CE 530 Molecular Simulation

Lecture 12
Dynamical Properties

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Review

- Several equivalent ways to formulate classical mechanics
  - *Newtonian, Lagrangian, Hamiltonian*
  - *Lagrangian and Hamiltonian independent of coordinates*
  - *Hamiltonian preferred because of central role of phase space to development*
- Molecular dynamics
  - *numerical integration of equations of motion for multibody system*
  - *Verlet algorithms simple and popular*

Dynamical Properties

- How does the system respond collectively when put in a state of non-equilibrium?
- Conserved quantities
  - *mass, momentum, energy*
  - *where does it go, and how quickly?*
  - *relate to macroscopic transport coefficients*
- Non-conserved quantities
  - *how quickly do they appear and vanish?*
  - *relate to spectroscopic measurements*
- What do we compute in simulation to measure the macroscopic property?

Macroscopic Transport Phenomena

- Dynamical behavior of conserved quantities
  - *densities change only by redistribution on macroscopic time scale*
- Differential balance

Mass

$$\frac{\partial c(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

Energy

$$c_p \frac{\partial T(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{q} = 0$$

Momentum

$$\rho \frac{D\mathbf{v}(\mathbf{r},t)}{Dt} + \nabla \cdot \underline{\underline{\tau}} = 0$$

- Constitutive equation

Fick's law

$$\mathbf{j} = -D\nabla c$$

Fourier's law

$$\mathbf{q} = -k\nabla T$$

Newton's law

$$\tau_{xy} = -\nu\nabla_y(\rho \mathbf{v}_x)$$

- Our aim is to obtain the phenomenological transport coefficients by molecular simulation
  - *note that the "laws" are (often very good) approximations that apply to not-too-large gradients*
  - *in principle coefficients depend on c, T, and* **v**

Approaches to Evaluating Transport Properties

- Need a non-equilibrium condition
- Method 1: Establish a non-equilibrium steady state
  - *"Non-equilibrium molecular dynamics" NEMD*
  - *Requires continuous addition and removal of conserved quantities*
  - *Usually involves application of work, so must apply thermostat*
  - *Only one transport property measured at a time*
  - *Gives good statistics (high "signal-to-noise ratio")*
  - *Requires extrapolation to "linear regime"*
- Method 2: Rely on natural fluctuations
  - *Any given configuration has natural inhomogeneity of mass, momentum, energy* (have a look)
  - *Observe how these natural fluctuations dissipate*
  - *All transport properties measurable at once*
  - *Poor signal-to-noise ratio*

Mass Transfer

- Self-diffusion
  - *diffusion in a pure substance*
  - *consider tagging molecules and watching how they migrate*
- Diffusion equations
  - *Combine mass balance with Fick's law*

$$\frac{\partial c}{\partial t} - D\nabla^2 c(\mathbf{r},t) = 0$$

  - *Take as boundary condition a point concentration at the origin*

$$c(\mathbf{r},t) = \delta(\mathbf{r})$$

For given configuration, each molecule represents a point of high concentration (fluctuation)

- Solution

$$c(\mathbf{r},t) = (2\pi Dt)^{-d/2} \exp\left(-\frac{r^2}{2Dt}\right)$$

- Second moment

$$\left\langle r^2(t) \right\rangle = \int r^2 c(\mathbf{r},t) d\mathbf{r} = 2dDt$$

RMS displacement increases as $t^{1/2}$

Compare to ballistic $r \sim t$

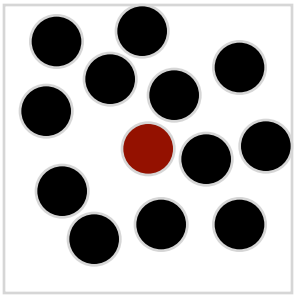
Interpretation

- Right-hand side is macroscopic property
  - *applicable at macroscopic time scales*

$$\left\langle r^2(t)\right\rangle = 2dDt$$

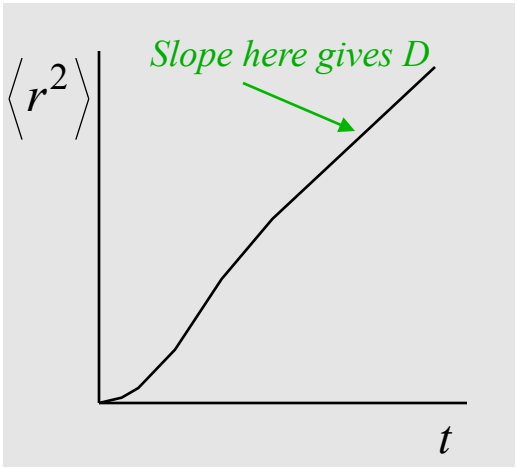
Einstein equation

- For any given configuration, each atom represents a point of high concentration (a weak fluctuation)



- View left-hand side of formula as the movement of this atom
  - *ensemble average over all initial conditions*

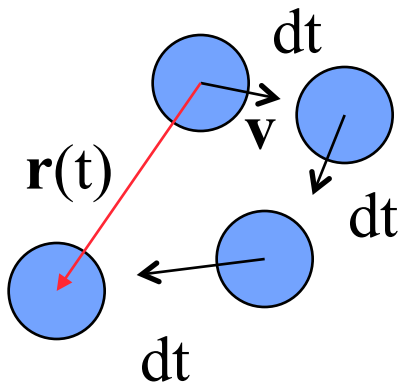
$$\left\langle r^2(t)\right\rangle = \int d\mathbf{p}^N \int d\mathbf{r}^N r_1^2(t)\left[\delta(\mathbf{r}_1)\pi(\mathbf{r}^N,\mathbf{p}^N)\right]_{t=0}$$



  - *asymptotic linear behavior of mean-square displacement gives diffusion constant*
  - *independent data can be collected for each molecule* $\left\langle r^2(t)\right\rangle = \frac{1}{N}\sum\left\langle r_i^2(t)\right\rangle$

Time Correlation Function

- Alternative but equivalent formulation is possible
- Write position **r** at time *t* as sum of displacements $\mathbf{r}(t) = \int_0^t \frac{d\mathbf{r}}{dt} d\tau = \int_0^t \mathbf{v}(\tau) d\tau$



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- Then

$$\left\langle r^2(t) \right\rangle = \left\langle \int_0^t \mathbf{v}(\tau_1) d\tau_1 \cdot \int_0^t \mathbf{v}(\tau_2) d\tau_2 \right\rangle$$

r^2 in terms of displacement integrals

$$= \int_0^t d\tau_1 \int_0^t d\tau_2 \left\langle \mathbf{v}(\tau_2) \cdot \mathbf{v}(\tau_1) \right\rangle$$

rearrange order of averages

$$= 2\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \left\langle \mathbf{v}(\tau_2) \cdot \mathbf{v}(\tau_1) \right\rangle$$

$\int\int(\tau_1 < \tau_2) + \int\int(\tau_1 > \tau_2) = 2\int\int(\tau_1 > \tau_2)$

$$= 2\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau_1 - \tau_2) \right\rangle$$

correlation depends only on time difference, not time origin

$$= 2\int_0^t d\tau_1 \int_0^t d\tau \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \right\rangle$$

substitute $\tau = \tau_1 - \tau_2$

$$2dDt = 2t\int_0^t d\tau \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \right\rangle \quad t \to \infty \quad \boxed{D = \frac{1}{d}\int_0^\infty d\tau \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \right\rangle}$$

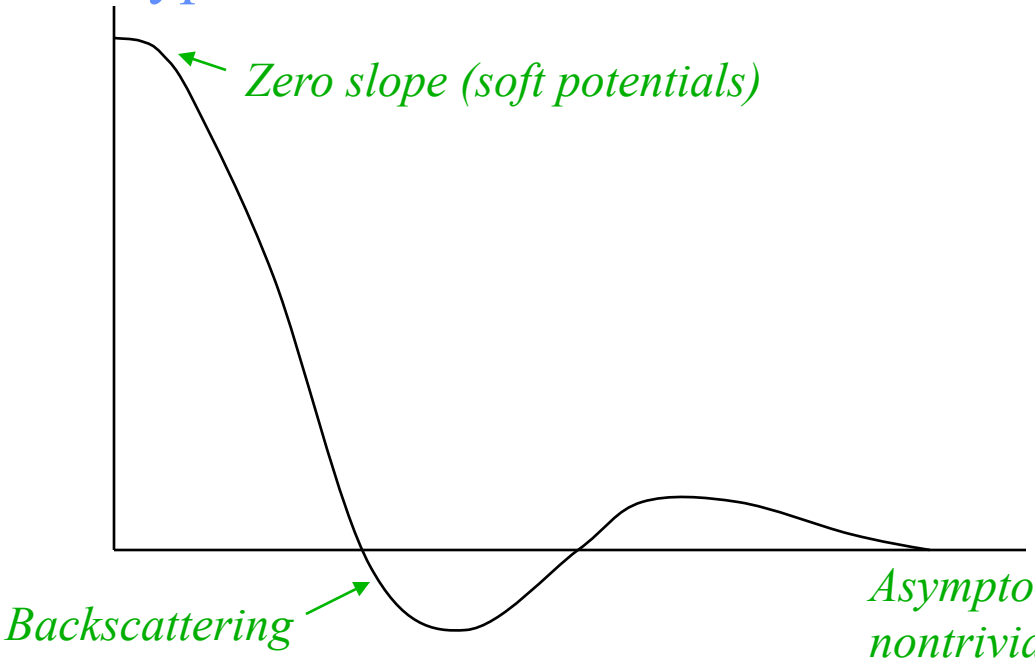
Green-Kubo equation

Velocity Autocorrelation Function

- Definition

$$C(t) \equiv \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \qquad C(0) = \langle v^2 \rangle = dkT/m$$

- Typical behavior



Diffusion constant is area under the curve

$$D = \frac{1}{d}\int_0^\infty d\tau \langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle$$

Asymptotic behavior ($t \rightarrow \infty$) is nontrivial (depends on d)

Other Transport Properties

- Diffusivity

$$D = \frac{1}{Vd\rho}\int_0^\infty dt \left\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\right\rangle \qquad \mathbf{v} = \sum_{i=1}^{N}[\mathbf{v}_i]$$

- Shear viscosity

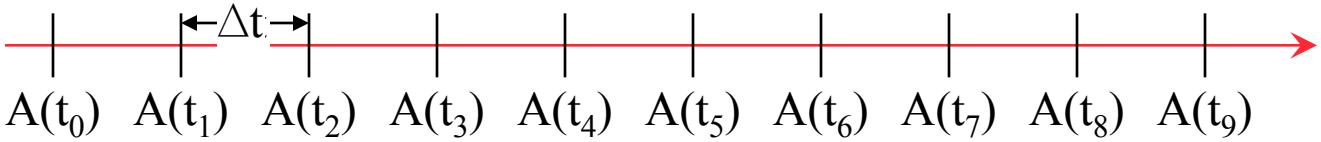
$$\eta = \frac{1}{VkT}\int_0^\infty dt \left\langle \sigma^{xy}(t)\sigma^{xy}(0)\right\rangle \qquad \sigma^{xy} = \sum_{i=1}^{N}\left[m_i v_i^x v_i^y + \frac{1}{2}\sum_{i\neq j} x_{ij} f_y(r_{ij})\right]$$

- Thermal conductivity

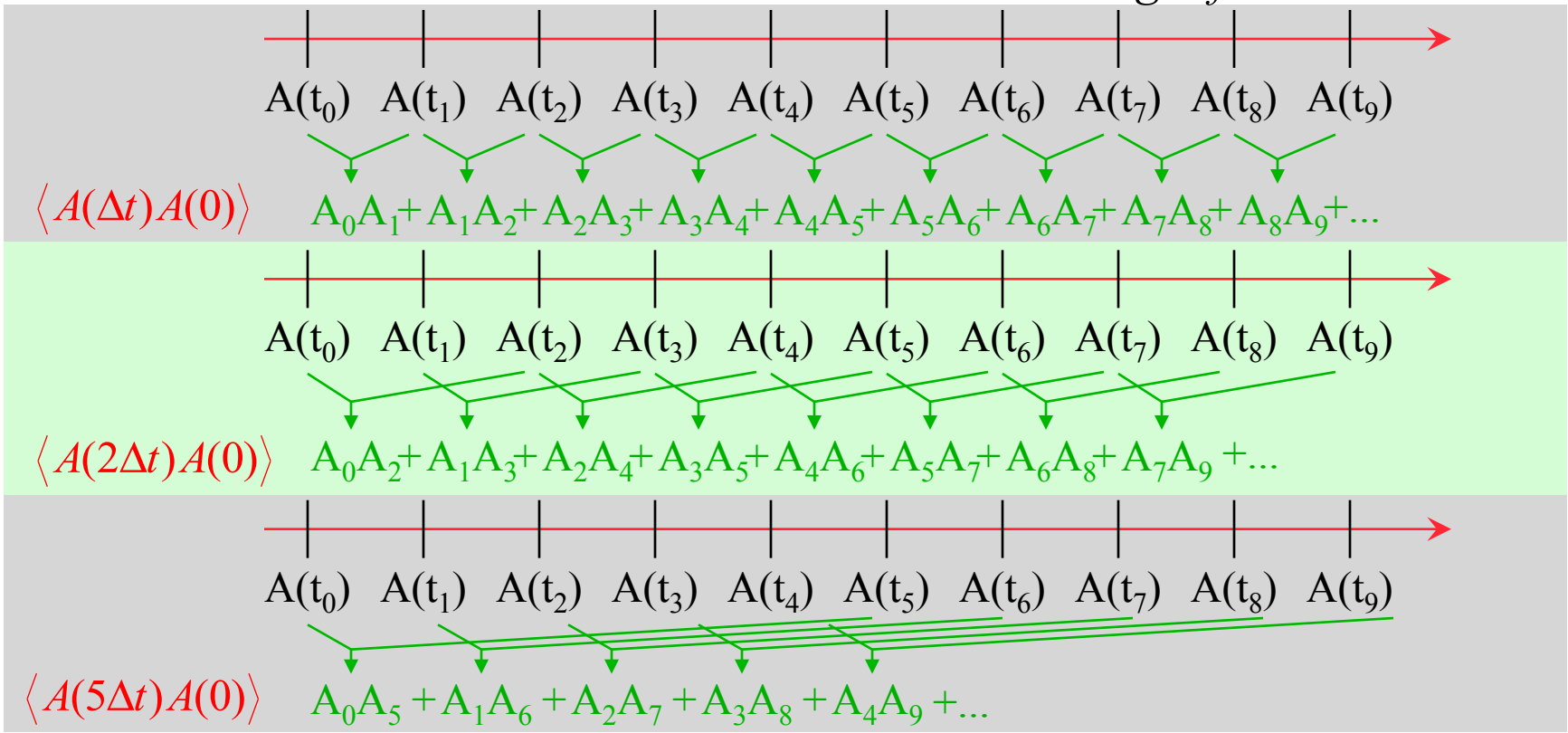
$$\lambda_T = \frac{1}{VkT^2}\int_0^\infty dt \left\langle q(t)q(0)\right\rangle \qquad q = \frac{d}{dt}\sum_{i=1}^{N}\left[\frac{1}{2}m_i v_i^2 + \frac{1}{2}\sum_{i\neq j} u(r_{ij})\right]$$

Evaluating Time Correlation Functions

- Measure phase-space property $A(\mathbf{r}^N,\mathbf{p}^N)$ for a sequence of time intervals

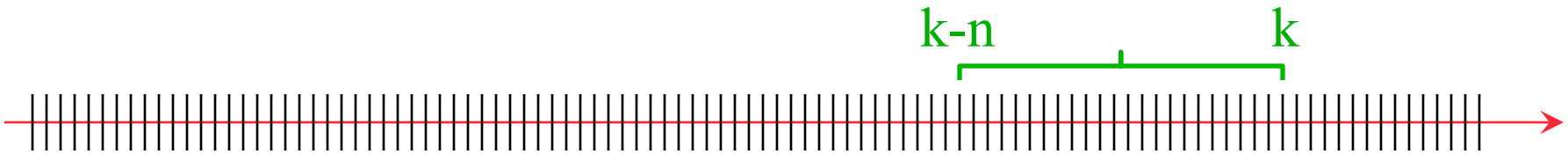


- Tabulate the TCF for the same intervals
  - *each time in simulation serves as a new time origin for the TCF*



Direct Approach to TCF

- Decide beforehand the time range $(0,t_{max})$ for evaluation of C(t)
  - *let* n *be the number of time steps in* t_{max}
- At each simulation time step, update sums for all times in $(0,t_{max})$
  - n *sums to update*
  - *store values of A(t) for past* n *time steps*
  - *at time step* k: $c_i += A_{k-i} A_k \quad i = 1,\ldots,n$



- Considerations
  - *trade off range of C(t) against storage of history of A(t)*
  - *requires* n^2 *operations to evaluate TCF*

Fourier Transform Approach to TCF

- Fourier transform

$$\hat{f}(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt \qquad f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \hat{f}(\omega) e^{+i\omega t} d\omega$$

- Convolution

$$C(t) = \int_{-\infty}^{+\infty} A(\tau) B(\tau + t) d\tau$$

- Fourier convolution theorem

$$\tilde{C}(\omega) = \tilde{A}(\omega)\tilde{B}(\omega)$$

- Application to TCF

$$C(t) = \sum_{t_0} \mathbf{v}(t_0) \cdot \mathbf{v}(t_0 + t)$$

Sum over time origins

$$\hat{C}(\omega) = \left[\hat{\mathbf{v}}(\omega)\right]^2$$

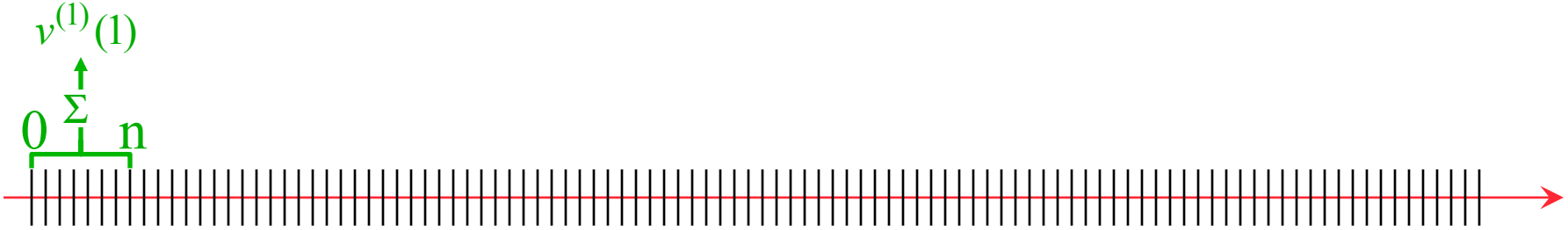
With FFT, operation scales as n ln(n)

Coarse-Graining Approach to TCF 1.

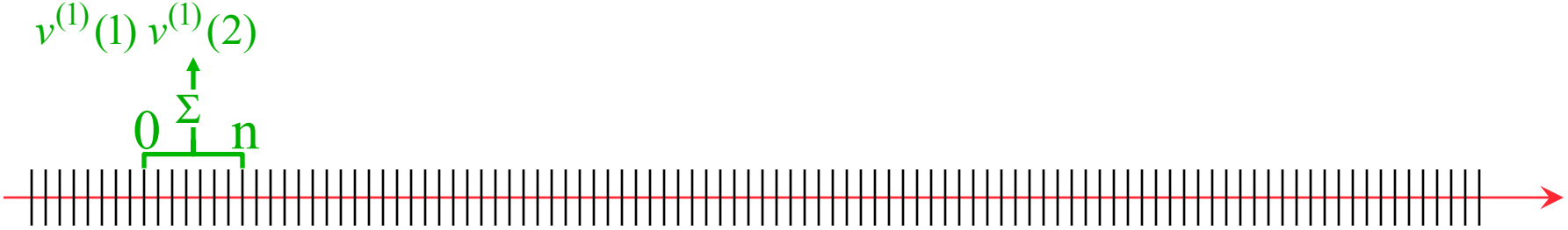
- Evaluating long-time behavior can be expensive
  - *for time interval* T, *need to store* T/δt *values (perhaps for each atom)*
- But long-time behavior does not (usually) depend on details of short time motions resolved at simulation time step
- Short time behaviors can be coarse-grained to retain information needed to compute long-time properties
  - *TCF is given approximately*
  - *mean-square displacement can be computed without loss*

Method due to Frenkel and Smit

Coarse-Graining Approach to TCF 2.



Coarse-Graining Approach to TCF 2.



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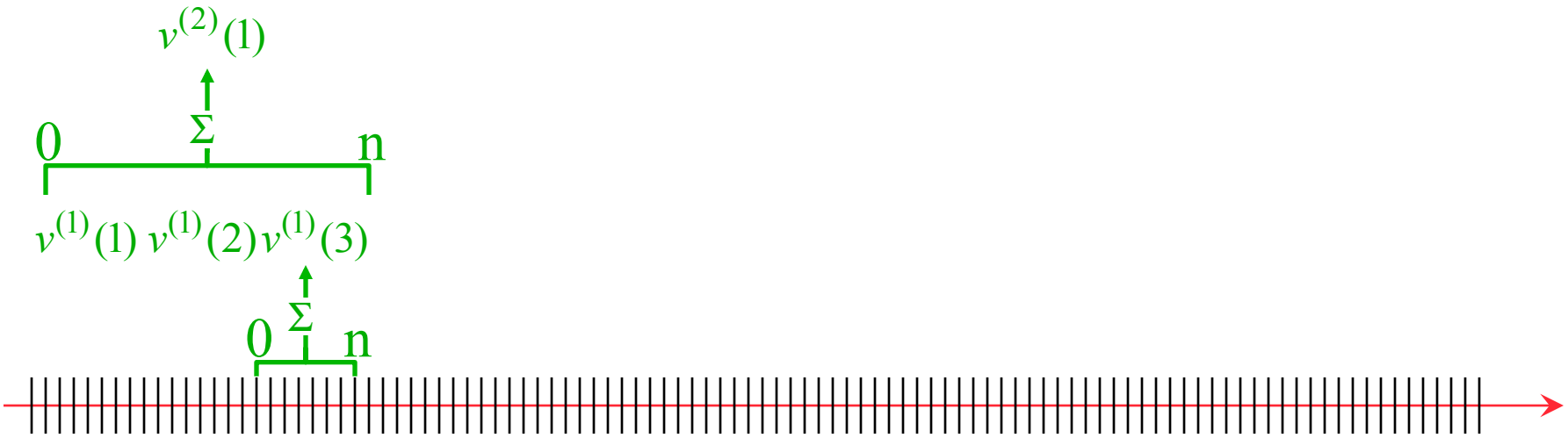

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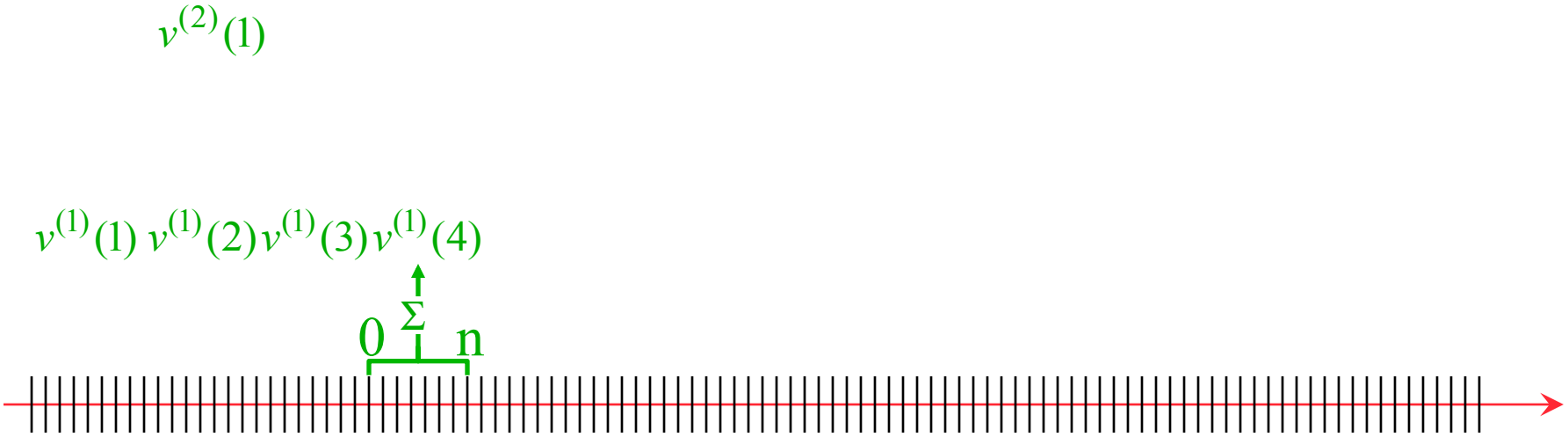
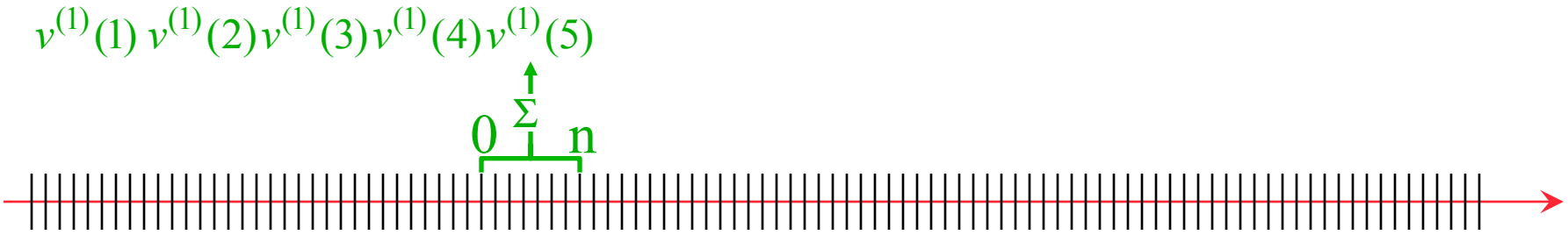


Coarse-Graining Approach to TCF 2.

$v^{(2)}(1)$



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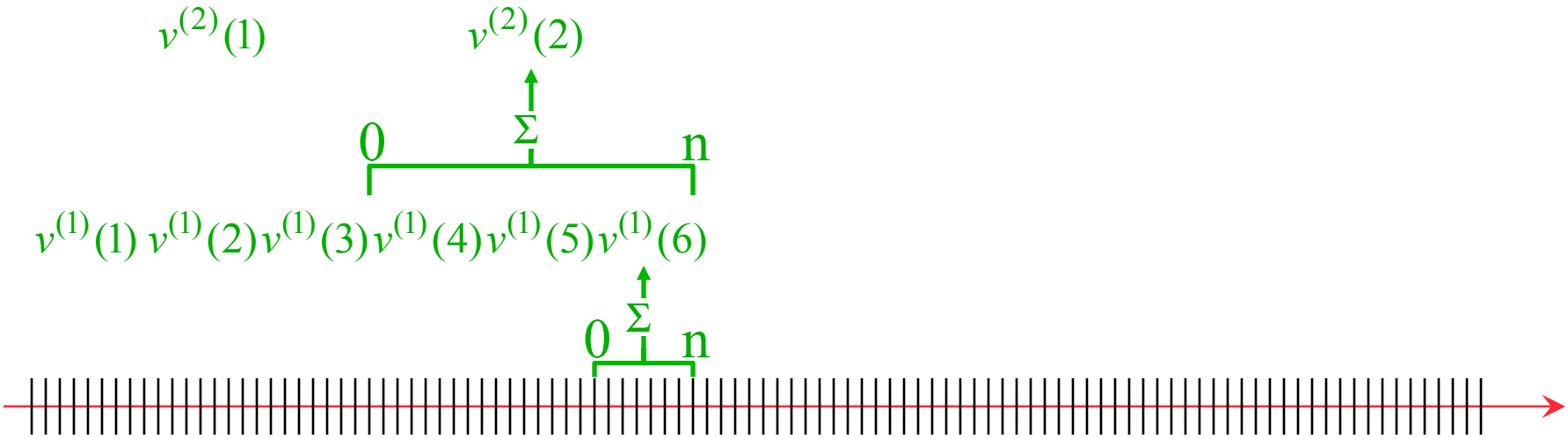


Coarse-Graining Approach to TCF 2.

$v^{(2)}(1)$ $v^{(2)}(2)$

$v^{(1)}(1)\ v^{(1)}(2)v^{(1)}(3)v^{(1)}(4)v^{(1)}(5)v^{(1)}(6)v^{(1)}(7)$

Σ

0 n

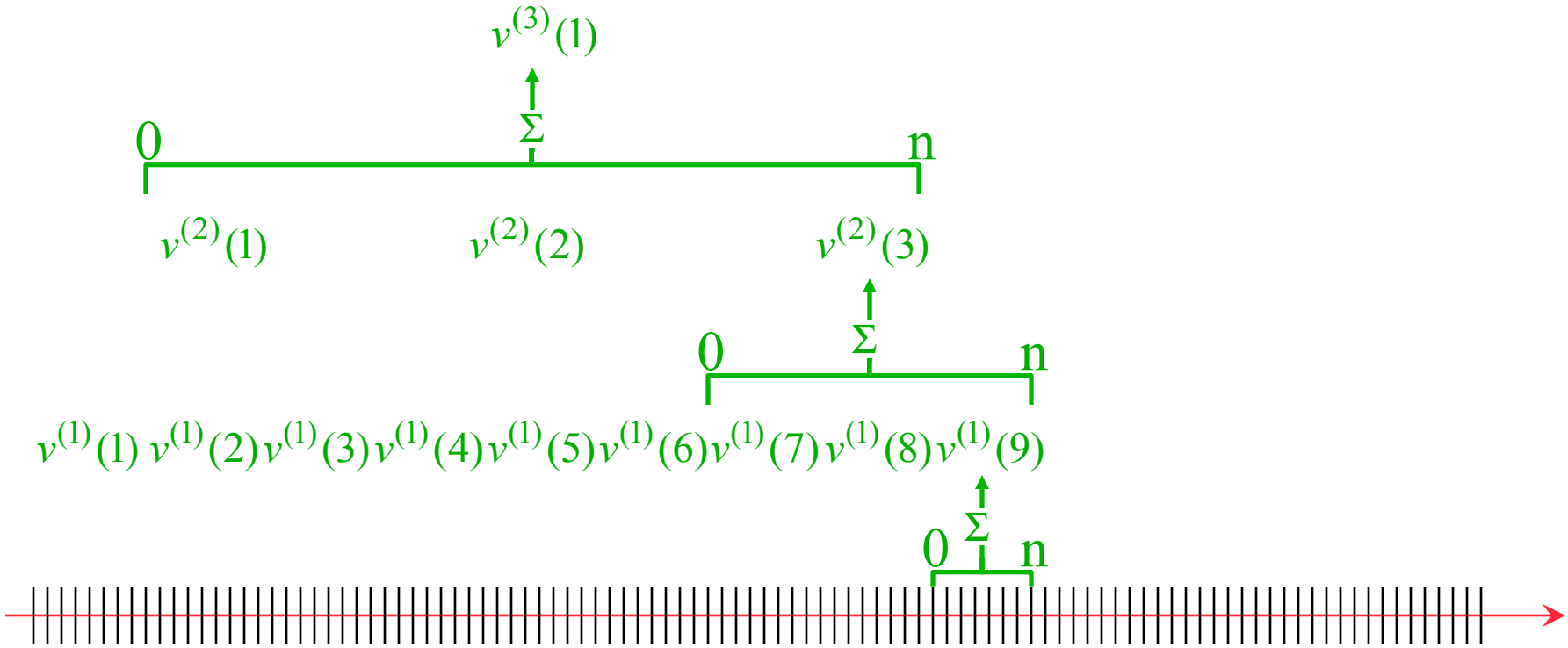
Coarse-Graining Approach to TCF 2.

$v^{(2)}(1)$ $v^{(2)}(2)$

$v^{(1)}(1)\ v^{(1)}(2)\ v^{(1)}(3)\ v^{(1)}(4)\ v^{(1)}(5)\ v^{(1)}(6)\ v^{(1)}(7)\ v^{(1)}(8)$

$0\ \Sigma\ n$

Coarse-Graining Approach to TCF 2.



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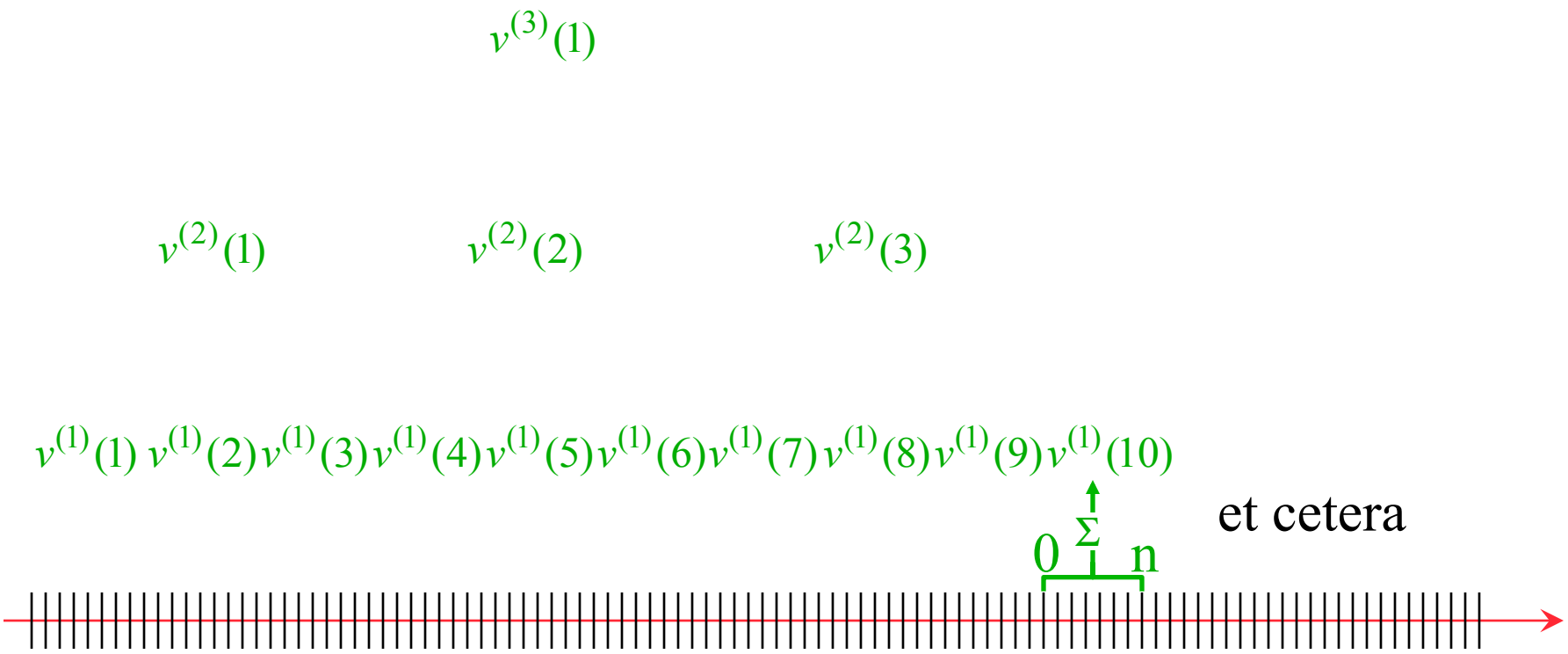
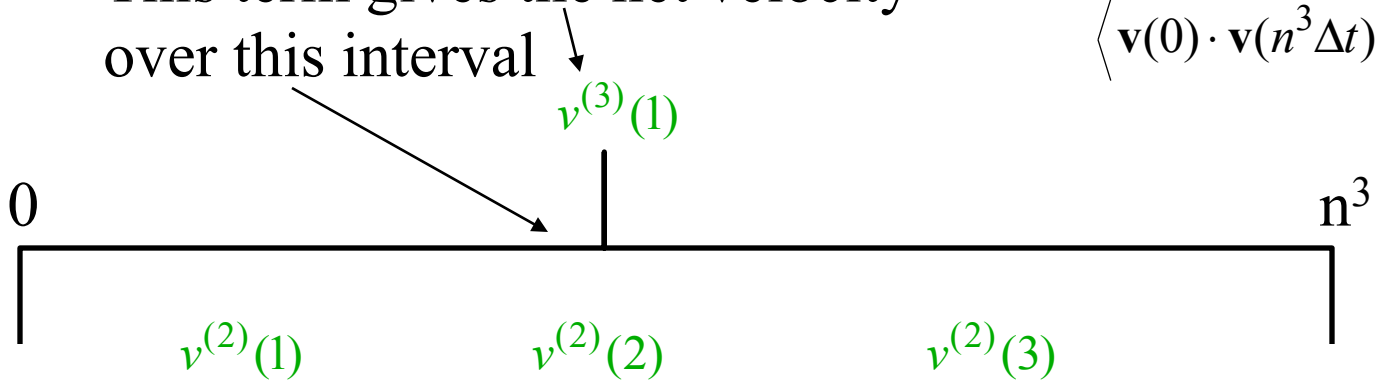


Coarse-Graining Approach to TCF 2.

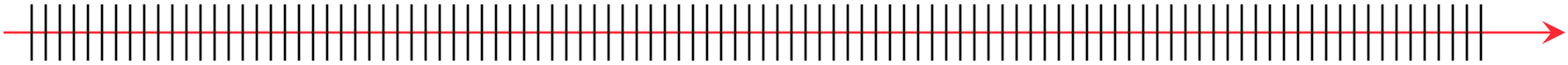
Approximate TCF

$$\left\langle \mathbf{v}(0)\cdot\mathbf{v}(n^3\Delta t)\right\rangle \approx \left\langle \mathbf{v}^{(3)}(0)\cdot\mathbf{v}^{(3)}(1)\right\rangle$$

This term gives the net velocity over this interval



$v^{(1)}(1)\ v^{(1)}(2) v^{(1)}(3) v^{(1)}(4) v^{(1)}(5) v^{(1)}(6) v^{(1)}(7)\ v^{(1)}(8) v^{(1)}(9) v^{(1)}(10)$



Coarse-Graining Approach: Resource Requirements

- Memory
  - *for each level, store n sub-blocks*
  - *for simulation of length* $T = n^k \Delta t$ *requires* $k \times n$ *stored values*

    compare to n^k values for direct method
- Computation
  - *each level j requires update (summing n terms) every* $1/n^j$ *steps*
  - *total*

$$T \times \frac{n}{\Delta t}\left(1+\frac{1}{n}+\frac{1}{n^2}+\ldots+\frac{1}{n^k}\right) = t \times \frac{n}{\Delta t}\frac{n-n^{-k}}{n-1}$$

$$\approx T \times \frac{n}{\Delta t}$$

  - *scales linearly with length of total correlation time*

    compare to T^2 or $T \ln(T)$ for other methods

Summary

- Dynamical properties describe the way collective behaviors cause macroscopic observables to redistribute or decay
- Evaluation of transport coefficients requires non-equilibrium condition
  - *NEMD imposes macroscopic non-equilibrium steady state*
  - *EMD approach uses natural fluctuations from equilibrium*
- Two formulations to connect macroscopic to microscopic
  - *Einstein relation describes long-time asymptotic behavior*
  - *Green-Kubo relation connects to time correlation function*
- Several approaches to evaluation of correlation functions
  - *direct: simple but inefficient*
  - *Fourier transform: less simple, more efficient*
  - *coarse graining: least simple, most efficient, approximate*