Nonequilibrium thermodynamics

Phase space
  Dimension - 6N
  Point in the phase space ("phase point") – determines the system
    - it moves
    - determines the dynamics of the system

Ensemble – subspace of phase space

Density of points in phase space: fraction of points inside $dq_1...dp_N$

$\int f_N(q, p, t)dpdq = 1$
Nonequilibrium thermodynamics

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Ensemble – subspace of phase space

Density of points in phase space: fraction of points inside \( dq_1 \ldots dp_N \)

\[
\int f_N(q, p, t) dpdq = 1
\]

Normalization condition

Number of phase points in \( \nu \)

\[
n = N \int_{\nu} f_N(q, p, t) dpdq
\]

The rate of change of number of Phase points

\[
\frac{dn}{dt} = N \int_{\nu} \frac{\partial f_N}{\partial t} dpdq
\]

\[
\frac{\partial f_N}{\partial t} + \nabla \cdot (f_N \mathbf{u}) = 0
\]

\[
\mathbf{u} = (q_1, \ldots, q_{3N}, \dot{q}_1, \ldots, \dot{q}_{3N})
\]

\[
\frac{dn}{dt} = -N \int_S f_N \mathbf{u} \cdot dS = -N \int_{\nu} \nabla \cdot (f_N \mathbf{u}) dpdq
\]
\[
\frac{\partial f_N}{\partial t} + \nabla \cdot (f_N \mathbf{u}) = 0
\]
Condition for conservation of phase points

\[
\nabla \cdot (f_N \mathbf{u}) = \sum_{j=1}^{3N} \frac{\partial}{\partial q_j} f_N \dot{q}_j + \sum_{j=1}^{3N} \frac{\partial}{\partial p_j} f_N \dot{p}_j = \sum_{j=1}^{3N} \left\{ \frac{\partial f_N}{\partial q_j} \dot{q}_j + \frac{\partial f_N}{\partial p_j} \dot{p}_j \right\} + \sum_{j=1}^{3N} \left[ \frac{\partial q_j}{\partial q_j} + \frac{\partial p_j}{\partial p_j} \right] f_N = 0
\]

\[
\frac{\partial f_N}{\partial t} + \sum_{j=1}^{3N} \frac{\partial f_N}{\partial q_j} \dot{q}_j + \sum_{j=1}^{3N} \frac{\partial f_N}{\partial p_j} \dot{p}_j = 0
\]
Hamilton’s equation of motion:

\[
\dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad \dot{q}_i = \frac{\partial H}{\partial p_i}
\]

\[
\frac{\partial f_N}{\partial t} + \frac{\partial f_N}{\partial q_j} \dot{q}_j + \frac{\partial f_N}{\partial p_j} \dot{p}_j = 0
\]
„Poisson bracket“ \{H,f_N\}

\[
\frac{\partial f_N}{\partial t} + H, f_N = 0
\]
Liouville equation

\[
\frac{\partial f_N}{\partial t} + \sum_{j=1}^{N} \frac{\mathbf{p}_j}{m_j} \cdot \nabla_{\mathbf{r}_j} f_N + \sum_{j=1}^{N} \mathbf{F}_j \cdot \nabla_{\mathbf{p}_j} f_N = 0
\]
In cartesian coordinates.
Same as Schrödinger equation

\[ \frac{i \partial f_N}{\partial t} = L f_N \]

Liouville operator

\[ L = -i \left( \sum_{j=1}^{N} \frac{p_j \cdot \nabla_{r_j}}{m_j} + \sum_{j=1}^{N} F_j \cdot \nabla_{p_j} \right) \]

\[ f_N \ p, r, t = e^{-iLt} f_N \ p, r, 0 \]

„Time displacement operator“ – it shifts \( f_N \) by time \( t \)
Ensemble average of dynamical variable at time $t$

$$\langle A(t) \rangle = \int A(p,q,t) f_N(p,q,t) \, dp \, dq$$

Time dependent ensemble average

It depends on only few variables

$$\langle U \rangle = \sum_{i,j} \int \cdots \int u(r_i, r_j) f_N(r_1, \ldots, p_N, t) \, dr_1 \cdots dp_N$$

Can be integrated of other (majority) of variables $\rightarrow$ Reduced distribution function

$$f^{(n)}_{N} \left(r_1, \ldots, r_n, p_1, \ldots, p_n, t\right) = \frac{N!}{(N-n)!} \int \cdots \int f_N(r_1, \ldots, p_N, t) \, dr_{n+1} \cdots dr_N \, dp_{n+1} \cdots dp_N$$
Distribution function

\( (N,V,T) \)

Probability that molecule 1 is in \( v \, dr_1 \) around \( r_1 \) ... \( N \, v \, dr_N \) around \( r_N \)

\[
P^{(N)}(r_1, ..., r_N)dr_1...dr_N = \frac{e^{-\beta U_N} dr_1...dr_N}{Z_N}
\]

Probability that molecule 1 is in \( dr_1 \) around \( r_1 \), ..., \( n \) in \( dr_n \) around \( r_n \) and other molecules are anywhere:

\[
P^{(n)}(r_1, ..., r_n)dr_1...dr_n = \int \ldots \int e^{-\beta U_N} dr_{n+1}...dr_N
\]

Probability that any molecule is in \( dr_1 \) around \( r_1 \), ..., \( n \) in \( dr_n \) around \( r_n \) and other molecules are anywhere:

\[
\rho^{(n)}(r_1, ..., r_n) = \frac{N!}{(N-n)!} P^{(n)}(r_1, ..., r_n)
\]

\[
\rho^{(1)}(r_1)dr_1 = \frac{N}{V} = \rho^{(1)} = \rho
\]

The simplest distribution function
Crystal – periodic function
Liquid – a constant
Ensemble average of dynamical variable at time $t$:

$$\langle A(t) \rangle = \int A(p, q, t) f_N \ p, q, t \ dpdq$$

Time dependent ensemble average.

Integration over other (majority of) variables $\rightarrow$ Reduced distribution function:

$$f_N^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n, \mathbf{p}_1, \ldots, \mathbf{p}_n, t) = \frac{N!}{(N-n)!} \int \cdots \int f_N(\mathbf{r}_1, \ldots, \mathbf{p}_N, t) \ dr_1 \ldots dr_N \ dp_{n+1} \ldots dp_N$$

Integration:

$$\frac{\partial f_N}{\partial t} + \sum_{j=1}^{N} \frac{p_j}{m_j} \cdot \nabla_{r_j} f_N + \sum_{j=1}^{N} X_j \cdot \nabla_{p_j} f_N + \sum_{i,j=1}^{N} F_{ij} \cdot \nabla_{p_j} f_N + \sum_{j=1}^{N} \int \int F_{j,n+1} \cdot \nabla_{p_j} f_N^{(n+1)} \ dr_{n+1} dp_{n+1} = 0$$

Bogoliubov, Born, Green, Kirkwood, Yvon hierarchy (BBGKY).

Time-dependent analogy of equilibrium equations (Kirkwood).

solution ???
Kirkwoodova equation

\[
kT \ln \rho^{(n)} 1, \ldots, n, \xi = kT \ln \rho + kT \ln \rho^{(n-1)}_{N-1} 2, \ldots, n - \xi \sum_{j=2}^{n} u(r_{ij}) + \frac{1}{N} \int_{V} \int_{V} u(r_{12}) \rho^{(2)}_{1,2,\xi} \ dr_{1} \ dr_{2} \ d\xi
\]

\[
- \int_{0}^{\xi} \int u(r_{1,n+1}) \rho^{(n+1)}_{1,\ldots,n,n+1,\xi} \ dr_{n+1} \ d\xi
\]

\[
-n=2
\]

\[
-kT \ln g^{2} 1, 2, \xi = \xi u(r_{12}) + \rho \int_{0}^{\xi} \int_{V} u(r_{13}) \left[ \frac{g^{(b)}_{1,2,3,\xi}}{g^{(2)}_{r,2,\xi}} - g^{(2)}_{1,3,\xi} \right] \ dr_{3} \ d\xi
\]

Cannot be solved without approximation
\[ \frac{\partial f^{(n)}}{\partial t} + \sum_{j=1}^{n} \frac{p_j}{m_j} \cdot \nabla_{r_j} f^{(n)} + \sum_{j=1}^{n} \mathbf{X}_j \cdot \nabla_{p_j} f^{(n)} + \sum_{i,j=1}^{n} F_{ij} \cdot \nabla_{p_j} f^{(n)} + \sum_{j=1}^{n} \int \int \mathbf{F}_{j,n+1} \cdot \nabla_{p_j} f^{(n+1)} \, d\mathbf{r}_{n+1} d\mathbf{p}_{n+1} = 0 \]

Solution for special cases only – gases with low density
- Intermolecular collisions are less likely
- Properties depends on single particle only
- Only reduced distribution function of the first order is required

\[ f_j^{(1)}(\mathbf{r}^n, \mathbf{p}^n, t) \quad \text{... „singlet“ distribution of component } j \]

- Central expression in the transport phenomena
- Description of mass transport

\[ f_j(\mathbf{r}, \mathbf{v}_j, t) \quad \text{Simplified notation for gases.} \]

Normalization conditions:
\[ \rho_j(\mathbf{r}, t) = \int f_j(\mathbf{r}, \mathbf{v}_j, t) \, d\mathbf{v}_j \quad \text{Density of particles } j \text{ around } \mathbf{r} \]
\[ N_j = \int \int f_j(\mathbf{r}, \mathbf{v}_j, t) \, d\mathbf{r} d\mathbf{v}_j \quad \text{Total number of molecules } j \]

Average velocity of molecules \( j \) in the vicinity of \( \mathbf{r} \)
\( \sim \) flow of molecules \( j \)
\[ \mathbf{v}_j(\mathbf{r}, t) = \frac{1}{\rho_j} \int \mathbf{v}_j f_j(\mathbf{r}, \mathbf{v}_j, t) \, d\mathbf{v}_j \]
Boltzmann equation

Assuming that it is sufficient to consider only two-particle interactions

Number of molecules in the phase space volume element $d\mathbf{r}d\mathbf{v}_j$ around $(\mathbf{r},\mathbf{v}_j)$:

$$f_j d\mathbf{r}d\mathbf{v}_j$$

No collision:

$$f_j \mathbf{r}, \mathbf{v}_j, t = f_j \left( \mathbf{r} + \mathbf{v}_j dt, \mathbf{v}_j + \frac{\mathbf{X}_j}{m_j} dt, t + dt \right) \quad (\mathbf{X} - \text{external forces})$$

Motion of molecules not colliding in $dt$

Molecules follow given trajectory (velocity $\mathbf{v} - \mathbf{v} + d\mathbf{v}$) around $\mathbf{r}$

- $\Gamma_{ji}^{(-)}$: Number of molecules diverged away from the trajectory due to collision with type $i$
- $\Gamma_{ji}^{(+)i}$: Number of molecules joining the trajectory due to collision with type $i$ molecules

$$f_j \left( \mathbf{r} + \mathbf{v}_j dt, \mathbf{v}_j + \frac{\mathbf{X}_j}{m_j} dt, t + dt \right) d\mathbf{r}d\mathbf{v}_j = f_j \mathbf{r}, \mathbf{v}_j, t \ d\mathbf{r}d\mathbf{v}_j + \sum_i \Gamma_{ji}^{(+)i} - \Gamma_{ji}^{(-)} \ d\mathbf{r}d\mathbf{v}_j dt$$

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_j \cdot \nabla \mathbf{r} f_j + \frac{\mathbf{X}_j}{m_j} \cdot \nabla \mathbf{v}_j f_j = \sum_i \Gamma_{ij}^{(+)i} - \Gamma_{ij}^{(-)}$$

„Streaming“ – changes
Due to motion without collisions

Changes due to
intermolecular collisions
Determining \[ \Gamma_{ji}^{(-)} \, drdv_j dt \]

Molecule \( j \) in \((r,v_j)\)

Impact parameter \((b,b+db)\)

Relative velocity \[ g_{ij} = (v_i - v_j) \]

\[ \Delta \ldots \text{Range of inter-molecular forces} \]

Number of molecules \( i \) in volume cylinder: \[ 2\pi f_i \, r, v_i, t \, g_{ij} bdb dt \]

Number of collision between \( i \) and \( j \) within \( dt \):

Number of molecules \( j \) in \( drdv_j \)

\[ f \, r, v_j, t \, drdv_j \]

\[ \Gamma_{ji}^{(-)} \, drdv_j dt = 2\pi drdv_j dt \iint f_j \, r, v_j, t \, f_i \, r, v_i, t \, g_{ij} bdb dv_i \]

\[ \Gamma_{ji}^{(-)} = 2\pi \iint f_j \, r, v_j, t \, f_i \, r, v_i, t \, g_{ij} bdb dv_i \]

Assumption that \( f_i \) and \( f_j \) do not correlate!

"Molecular chaos assumption"
\[ \Gamma^{(+)}_{ji} = 2\pi \int \int f_i \cdot r, v_j, t, f_j \cdot r, v_i, t \; g_{ij} bdbd v_i' = 2\pi \int \int f_i' f_j' g_{ij} bdbd v_i' \]

\[ \frac{\partial f_i}{\partial t} + v_j \cdot \nabla_r f_j + \frac{X_j}{m_j} \cdot \nabla_{v_j} f_j = \sum_i \Gamma^{(+)}_{ij} - \Gamma^{(-)}_{ij} \]

\[ \frac{\partial f_i}{\partial t} + v_j \cdot \nabla_r f_j + \frac{X_j}{m_j} \cdot \nabla_{v_j} f_j = 2\pi \sum_i \int \int f_i' f_j' - f_i f_j \; g_{ij} bdbd v_i \]

**Boltzmannova rovnice**

Nonliner integro-differential equation
Solution – approximations – Hilbert, Chapman, Enskog
Separately for each component of gas phase
Dependence on the character of inter-molecular potentials – \( f_i' \)
Time-correlation function

Green, Kubo

Time-correlation function – nonequilibrium statistical mechanics
- it corresponds to partition function in equilibrium statistical mechanics
Hold in classical limit as well as in quantum description

Phase space: \( p(0), q(0) \rightarrow p(t), q(t) \)

\[
\begin{align*}
p(t) &= p(p, q; t) \\
q(t) &= q(p, q; t)
\end{align*}
\]

\[
A(p(t), q(t)) = A(p, q; t) = A(t)
\]

\[
C(t) = \langle A(0)A(t) \rangle = \int \cdots \int dpdq A(p, q; 0) A(p, q; t) f(p, q)
\]

Classical t-c function

\[
C(t) = \langle A(0)A(t) \rangle = \int \cdots \int dpdq A(p, q; 0) A(p, q; t) f(p, q)
\]

Equilibrium distribution function
Simple example – $A$ is a velocity of particular molecule:

$$C(t) = \langle v(0) v(t) \rangle$$

$$C(t) = \int \cdots \int dp dq v(p, q; 0) v(p, q; t) f(p, q)$$

- solving equation of motion for particle surrounded by other particles
- averaging initial conditions over equilibrium ensemble
- complicated solution

Advantage – access to otherwise hard-to-get properties (transport coeff.)
- suitable for numerical solution

$$D = \frac{1}{3} \int_{0}^{\infty} \langle v(0) v(t) \rangle dt$$

Diffusion coefficient – can be obtained for:
- any density
- any interaction potentials (including anisotropic)
- polyatomic molecules

For particular transportation phenomenon – need for appropriate time-correlation function
\[ C(t) = \langle v(0)v(t) \rangle \] Correlation function for particle velocity

\[ C(0) = \langle v(0)v(0) \rangle \] Corresponds to average \( v^2 \) ... \( (3kT/m) \)

With increasing time the number of collision increases and the velocity deviates from the initial one. After a time \( t \) the velocity will not be correlated with the initial one: \( C(t) = 0 \)

\[ C(0) = 3kT/m \]
\[ C(t) = 0 \] Approximation:

Exponential decay

\[ C(t) = (3kT/m)\exp(-t/\tau) \]

Application of TC methodology:
Time dependent perturbation – time dependent response:
Fourier analysis of "frequency dependent susceptibility"
Example – time-dependent external electric field – time-dependent current in conductor
Current density described via frequency-dependent conductance \( \sigma(\omega) \)
(interaction of molecules with light)

\[ \sigma(\omega) = \frac{1}{kT} \int_0^\infty dte^{-i\omega t} \langle J(0)J(t) \rangle \]

\[ J(t) = \sum_j q_j v_j \] Charge

Velocity along the field direction

Fourier-Laplace transformation
In general – application of time-dependent perturbation – analysis of „response“
Response is linearly dependent on the perturbation: **LINEAR RESPONSE THEORY**

Correlation of two different properties:

$$
\psi(\omega) = \int_0^\infty dt e^{-i\omega t} \langle A(0)B(t) \rangle
$$

<table>
<thead>
<tr>
<th>Correlation</th>
<th>( p(t), q(t) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>p(t), q(t)</td>
</tr>
<tr>
<td>B</td>
<td>p(t), q(t)</td>
</tr>
</tbody>
</table>

\( \psi \) ... Generalized susceptibility

**Example:** **Absorption of light**

The shape of IR bends can be obtained by Fourier-Laplace transformation of autocorrelation function of dipole moment!

System of \( N \) interacting molecules in quantum state \( i \)
System interacts with electric field having frequency \( \omega \)

\[
E(t) = E_0 E \cos \omega t = \frac{E_0 E}{2} e^{i\omega t} + e^{-i\omega t}
\]
Interaction between the field and molecule:

\[ H^{(1)}(t) = -\mathbf{M} \cdot \mathbf{E}(t) \]

Operator of total dipole moment

Golden rule: transition probability

\[
P_{i \rightarrow f}(\omega) = \frac{\pi E_0^2}{2\hbar^2} \left| \langle f | \mathbf{\varepsilon} \cdot \mathbf{M} | i \rangle \right|^2 \left[ \delta \omega_f - \omega + \delta \omega_f + \omega \right]
\]

Multiplying by \(\hbar \omega/2\pi \rightarrow\) energy lost velocity transition to (final) state \(f\)

Summing over all \(i\) and \(f \rightarrow\) total lost

Multiplying by the probability that the system is in state \(i\)

\[
-\dot{E}_{rad} = \sum_i \sum_f \rho_i \hbar \omega_f P_{i \rightarrow f}(\omega) = \frac{\pi E_0^2}{2\hbar^2} \sum_f \sum_i \omega_f \rho_i \left| \langle f | \mathbf{\varepsilon} \cdot \mathbf{M} | i \rangle \right|^2 \left[ \delta \omega_f - \omega + \delta \omega_f + \omega \right]
\]

System in equilibrium:

\[
\rho_f = \rho_i e^{-\beta \hbar \omega_f} \quad \rho_i - \rho_f = \rho_i (1-e^{-\beta \hbar \omega_f})
\]

\[
-\dot{E}_{rad} = \frac{\pi E_0^2}{2\hbar^2} 1-e^{-\beta \hbar \omega} \omega \sum_i \sum_f \rho_i \left| \langle f | \mathbf{\varepsilon} \cdot \mathbf{M} | i \rangle \right|^2 \delta \omega_f - \omega
\]
\( dE_{rad} \) ... Radiation intensity (expressed as a flux) \textit{times} transition probability (cross section)

\[
S = \frac{v}{8\pi} \varepsilon E_0^2 = \frac{c}{8\pi} nE_0^2
\]

Poynting vector ... incident flux of radiation

\[
\left( -\frac{\dot{E}_{rad}}{S} \right) = \alpha(\omega) = \frac{4\pi^2}{\hbar c n} \left( 1 - e^{-\beta \hbar \omega} \right) \omega \sum_f \sum_i \rho_i \left| \langle f | \mathbf{\varepsilon} \cdot \mathbf{M} | i \rangle \right|^2 \delta \omega_i - \omega
\]

"Absorption lineshape“ \textit{I}

\[
I(\omega) = \frac{3\hbar c n \alpha(\omega)}{4\pi^2 \omega \left( 1 - e^{-\beta \hbar \omega} \right)} = 3 \sum_f \sum_i \rho_i \left| \langle f | \mathbf{\varepsilon} \cdot \mathbf{M} | i \rangle \right|^2 \delta \omega_i - \omega
\]

\textbf{Time dependency of wavefunction \textit{vs.} Time dependency of operator}

\[
\chi(0), A(t)\psi(0) = \chi(t), A(0)\psi(t)
\]

\[
i\hbar \frac{\partial \psi}{\partial t} = H\psi
\]

\[
\psi(t) = \exp \left( -\frac{iHt}{\hbar} \right) \psi(0) = U(t)\psi(0)
\]

\[
\chi(0), A(t)\psi(0) = \chi(t), A(0)\psi(t) = U(t)\chi(0), A(0)U(t)\psi(0) = \chi(0), U(t)^* A(0)U(t)\psi(0)
\]

\[
A(t) = e^{iHt/\hbar} A(0)e^{-iHt/\hbar}
\]
\[ I(\omega) = \frac{3\hbar cn(\omega)}{4\pi^2 \omega} \left[ 1 - e^{-\beta \hbar \omega} \right] = 3 \sum_f \sum_i \rho_i \left| \langle f | \mathbf{\varepsilon} \cdot \mathbf{M} | i \rangle \right|^2 \delta(\omega_{fi} - \omega). \]

Transformation to Heisenberg form using FT delta function

\[ \delta(\omega) = \frac{1}{2\pi} \int_0^\infty e^{i\omega t} dt \]

\[ I(\omega) = \frac{3}{2\pi} \sum_f \sum_i \rho_i \langle i | \mathbf{\varepsilon} \cdot \mathbf{M} | f \rangle \langle f | \mathbf{\varepsilon} \cdot \mathbf{M} | i \rangle \int_{-\infty}^\infty dt \cdot \exp \left[ \frac{E_f - E_i}{\hbar} - \omega \right] it. \]

\(i\) and \(f\) are eigenfunction of \(H\):

\[ e^{-iE_i t/\hbar} |i\rangle = e^{-iH_0 t/\hbar} |i\rangle \]

\[ \langle f | e^{iE_f t/\hbar} = \langle f | e^{iH_0 t/\hbar} \]

\[ I(\omega) = \frac{3}{2\pi} \int_{-\infty}^\infty dt \cdot e^{-i\omega t} \sum_f \sum_i \rho_i \langle i | \mathbf{\varepsilon} \cdot \mathbf{M} | f \rangle \langle f | \mathbf{\varepsilon} \cdot \mathbf{M}(t) | i \rangle \]

\[ \mathbf{M}(t) = e^{iH_0 t/\hbar} \mathbf{M} e^{-iH_0 t/\hbar} \]
\[ I(\omega) = \frac{3}{2\pi} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \sum_i \rho_i \langle i | \mathbf{\varepsilon} \cdot \mathbf{M}(0) \mathbf{\varepsilon} \cdot \mathbf{M}(t) | i \rangle \]

Sumation over \( i \) – this is just equilibrium ensemble average

\[ I(\omega) = \frac{3}{2\pi} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \langle \mathbf{\varepsilon} \cdot \mathbf{M}(0) \mathbf{\varepsilon} \cdot \mathbf{M}(t) \rangle \]

For an isotropic fluid – \( \varepsilon \) averaged over all directions

\[ I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle \]

Lineshape is just FT of the time-correlation function of the dipole moment operator of the absorbing molecules in the absence of the field !!
\[
I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \cdot e^{-i\omega t} \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle
\]

Overall dipole moment of the system must be known:

\[
\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle = \left( \sum_{i=1}^{N} \mu_i(0) \right) \cdot \left( \sum_{j=1}^{N} \mu_j(t) \right)
\]

"cross-terms" between molecules \( i \) and \( j \) are present as well.
In general it cannot be interpreted as a change of dipole moment orientation.

In case of sufficient dilution the cross-terms can be neglected:

\[
\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle = \left( \sum_{j=1}^{N} \mu_j(0) \cdot \mu_j(t) \right) = N \langle \mu_j(0) \cdot \mu_j(t) \rangle
\]

Knowing the whole spectra for the region – back FT transformation provides correlation function!

\[
\langle \mu_j(0) \cdot \mu_j(t) \rangle = \int_{\text{band}} I(\omega)e^{i\omega t} d\omega
\]