BASIC OF THE LINEAR RESPONSE THEORY AND ITS APPLICATIONS

Jiawei Xu

April 2009

OUTLINE

✖ Linear Response Theory

✖ Static Linear Response

✖ Dynamic Linear Response

✖ Frequency Dependent Response

✖ Applications

    1. THE MOBILITY OF A SINGLE ION IN SOLUTION

    2. MAGNETIC SUSCEPTIBILITY

    3. SOLVATION DYNAMICS

    4. PROTEIN STRUCTURAL CHANGE UPON LIGAND   BINDING

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

LINEAR RESPONSE THEORY

✖ 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

LINEAR RESPONSE THEORY

- 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

LINEAR RESPONSE THEORY

- 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.

STATIC LINEAR RESPONSE

- 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.

STATIC LINEAR RESPONSE

- 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

STATIC LINEAR RESPONSE

× 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

STATIC LINEAR RESPONSE

- The expansion of the perturbed distribution is :

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

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

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

STATIC LINEAR RESPONSE

- The average of any dynamical variable *A(X)*, denoted by *<A; E> :*

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

- Where the coefficient χ_{AM} is given by:

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

- χ_{AM} describes the average linear response *<A; E>* produced by the applied field.

- If A → electric dipole moment , χ_{AM} is the dielectric susceptibility. If A → magnetic moment, χ_{AM} is the of magnetic susceptibility.

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

STATIC LINEAR RESPONSE

✖ 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

DYNAMIC LINEAR RESPONSE

- 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

DYNAMIC LINEAR RESPONSE

- 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,

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

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

DYNAMIC LINEAR RESPONSE

✖ Then we can obtain the time-dependent average of some dynamic variable *A(X),* such as the electric dipole moment or the magnetic moment,

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

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

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

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

DYNAMIC LINEAR RESPONSE

- 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

DYNAMIC LINEAR RESPONSE

- 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 :

$$\phi_{AM}(t) = -\beta \langle A(t) L_0 \tilde{H}_1 \rangle_{eq}$$

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:

$$\langle A \rangle_\omega = \sigma_{AM}(\omega) E_\omega \quad \sigma_{AM}(\omega) = \int_0^\infty dt\, e^{i\omega x}\, \phi_{AM}(t)$$

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 MOBILITY OF A SINGLE ION IN SOLUTION

- 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*),

$$A = x \doteq v$$

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

THE MOBILITY OF A SINGLE ION IN SOLUTION

- 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:

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

- 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.

  A is the magnetization M/V, where V is the volume of the system.

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

MAGNETIC SUSCEPTIBILITY

* 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:

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

* Or, written as another expression,

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

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

SOLVATION DYNAMICS

- 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.

SOLVATION DYNAMICS

✖ In the experiment, the dynamical response of the solvent is described by the experimental response function:

$$S(t) = \frac{\overline{\Delta U}(t) - \overline{\Delta U}(\infty)}{\overline{\Delta U}(0) - \overline{\Delta U}(\infty)}$$

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

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

SOLVATION DYNAMICS

* 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:

$$\delta\Delta U(t) = \Delta U(t) - \langle\Delta U(t)\rangle$$

Edson Bernardi, etc. Chemical Physics Letters 407 (2005) 171-175

SOLVATION DYNAMICS

✖ 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:

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

σ : size parameter representing changes in the molecular geometry with electronic excitation.

ε : polarizability parameter representing the well-depth of intermolecular interactions.
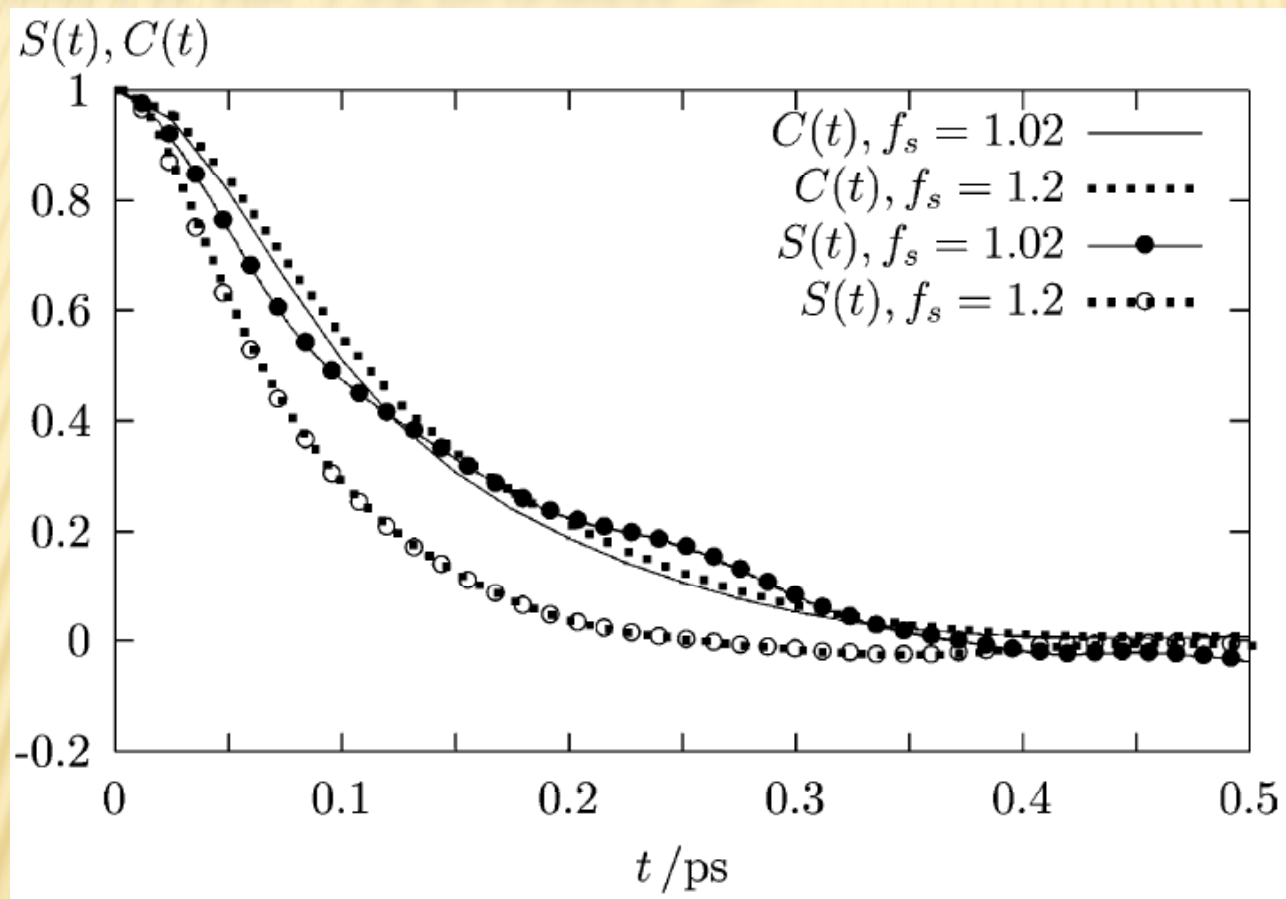
Edson Bernardi, etc. Chemical Physics Letters 407 (2005) 171-175

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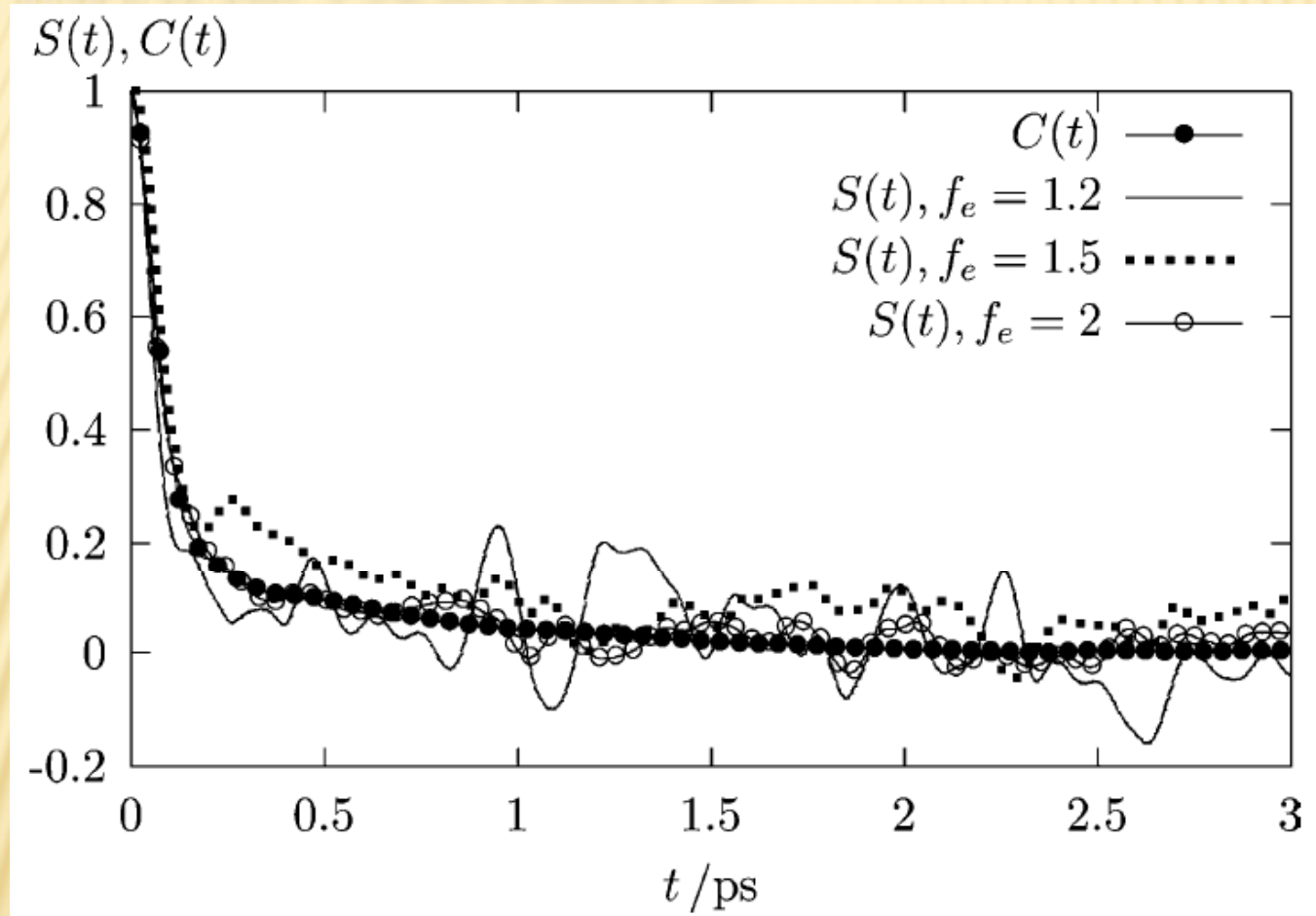
Comparison between S(t) and C(t) with changing of the well-depth parameter

Edson Bernardi, etc. Chemical Physics Letters 407 (2005) 171-175

SOLVATION DYNAMICS

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

Edson Bernardi, etc. Chemical Physics Letters 407 (2005) 171-175

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)

PROTEIN STRUCTURAL CHANGE UPON LIGAND BINDING

- The Hamiltonian of the bound state,

$$H_1 = H_0 + \sum_l \int dr V_1(r)\phi_1(r) \qquad \phi_1(r) = \delta(r - r_l)$$

- 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)

PROTEIN STRUCTURAL CHANGE UPON LIGAND BINDING

✖ 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:

$$\Delta r_i = \int dr\, r\, \delta\rho_i(r) \cong \beta \sum_j \langle \Delta r_i \Delta r_j \rangle_0 \, f_j$$

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.

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

PROTEIN STRUCTURAL CHANGE UPON LIGAND BINDING
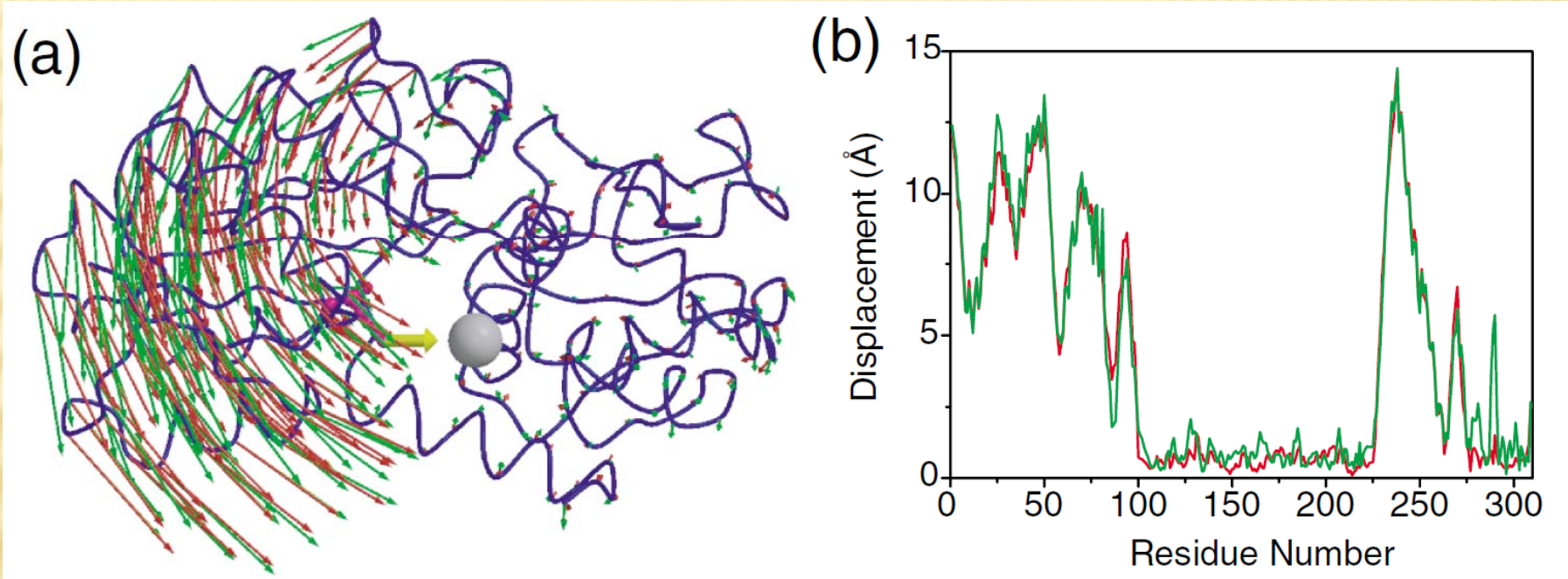
Structure change of FBP upon binding of Fe^{3+}.
Red: Experimental structural changes of C-alfa atoms
Green: predicted structural changes of C-alfa atoms

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

THE END
THANKS