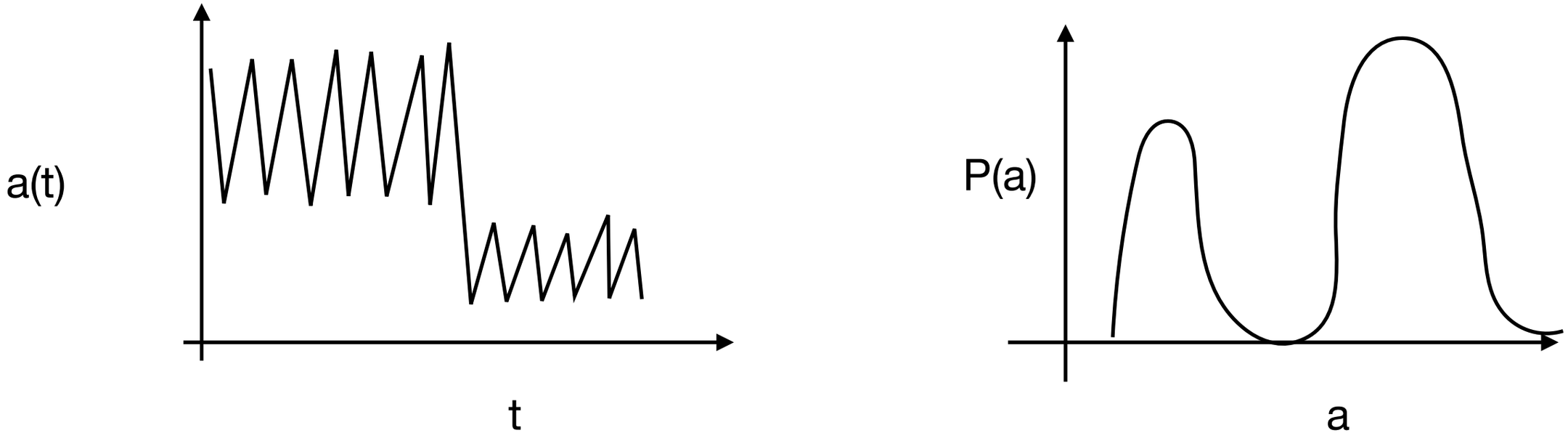
Lecture 10

CHM695
Feb. 6

Distribution functions



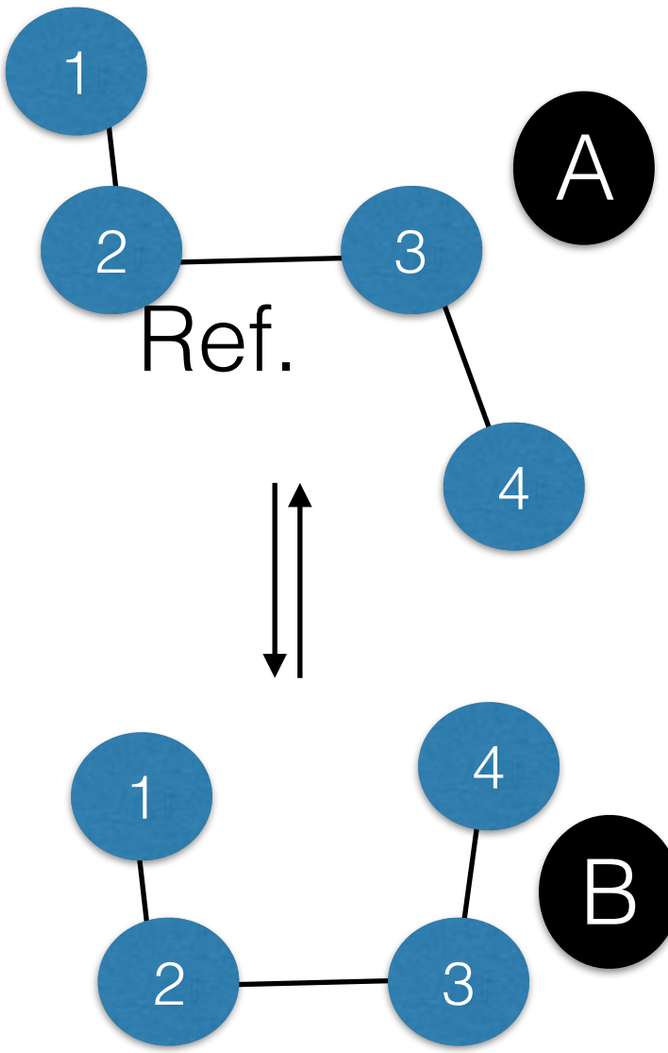
$$P(a) = \frac{1}{Z} \int d\mathbf{R}\, \delta(a(\mathbf{R}) - a) = \langle \delta\left(a(\mathbf{R}) - a\right) \rangle$$

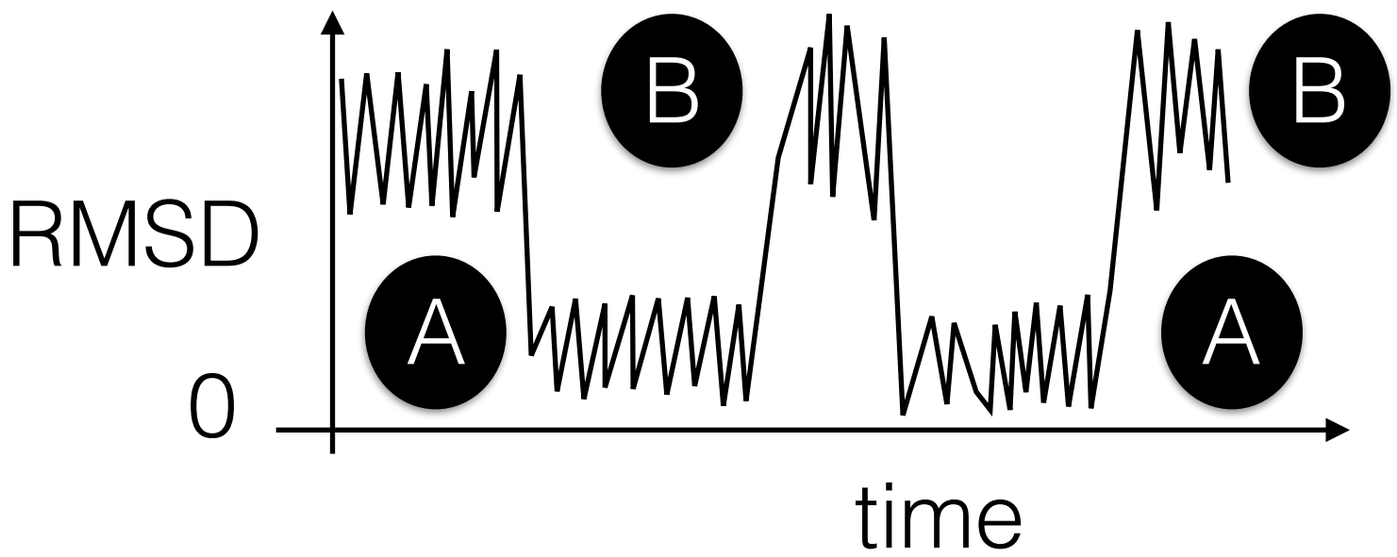
```
CALL read_trajectory( R )
READ *, grid_min, grid_max, grid_width
ngrids=int((grid_max-grid_min)/grid_width)+1
ALLOCATE(P(ngrids))
DO isteps=1,nsteps
    CALL compute_a( R , a)
    igrid=int( (a-grid_min)/grid_width) + 1
    P(igrid)=P(igrid)+1.0
END DO
int=0.0
DO igrid=1,ngrids
  int=int+P(igrid)*grid_width
END DO
P(1:ngrids)=P(1:ngrids)/int
CALL print_P(P)
```

Root Mean Square Displacement or RMSD

$$\mathrm{RMSD} = \sqrt{\frac{1}{N}\sum_{I}^{N}\delta_I^2}$$

$$\delta_I = \left|\mathbf{R}_I - \mathbf{R}_I^{\mathrm{ref}}\right|$$

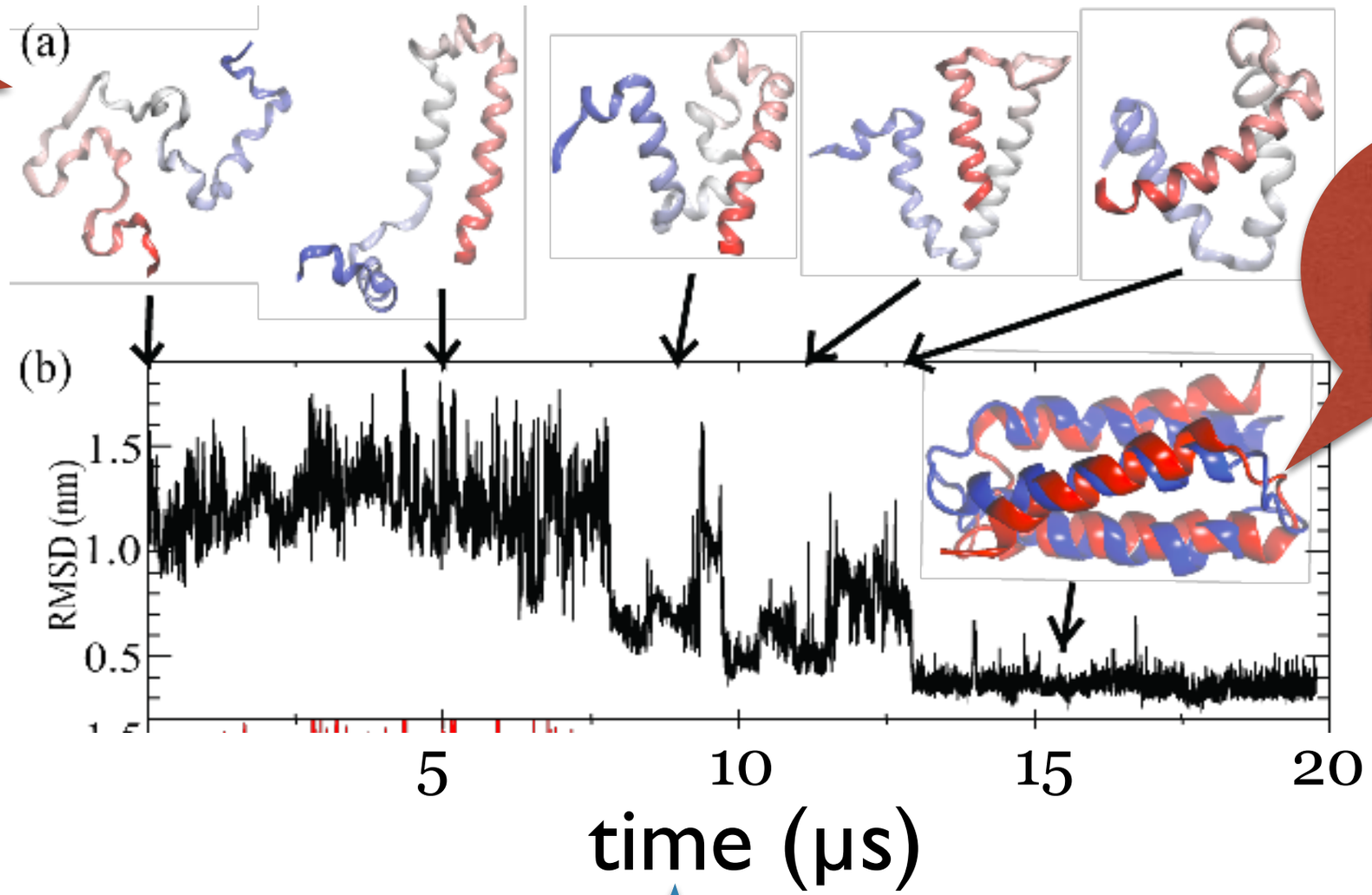




RMSD

high RMSD

RMSD w.r.t. X-ray structure is plotted here



low RMSD

MD time

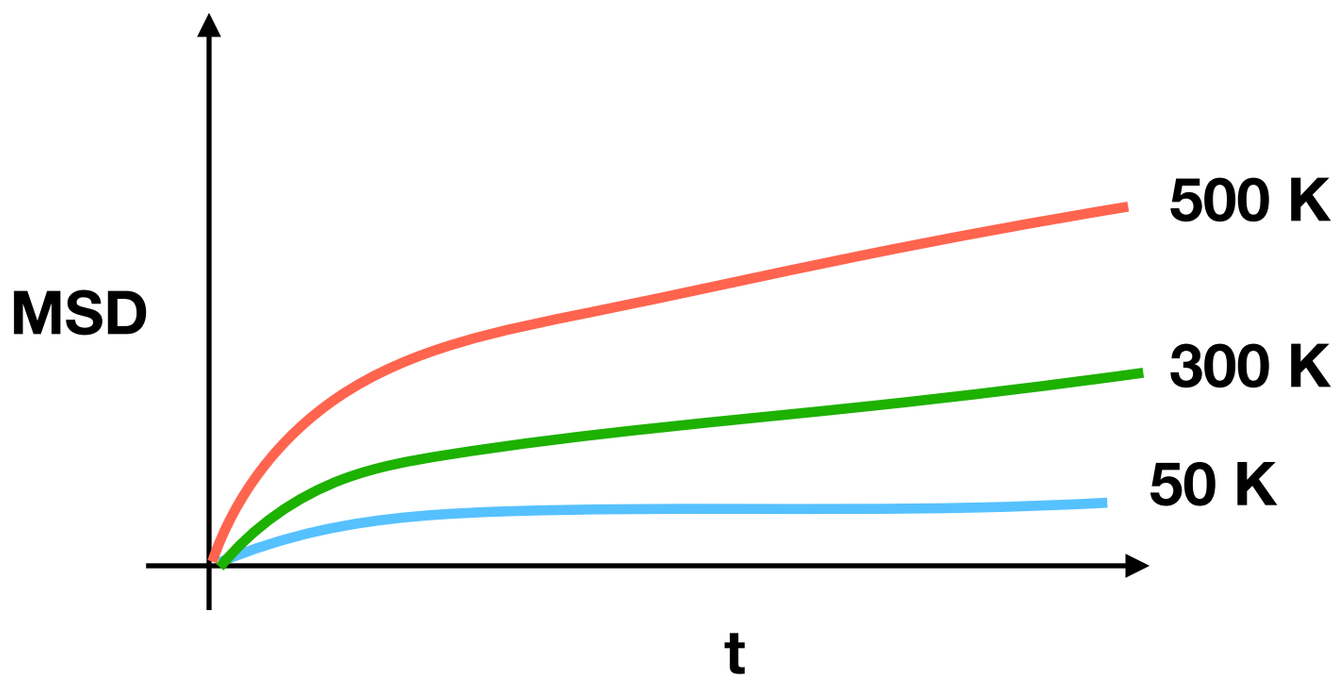
Mean Square Displacement

$$\left\langle \Delta r^2 \right\rangle = \frac{1}{N} \sum_{I}^{N} \Delta \mathbf{R}_I(t)^2$$

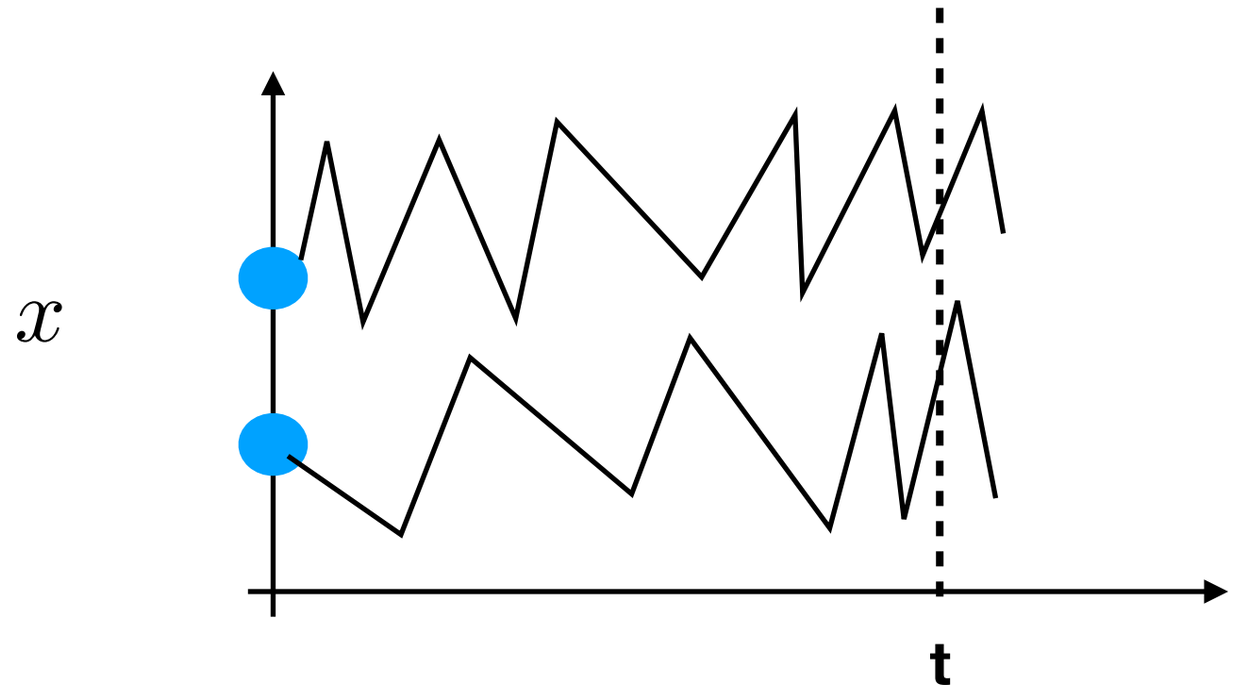
distance travelled by atom *I* in time *t*

$$\frac{\partial \left\langle \Delta r^2 \right\rangle}{\partial t} = 2dD$$

Connection to diffusion coefficient



Dynamic Properties: Correlation Functions



$$C_{AA}(t) = \langle a(0)a(t)\rangle = \int dx\, f(x)\, a(x)\, a(x_t(x))$$

distribution

dynamic property

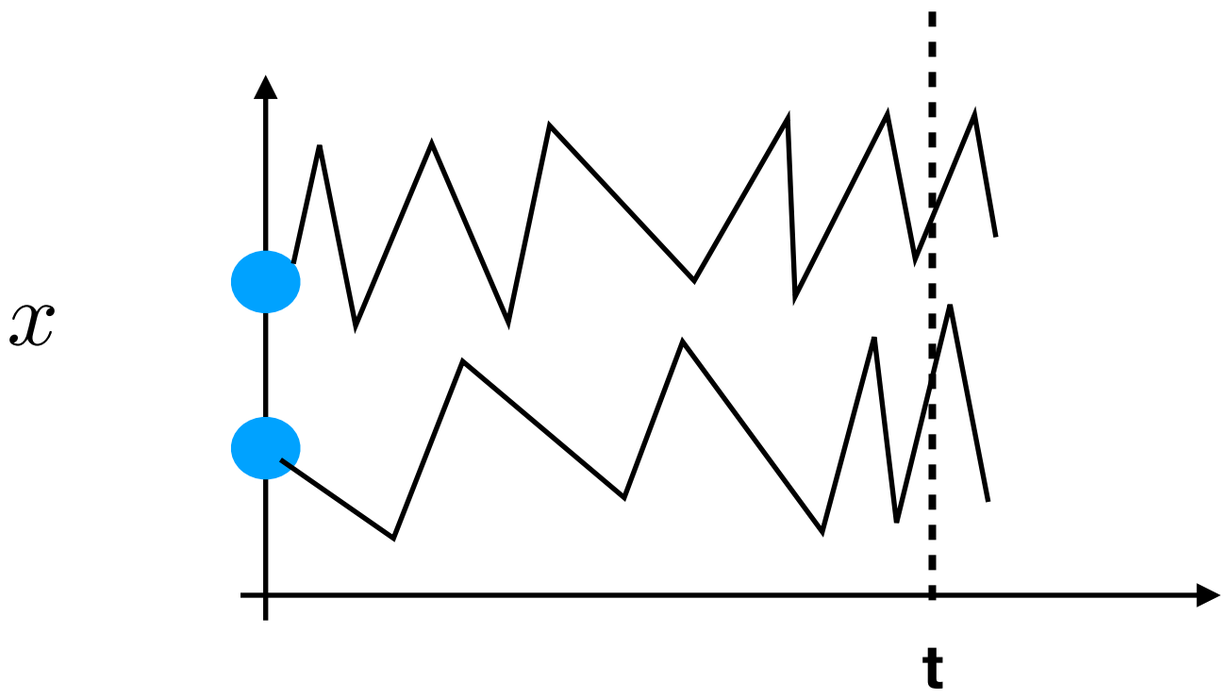
For short time, x_t and x are not very different ⇒ highly correlated

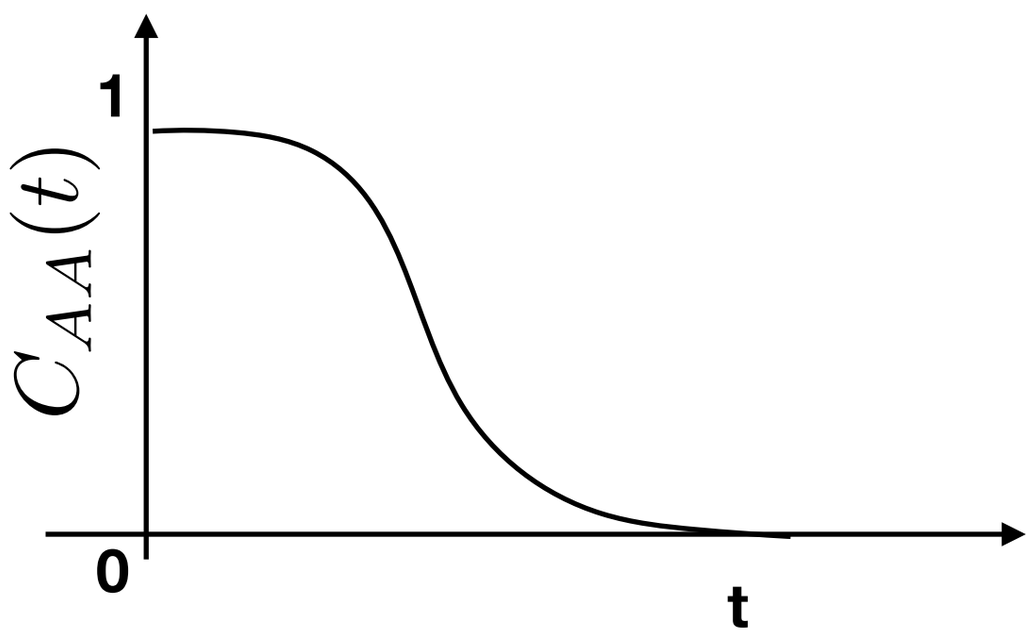
For long time, x_t and x could be highly uncorrelated due to non-linear forces

⇒ trajectory looses memory

Correlation time: time upto which the properties remains correlated

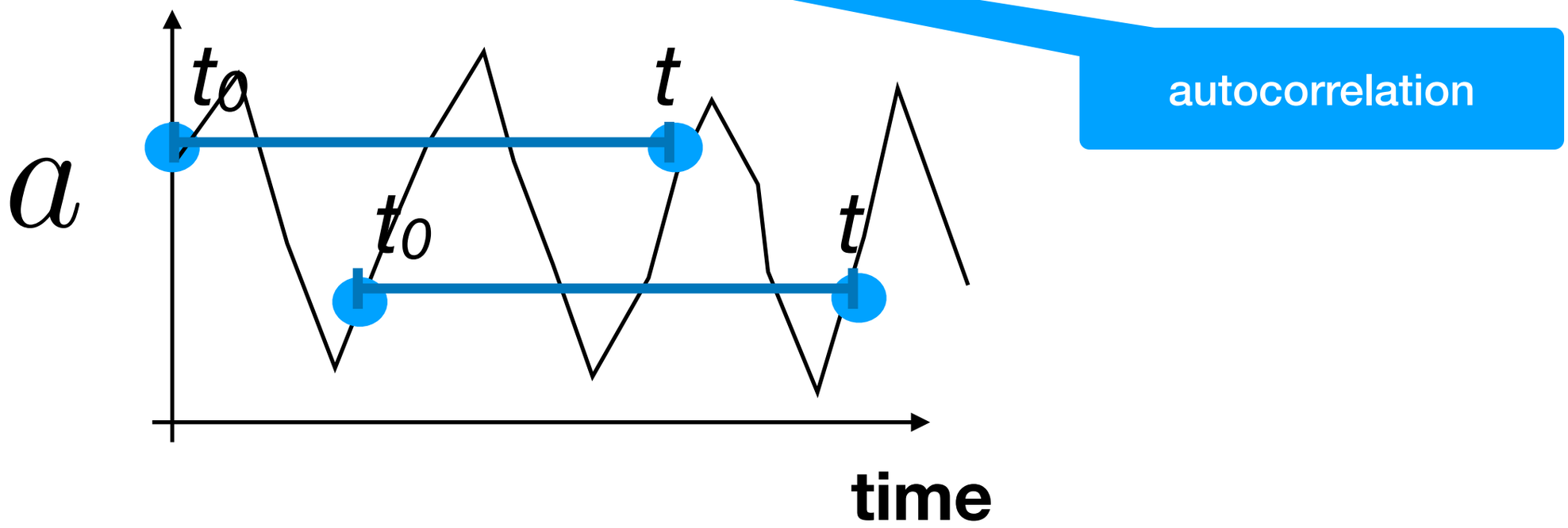
Correlation length depends on the nature of the system





$$C_{AA}(t) = \langle a(t_0)a(t_0+t)\rangle = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^{\tau} dt_0\, a(t_0)a(t_0+t)$$

autocorrelation



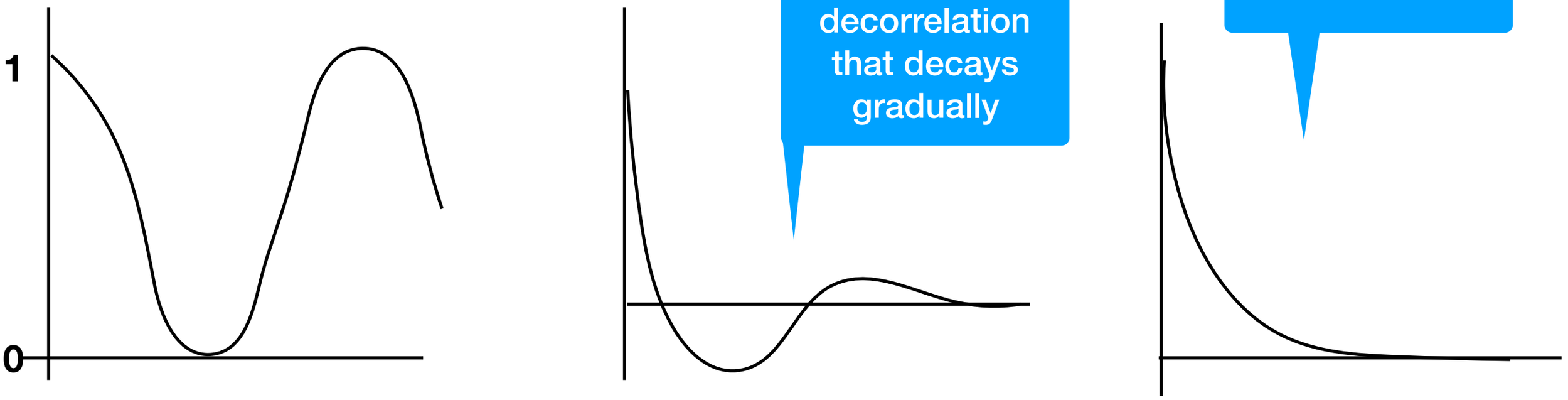
shift time origin from τ=0 to some time τ and average over all these different time origin

$$C_{AB}(t) = \langle a(t_0)b(t_0+t)\rangle$$

cross-correlation

Normalized correlation:

$$C_{AB}(t) = \frac{\langle a(t_0)b(t_0+t)\rangle}{\langle a(t_0)b(t_0)\rangle}$$



Implementation:

$$C_{AB}(t) = \frac{1}{t_{\max}} \sum_{t_0}^{t_{\max}} a(t_0) b(t_0 + t)$$

Computing diffusion coefficient:

$$D = \int_0^\infty dt\, C(t)$$

diffusion coefficient

$$C(t) = \frac{1}{3N} \left\langle \sum_I^N \mathbf{V}_I(t_0) \cdot \mathbf{V}_I(t_0 + t) \right\rangle$$

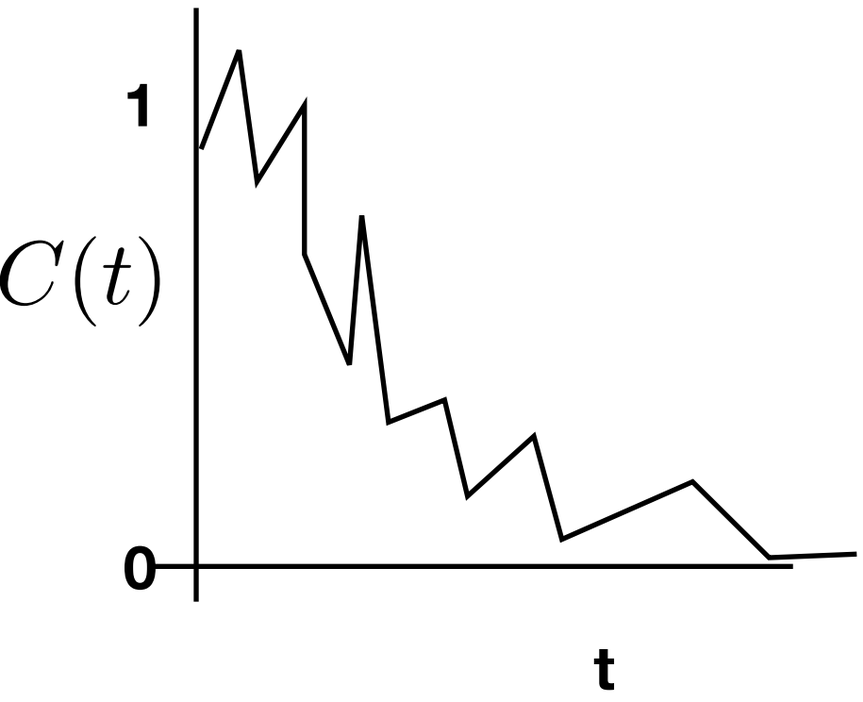
Fourier Transform of Velocity autocorrelation

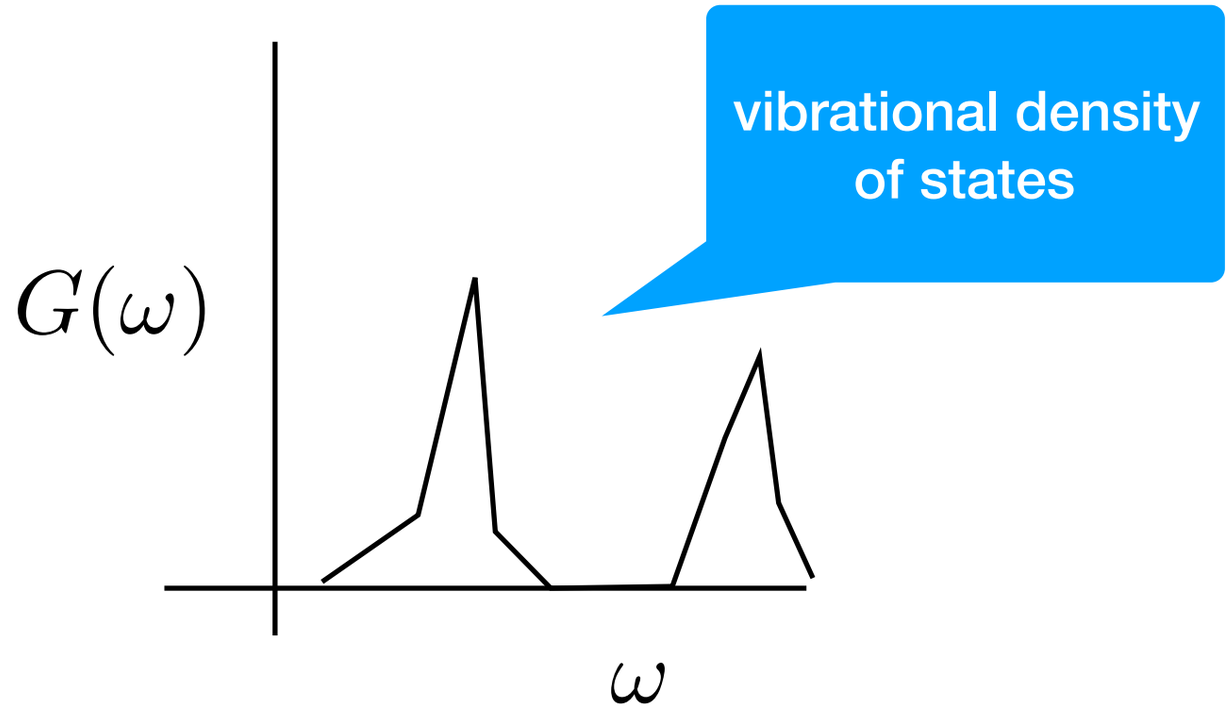
$$G(\omega) = \int_{-\infty}^{\infty} dt C(t) \exp(-2\pi i \omega t)$$

Discrete Fourier Transform:

$$G_k = \sum_{j=0}^{N-1} C_j \exp(-i\, 2\pi j k / N)$$

for N points

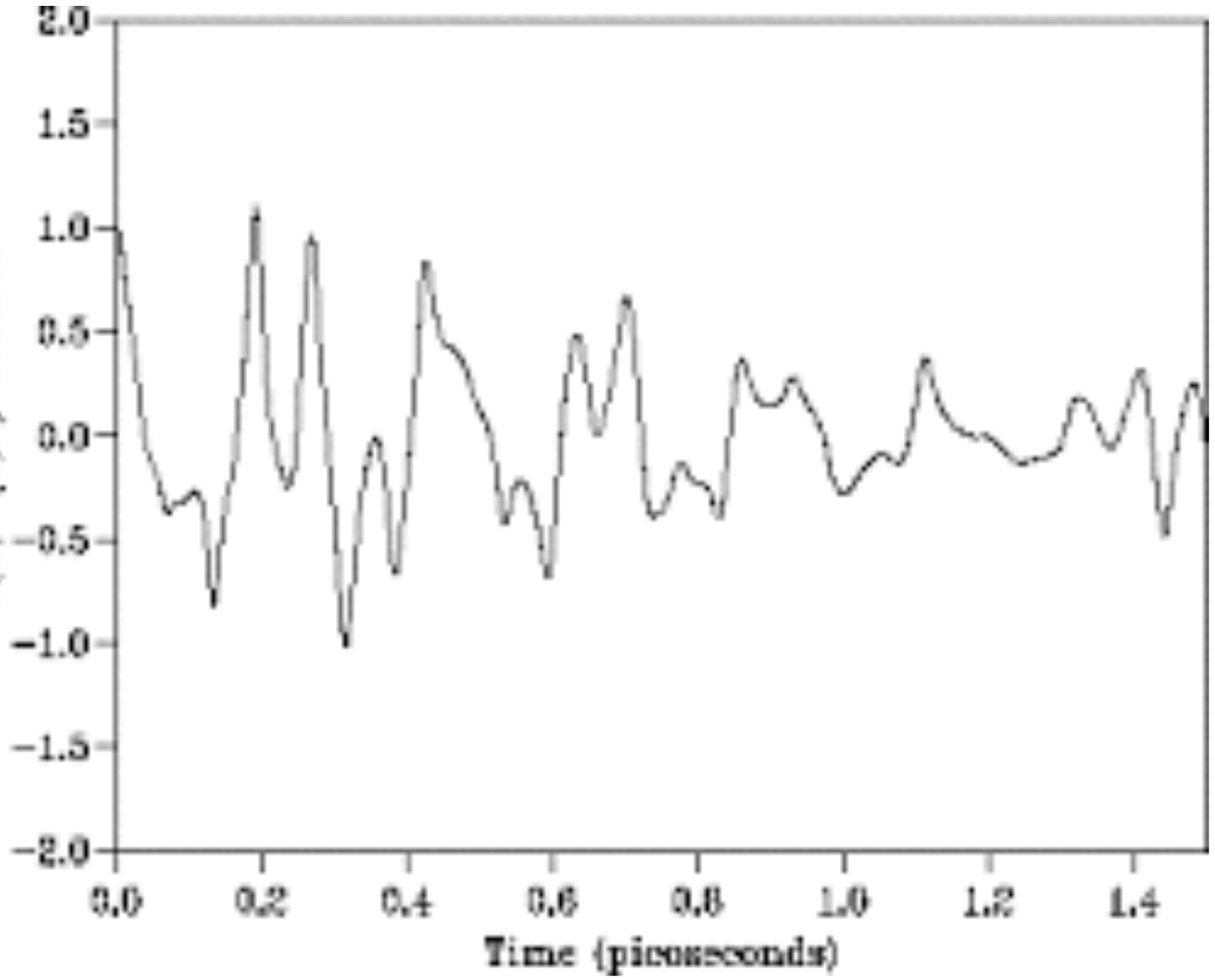


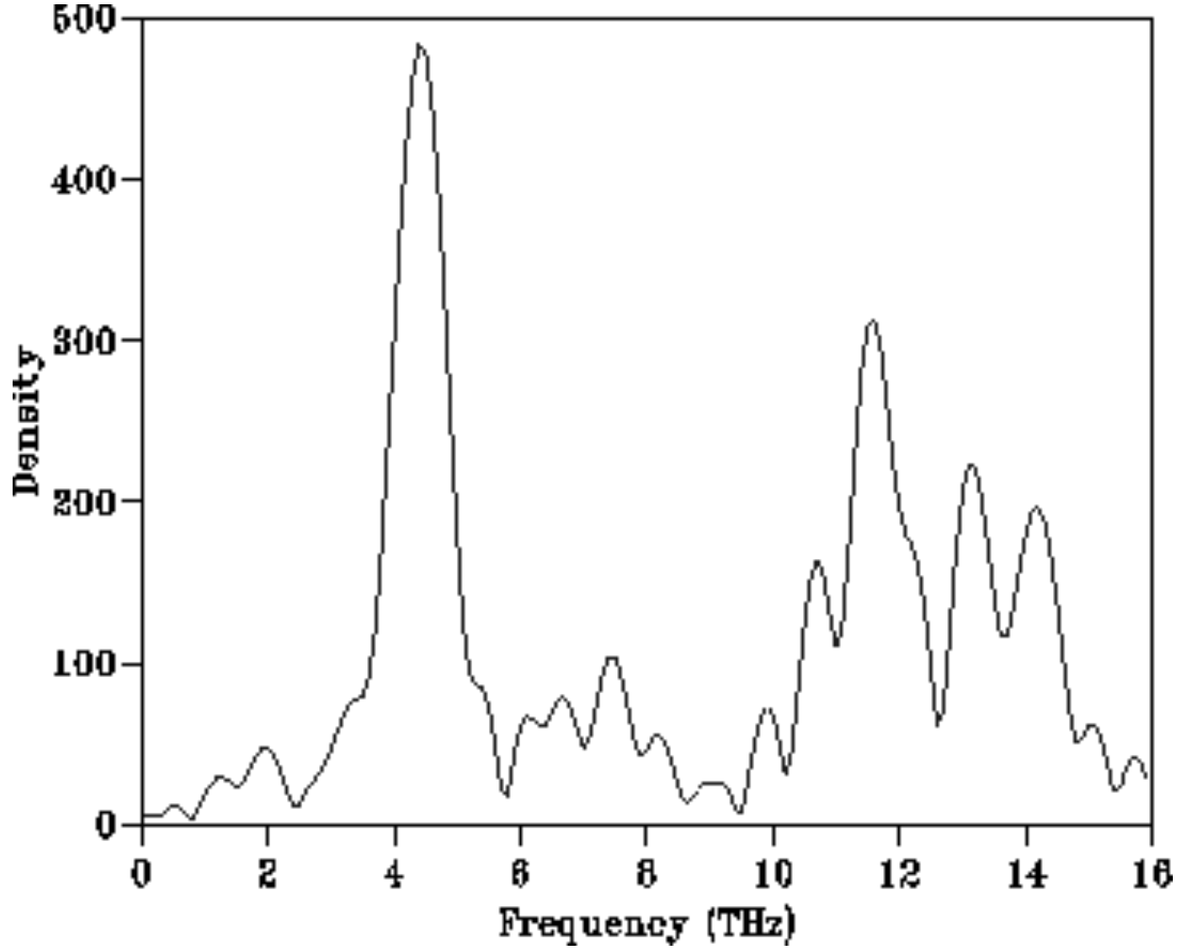


FT of dipole-Dipole autocorrelation can be compared to IR spectrum (intensity as well)

FT of velocity autocorrelation can be compared with vibrational spectrum (not intensity but peak positions)

G(w) is called vibrational density of states (if velocities are majorly contributed by the vibrational motion): area under the curve is proportional to the number of degrees of freedom contributing to that vibrational mode


2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
<v(0).v(t)>/<v0.v0>
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Time (picoseconds)


500
400
300
200
100
0
Density
0
2
4
6
8
10
12
14
16
Frequency (THz)

Home work set 3 a)

Write a program for computing velocity autocorrelation function.

Write a program to convert velocity autocorrelation function to power spectrum.

Test the above for a simple harmonic oscillator in NVE ensemble.

Test the above for a simple harmonic oscillator connected with Langevin thermostat in NVT ensemble.