BASIC OF THE LINEAR RESPONSE THEORY AND ITS APPLICATIONS

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LINEAR RESPONSE THEORY

- An ordinary system, if left alone, will sooner or later attain an equilibrium state.

- This equilibrium state depends on the temperature of the environment and on external parameters.

- If temperature or the external parameters change slowly enough, the system can attain the new equilibrium state practically instantaneously, and we speak of a *reversible* process.

- On the other hand, if the external parameters vary so rapidly that the system has no chance to adapt, it remains away from equilibrium, and we speak of *irreversibility*.

Peter Hertel, Lectures on Theoretical Physics, Linear Response Theory, University of Osnabruck, Germany
When an external field is applied to a system which is at equilibrium, properties of the system that couple to the external field change accordingly.

For low enough field, this change is proportional to the external field. The proportionality constant is usually called the linear response function and provides valuable information of the system.

Ryogo Kubo, Journal of The Physical Society of Japan, 12, 6, (1957), 570
There is an intimate relation between the time dependent response functions and dynamical properties of the system at equilibrium.

This relation is expressed by linear response theory (LRT), first clearly formulated by Kubo in an important paper in 1957\(^1\).

LRT is valid when the applied field is very small.

1. Ryogo Kubo, Journal of The Physical Society of Japan, 12, 6, (1957), 570
Examples of static response functions are specific heat, magnetic and electric susceptibility, isothermal compressibility etc.

These are very important properties of the system.

In the case of time (or frequency) dependent perturbation, the response also becomes time or frequency dependent.
LINEAR RESPONSE THEORY

- If the applied field is held constant for a very long time, so that the system can come to equilibrium in the presence of the field, finding the response is a problem of equilibrium statistical mechanics.

- But if we want to know the *transient response* to the applied field, or if the field varies periodically in time, then it is necessary to go beyond equilibrium statistical mechanics.

- We will deal with the response to a static force first. Then the theory for a time dependent force will be presented.
Let’s see how the equilibrium linear response is determined.

An equilibrium system is described by an unperturbed Hamiltonian $H(X)$.

The small applied field is denoted by $E$ (magnetic field or electric field).

The coupling of the system to the field is described by the energy $-M(X)E$.

$M(X)$ (magnetic moment or dipole moment) is some known function of the state of the system.
The perturbed Hamiltonian is:

\[ H(X, E) = H(X) - M(X)E \]

In classical mechanics, the unperturbed distribution function denoted \( f(X) \) is:

\[ f(X) = \frac{1}{Q} e^{-\beta H(X)} \]

where \( Q \) is the unperturbed partition function:

\[ Q = \int dX e^{-\beta H(X)} \]

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The corresponding perturbed quantities are:

\[ f(X, E) = \frac{1}{Q(E)} e^{-\beta H(X) + \beta M(X)E} \]
\[ Q(E) = \int dX e^{-\beta H(X) + \beta M(X)E} \]

In classical statistical mechanics, the perturbed system can be expanded about the unperturbed system. To first order, it is in linear response:

\[ e^{-\beta H(X) + \beta M(X)E} = \{1 + \beta ME + O(E^2)\} e^{-\beta H(X)} \]
\[ Q(E) = \{1 + \beta \langle M \rangle E + O(E^2)\} \]

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The expansion of the perturbed distribution is:

\[ f(X, E) = \left(1 + \beta[M(X) - \langle M \rangle]E\right)f(X) + O(E^2) \]

These equations contain the unperturbed equilibrium average \( \langle M \rangle \), coming from the first-order expansion of \( Q(E) \). For simplicity, from here on we restrict the discussion to cases where \( \langle M \rangle = 0 \).

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The average of any dynamical variable $A(X)$, denoted by $\langle A; E \rangle$:

$$\langle A; E \rangle = \langle A \rangle + \chi_{AM} E + O(E^2)$$

Where the coefficient $\chi_{AM}$ is given by:

$$\chi_{AM} = \beta \langle AM \rangle$$

$\chi_{AM}$ describes the average linear response $\langle A; E \rangle$ produced by the applied field.

If $A \rightarrow$ electric dipole moment, $\chi_{AM}$ is the dielectric susceptibility. If $A \rightarrow$ magnetic moment, $\chi_{AM}$ is the magnetic susceptibility.

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The quantum mechanical version has a similar form of the average of any dynamical variable $A(X)$.

The only difference is the replacement of $M$ by its Kubo transform $\tilde{M}$ to represent the susceptibility:

$$\chi_{AM} = \beta \langle A\tilde{M} \rangle$$

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
**DYNAMIC LINEAR RESPONSE**

- Considering a time-dependent external field $E(t)$
  
  (magnetic field or electric field)

- To find the time-dependent average of a dynamical variable $A$, we use the time-dependent distribution function $f(X; t)$, instead of $f(X)$ for the static case.

- Then we look for the way that $f(X; t)$ is affected by the extra perturbing Hamiltonian $-M(X)E(t)$.

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The time-dependent distribution function obeys the Liouville equation:

\[ \frac{\partial f}{\partial t} = -L_0 f - L_1 E(t) f \]

in which \(L_0\) is the unperturbed Liouville operator. \(L_0 f\) is the Poisson bracket of \(H\) and \(f\), and \(L_1 f\) is the Poisson bracket of \(-M\) and \(f\).

Poisson bracket

\[ (A, B) = \sum \left( \frac{\partial A}{\partial q} \frac{\partial B}{\partial p} - \frac{\partial A}{\partial p} \frac{\partial B}{\partial q} \right) \]

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
To find the first-order response to $E(t)$, we expand $f$ in powers of $E$, using $f_0$ and $f_1$ to denote the terms of zeroth and first order in $E$:

$$f = f_0 + f_1 + O(E^2)$$

- $f_0$ is the initial equilibrium condition, $f_0(t) = f_{eq}$
- $f_1$ is the perturbation term,

$$f_1(t) = \int_0^t ds \beta E(s) e^{-(t-s)L_0 M} f_{eq}$$

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
Then we can obtain the time-dependent average of some dynamic variable $A(X)$, such as the electric dipole moment or the magnetic moment,

$$\langle A; t \rangle = \langle A \rangle + \beta \int_0^t ds E(s) \int dX A(X) e^{-(t-s)L_0 M} f_{eq}$$

In typical applications, the equilibrium averages of both $A$ and $M$ vanish. Then an equilibrium average can be obtained,

$$\langle A; t \rangle = \beta \int_0^t ds E(s) \langle A(t - s) M(0) \rangle_{eq} + \cdots$$

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
If we define the time-dependent response function analog of the static susceptibility,

\[ \phi_{AM}(t) = \beta \langle A(t) \dot{M}(0) \rangle_{eq} \]

Then we obtain the standard linear response formular:

\[
\langle A; t \rangle = \beta \int_0^t ds \phi_{AM}(s)E(t - s) + O(E^2)
\]

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The quantum mechanical version has a similar form of the average of any dynamical variable $A(X, t)$.

The only difference is the form of the response function:

$$\phi_{AM}(t) = -\beta \langle A(t)L_0 H_1 \rangle_{eq}$$

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
FREQUENCY DEPENDENT RESPONSE

- Periodically varying external fields are often used in experiments, then the response at the frequency of the perturbation can be measured.

- With a Fourier transform, the standard linear response formular can be written as:

\[ \langle A \rangle_\omega = \sigma_{AM}(\omega)E_\omega \]

\[ \sigma_{AM}(\omega) = \int_0^\infty dt e^{i\omega t} \phi_{AM}(t) \]

where the response function \( \sigma_{AM}(\omega) \) is a one-sided Fourier transform of \( \phi_{AM}(t) \).

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The calculation of the mobility of a single ion in solution.

The ion has a charge e and interacts with an external uniform electric field \( E \) in the \( x \) direction.

The perturbation Hamiltonian is \(-eE(t)x\).

The quantity \( M \) is \( ex \).

The mobility of the ion is its average velocity (\( v \)),

\[ A = x = v \]

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The frequency-dependent average of the mobility of the ion can be calculated by:

\[ \langle v \rangle_\omega = \mu(\omega)E_\omega \]

The response function \( \mu(\omega) \) can be written as:

\[ \mu(\omega) = \int_0^\infty dt e^{-i\omega t} \beta \langle v(t)v(0) \rangle \]

Where the velocity correlation function decays exponentially,

\[ \langle v(t)v(0) \rangle_{eq} = \frac{kT}{m} e^{-\xi t/m} \]

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
MAGNETIC SUSCEPTIBILITY

- Finding an expression for the frequency-dependent magnetic susceptibility of a material.
- The external field is a time-dependent magnetic field $B(t)$.
- The quantity $M$ is the total magnetic moment of the system.
  $\mathcal{A}$ is the magnetization $M/V$, where $V$ is the volume of the system.

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The frequency-dependent average of the variable, $A$, is

$$\frac{1}{V} \langle M \rangle_\omega = \chi(\omega) B_\omega$$

The response function $\chi(\omega)$, which is also the frequency-dependent magnetic susceptibility, can be written as:

$$\chi(\omega) = \frac{\beta}{V} \int_0^\infty dt e^{-i\omega t} \langle M(t) L_0 \bar{M} \rangle$$

Or, written as another expression,

$$\chi(\omega) = \frac{\beta}{V} \langle M \bar{M} \rangle_{eq} \frac{1}{1 + i\omega\tau}$$

Robert Zwanzig, Nonequilibrium Statistical Mechanics, Oxford University Press, 2001
The dynamical response of the solvent is importance in the understanding of chemical reaction rates in solution.

The dynamical response of the solvent is originated at changes in the interaction potential with the solute.

The linear response theory can be applied to describes the solvation dynamics by the time correlation function for fluctuations in the solvation energy.
In the experiment, the dynamical response of the solvent is described by the experimental response function:

\[ S(t) = \frac{\Delta U(t) - \Delta U(\infty)}{\Delta U(0) - \Delta U(\infty)} \]

Where \( \Delta U(t) \) is the difference of the interaction energies:

\[ \Delta U(t) = U_{ex}(t) - U_0(t) \]

Within linear response theory, the solvation dynamics is described by the time correlation function:

\[ C(t) = \frac{\langle \delta \Delta U(0) \delta \Delta U(t) \rangle}{\langle \delta \Delta U^2 \rangle} \]

Where \( \delta \Delta U(t) \) is the fluctuations in the solvation energy:

\[ \delta \Delta U(t) = \Delta U(t) - \langle \Delta U(t) \rangle \]

The comparison of the solvation dynamics described by the experimental response function, $S(t)$, and the theoretical time correlation function, $C(t)$, clarifies whether linear response theory is valid or not for a system under investigation.

SOLVATION DYNAMICS

- Invested system: 255 solvent argon atoms, and a single argon solute atom.
- MD simulations were performed.
- The solvent-solvent and solvent-solute interactions were described by the Lennard-Jones potential:

\[ u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

\[ \sigma : \text{ size parameter representing changes in the molecular geometry with electronic excitation.} \]

\[ \varepsilon : \text{ polarizability parameter representing the well-depth of intermolecular interactions.} \]

Comparison between $S(t)$ and $C(t)$ with changing of the well-depth parameter

Comparison between $S(t)$ and $C(t)$ with changing of the size parameter

PROTEIN STRUCTURAL CHANGE UPON LIGAND BINDING

- Linear Response Theory can be used to explain and predict the structural change of proteins upon ligand binding.

- By regarding ligand binding as an external perturbation, the structural change as a response is described by atomic fluctuations in the ligand-free form and the protein-ligand interactions.

Mitsunori Ikeguchi, etc. Physical Review Letters, 94 078102 (2005)
The Hamiltonian of the bound state,

\[ H_1 = H_0 + \sum_i \int dr v_i(r) \phi_i(r) \]

\[ \phi_1(r) = \delta(r - r_1) \]

The response,

\[ \delta \rho_1(r) \cong -\beta \sum_j \int dr' \langle \delta \phi_1(r) \delta \phi_j(r') \rangle_0 v_j(r') \]

with the response function,

\[ \langle \delta \phi_1(r) \delta \phi_j(r') \rangle_0 \]

Mitsunori Ikeguchi, etc. Physical Review Letters, 94 078102 (2005)
What we are interested in is the expectation of the coordinate shift of atom \( i \) in the protein with the perturbation of the ligand binding:

\[
\Delta r_i = \int \, drr \, \delta \rho_i (r) \approx \beta \sum_j \langle \Delta r_i \Delta r_j \rangle_0 f_j
\]

where \( f_j \) is the external force acting on atom \( j \), and \( \langle \Delta r_i \Delta r_j \rangle_0 \) is the variance-covariance matrix of the atomic fluctuations in the ligand-free state.
Structure change of FBP upon binding of Fe$^{3+}$.
Red: Experimental structural changes of C-alfa atoms
Green: predicted structural changes of C-alfa atoms

Mitsunori Ikeguchi, etc. Physical Review Letters, 94 078102 (2005)
THE END
THANKS