t-t'')\; v_x(0) \rangle$$

Next, we apply the change of variable $\tau = t - t''$:

$$= \lim_{t \to \infty} \int_t^0 -d\tau \langle v_x(\tau)\; v_x(0) \rangle$$

$$D = \int_0^\infty d\tau \langle v_x(\tau)\; v_x(0) \rangle$$

Velocity-velocity autocorrelation function

$$D = \int_0^\infty d\tau \, \langle \, v_x(\tau) \; v_x(0) \, \rangle$$

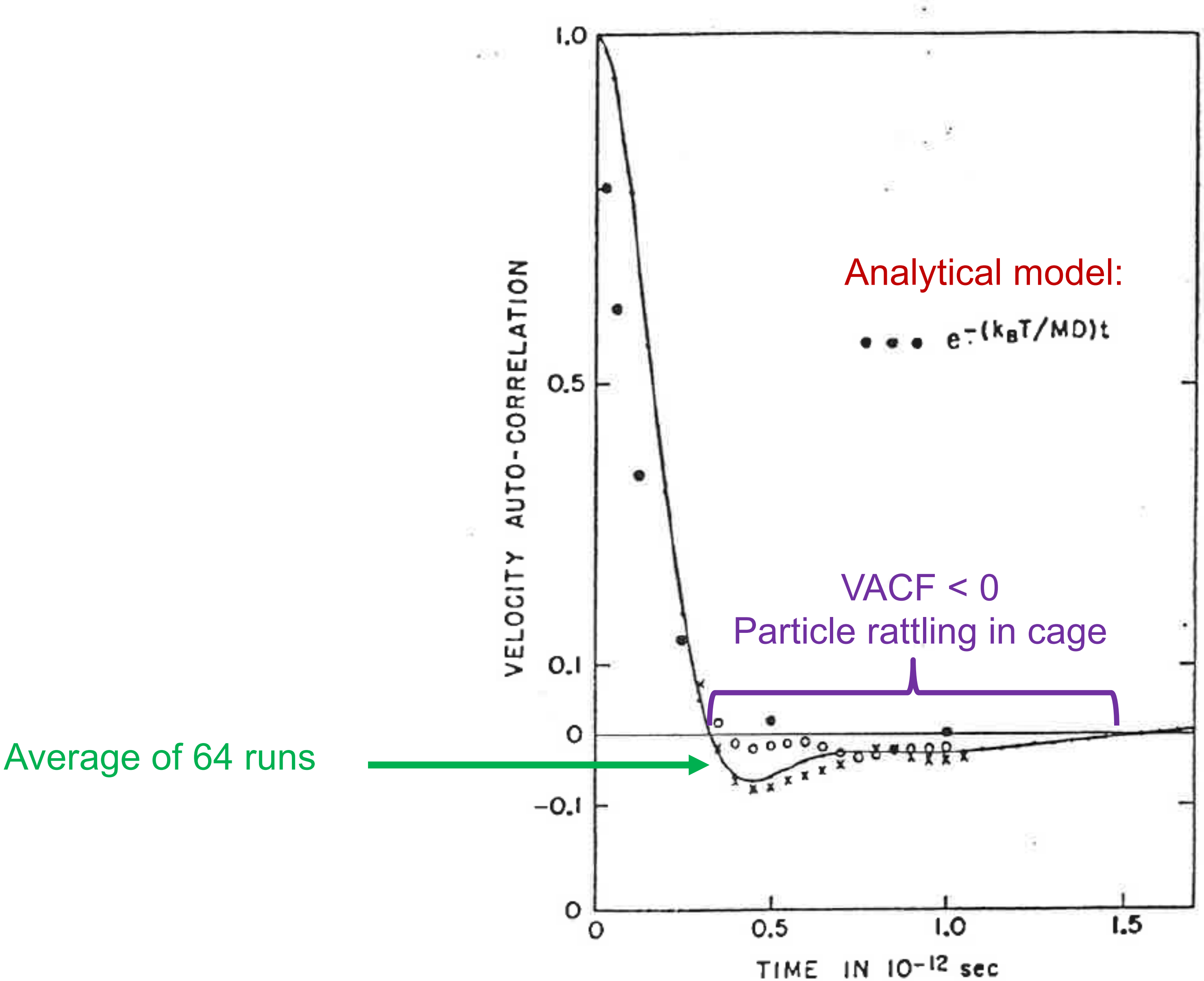
$\langle \, v_x(\tau) \, v_x(0) \, \rangle = \frac{1}{3} \langle \, \vec{v}(\tau) \cdot \vec{v}(0) \, \rangle$ for isotropic systems, *x*, *y* and *z* are equivalent

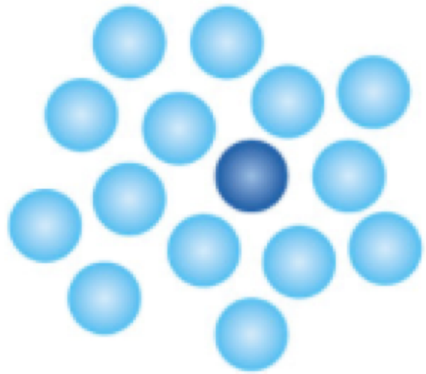
Definition of velocity-velocity autocorrelation function (VACF):

$$\mathrm{VACF}\,(\tau) = \frac{\langle \, \vec{v}(\tau) \cdot \vec{v}(0) \, \rangle}{\langle \, \vec{v}(0) \cdot \vec{v}(0) \, \rangle}$$

normalized so that VACF (τ = 0) = 1

VACF of Lennard-Jones liquid





Videos on the internet

Molecular dynamics simulation of liquid argon (duration: 8 s)

https://www.youtube.com/watch?v=MAr2-KJX62o

Diffusion of tagged particle in liquid argon (duration: 9 s)

https://www.youtube.com/watch?v=mZe-krsr87k

Ab initio molecular dynamics of liquid water (duration: 1 min 19 s)

https://www.youtube.com/watch?v=Zl74NCVbA5A

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