

An Overview of Continuum Models for Nonequilibrium Solvation: Popular Theories and New Challenge

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The effect of solvent on the electron transfer (ET) and spectral shifts has been the focus of experimental and theoretical studies and a key quantity in these studies is the solvent reorganization energy. There are a number of theoretical models toward the evaluation of nonequilibrium solvation free energy that were proposed decades ago and have been applied widely. In the past decade, however, we revisited the original theoretical derivations and identified a serious defect in the popular nonequilibrium solvation models which causes the significant overestimation of solvent reorganization energy and hence predicts a much lowered rate constant for ET in some cases. A rigorous derivation by means of constrained

equilibrium principle of thermodynamics was subsequently conducted for the study of nonequilibrium solvation. In this review, the author outlined the intimate interplays among the representative models and analyzed what the possible problem could be. The key idea presented in our recent papers was highlighted. The constrained equilibrium principle in classical thermodynamics and its application to the nonequilibrium solvation were detailed, and a few argumentative examples in literature were taken for the validation of our theory. © 2015 Wiley Periodicals, Inc.

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Introduction

The theoretical evaluation of solvent effects has aroused the interest of many people over a long time, and properties of solvents and their impacts on processes lie at the heart in many sectors. Recently, concern is growing over solvent effects in electron transfer (ET),^[1–4] molecular excitation^[5–10] in solution and ionic fluids.^[11,12] The influence of a polarizable medium on the properties of a molecular system has attracted the attention of many chemists. In this context, explicit solvent methods that intend to account for the microscopic structure of solvent molecules are more advanced than implicit solvent models. Nevertheless, such methods are yet not to be mature for general purposes. To simplify theoretical treatments and reduce computational demands, often the solvent is replaced by a homogeneous continuous medium characterized by its macroscopic dielectric constant,^[13] and the electrostatic interactions between solute species and solvent molecules are accounted for by means of the reaction field theory.

Continuum models have two primary advantages.^[14] First, the number of degrees of freedom for the system is greatly reduced. If we explicitly take a few of solvent layers which involve hundreds of solvent molecules, a huge number of degrees of freedom will need to be dealt with. As a consequence, we must face with a huge number of possible conformations. Furthermore, explicit models are usually used with empirical force fields whose parameterization is a concern as well, and the descriptions of the solute-solvent interface with nonpolarizable force fields are notably imperfect while applications of the polarizable force fields are still limited. Second, continuum models are appropriate for describing the strong and long-range electrostatic forces that dominate many solvation phenomena.

For equilibrium solvation, there already exist quite a lot of techniques with broad applications from simple models such

as dipolar hard spheres to complex models such as realistic models of methanol.^[15,16] In a previous review by Tomasi and Persico,^[17] various approximations based on continuous medium theory, especially for the equilibrium solvation, have been discussed. Of particular, the polarizable continuum model (PCM), which is parameterized with bulk properties of the solvent and the shape of the solute, has been extensively used.^[17,18] PCM has several versions to account for different electrostatic boundary conditions, but these versions are largely similar with only minor differences. For instance, the original D-PCM,^[19,20] the so-called Conductor-like-screening model (C-PCM),^[20,21] and the integral equation formalism integral equation formulation polarizable continuum model (IEF-PCM)^[17,22] which uses isodensity surface of the molecular solute as a cavity surface, have been coded in several popular quantum chemistry packages. Scalmani and Frisch introduced a continuous surface charge approach that leads to a smooth and robust formalism for the PCM model.^[23] The original C-PCM was developed by Klamt, and its central point is to approximate the medium as conductor.^[21] In the surface volume explicit polarization model^[24] by Chipman, the penetration of the solute charge distribution into the medium is taken into account.

Besides the structure and properties of a thermodynamically equilibrated solute-solvent system, a process that takes place on a sufficiently long timescale may legitimately be treated as

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equilibration with respect to solvent polarization. Still, how to apply continuum models to very fast processes is worthy of consideration. For instance, a transition state structure may live for only a single period of vibration, during which the solvent may not have enough time to respond to the electronic change of the solute at the position of the transition state. By the assumed equilibration, the solvation free energy would be overestimated. In fact, many processes such as ET, spectral shift, and vibrational spectrum are intimately related to the so-called nonequilibrium solvation phenomena in solution.^[18,25] Among them, the solvent reorganization energy in the ET reactions^[26–29] and the spectral shifts^[30–35] is a key quantity that has attracted most attention. Moreover, nonequilibrium solvation problem also exists in some other processes such as proton transfer.^[4,36–40]

In most quantum chemistry software packages, time-dependent density functional theory (TDDFT) coupled with PCM turns out to be a general-purpose procedure for the computation of excitation energies. Implementation of analytical gradient for excited states based on TDDFT including solvent effects by means of the PCM^[41,42] has been reported by several groups. TDDFT/PCM can provide helpful insights into the photophysical and photochemical pathways in solution. Some even new progresses on the combination of continuum models for excited state and advanced quantum chemistry methods have been made. For example, implementation of the first and second analytical energy derivatives of excited state with TDDFT/CPCM into a locally modified Q-Chem has been reported recently.^[43–46]

Although the remarkable success of continuum solvent models in describing the electrostatic interaction between the solvent and the solute molecules in both equilibrium and non-equilibrium solvation cases, there are still certain unsolved questions. In the past decade, we initiated a discussion on the reliability of traditional theories on nonequilibrium solvation, in particular the derivations for the nonequilibrium solvation free energy and the solvent reorganization energy, and have been developing a new approach which can remedy the issues in previous models. In the following section, a brief overview is presented to clarify the defects in the popular nonequilibrium solvation theories and application models. The constrained equilibrium principle in classical thermodynamics and its application to the nonequilibrium solvation are discussed in the Nonequilibrium Solvation Theory Based on Constrained Equilibrium Principle section while the derivation of the solvent

reorganization energy is laid out in the Solvent Reorganization Energy section. Finally, a conclusion is made in the Conclusion section.

Traditional Theories on Nonequilibrium Solvation

Lippert–Mataga equation

In 1950, Ooshika proposed different treatments for two classes of polarizations in solution; the first class of polarizations is due to the orientation of the permanent dipoles of solvent molecules and the second one results from the electronic polarizability.^[47] It is believed that the electronic polarization responds simultaneously to the motion of solute electrons while the orientation of the permanent dipoles is well behind the motion of solute electrons. A typical situation is that the light absorption of a solute molecule is determined not only by the total dielectric constant of the solvent. To describe the solvent effects, Ooshika introduced a perturbation method.^[47] By considering a transition from the ground state to the excited state of the solute, the perturbation method was applied to account for the solvation energy. In terms of “reaction field” originally put forward by Onsager^[48] and based on the first-order perturbation and the second-order energy correction, Mataga et al. gave the spectral shift of light absorption as^[49,50]

$$\Delta(h\nu_{ab}) = - \left[R_s \mu_1 + \frac{1}{2} R_{op} (\mu_2 - \mu_1) \right] \cdot (\mu_2 - \mu_1) \quad (1)$$

with

$$R_s = \frac{2(\epsilon_s - 1)}{(2\epsilon_s + 1)a^3} \quad (2)$$

$$R_{op} = \frac{2(\epsilon_{op} - 1)}{(2\epsilon_{op} + 1)a^3} \quad (3)$$

where ϵ_s and ϵ_{op} denote the static and optical dielectric constant of the solvent, respectively, a stands for the cavity radius, and μ_1 and μ_2 are the dipole moments of the solute at the ground state and the excited state, respectively.

For the fluorescence spectrum, the excited state with an equilibrium polarization of the solvent environment is

considered as the starting point, while the orientations of the permanent dipoles of the solvent keep fixed after the solute changes its dipole from μ_2 to μ_1 . Therefore, the spectral shift in this transition is expressed as^[49,50]

$$\Delta(h\nu_{\text{em}}) = (\mu_2 - \mu_1) \cdot \left[R_s \mu_2 - \frac{1}{2} R_{\text{op}} (\mu_2 - \mu_1) \right] \quad (4)$$

Here, a positive value of $\Delta(h\nu_{\text{ab}})$ corresponds to a blue shift but the same sign for $\Delta(h\nu_{\text{em}})$ to a red shift. Taking a sum of Eqs. (3) and (4), the total shift, that is, the Stokes shift, is given by^[49,50]

$$\Delta(h\nu_{\text{sum}}) = \Delta(h\nu_{\text{ab}}) + \Delta(h\nu_{\text{em}}) = (R_s - R_{\text{op}})(\mu_2 - \mu_1)^2 \quad (5)$$

Equation (5) is called the Lippert–Mataga equation and has been widely applied in the experimental fittings of spectral shifts.

Marcus theory

Marcus pioneered the systematic formulation for nonequilibrium solvation free energy. The central hypothesis is the separation of the orientational and electronic polarizations of solvent.^[51–53] Such a separation eventually leads to the same expression as that given by Ooshika,^[47] Lippert,^[50] and Mataga.^[49] Here, the term “orientational” is used to represent the total of the orientational and atomic parts. In the case of nonequilibrium polarization, the orientational polarization is not in equilibrium with the given solute charge distribution and is quite independent of it. The contribution from this type to the total polarization $\mathbf{P}(\mathbf{r})$ at position \mathbf{r} is denoted as $\mathbf{P}^{\text{or}}(\mathbf{r})$. Conversely, the contribution from the electronic type of polarization is denoted as $\mathbf{P}^{\text{op}}(\mathbf{r})$, and is assumed to equilibrate with the distribution of the solute charge at any time. Such a partition in fact implies an approximation that the continuous response frequencies are classified into two parts; one can match the electronic motion of the solute and the other cannot. Consequently, the nonequilibrium state is such a state in which $\mathbf{P}^{\text{op}}(\mathbf{r})$ reaches the nonequilibrium with the final distribution of solute charge but $\mathbf{P}^{\text{or}}(\mathbf{r})$ is the same as that in the previous equilibrium state. Throughout this review, for the sack of simplicity the position coordinate \mathbf{r} will be dropped unless necessary. The concept of nonequilibrium solvation has led to great progresses in understanding the physics of fast processes in solution, especially in ET reactions and photon absorption/emission. With the definition of the above two kinds of polarizations, that is, orientational and electronic, the reversible work method was adopted to derive the nonequilibrium free energy,^[51–53] based on which ET reactions in solution have been intensively studied for several decades. Significantly, Marcus two-sphere model for solvent reorganization energy has been a very useful tool for qualitative depictions of ET reactions in solution.

Nonequilibrium solvation theories for continuous media are still ongoing topics.^[54,55] In this context, the concept of nonequilibrium free energy plays the key role in the understanding of the physics of fast processes in solutions. For half a century,

Marcus theory^[51–53,56] for nonequilibrium solvation has been the main avenue for elucidating nonequilibrium solvent effects. In the landmark papers by Marcus,^[51,52] the free energy change from the initial equilibrium state to the nonequilibrium state was attained by the simple reversible work integration, directly along the pathway from the initial equilibrium to the nonequilibrium, that is,

$$[\rho=0, \Phi=0] \xrightarrow{A1, \epsilon_s} [\rho_1, \Phi_1^{\text{eq}}] \xrightarrow{A2, \epsilon_{\text{op}}} [\rho_2, \Phi_2^{\text{non}}] \quad (6)$$

where Φ denotes the total electric potential including both the potential ψ due to the solute charge in vacuum and polarization potential φ due to the medium. The solute charge is also referred to as “free charge” from the standpoint of electrostatics, which in principle represents the charge that can move about through the material. In practice, what this ordinarily means is that free charge is not associated with any particular nucleus, but roams around at will. By contrast, the bound charges or the polarization charges in medium are attached to specific atoms or molecules. They are on a tight leash and can move only a bit within each atom or molecule. Such microscopic displacements are not as dramatic as the wholesale rearrangement of the solute charges, but their cumulative effects account for the characteristic behaviors of dielectric materials. For convenience, we call hereafter ψ the vacuum potential while φ the polarization potential. We do not distinguish “free charge” and “solute charge” and use ρ to denote the continuous bulk distribution of the solute charge. The superscripts “eq” and “non” in Eq. (6) are abbreviations of equilibrium and nonequilibrium, respectively.

In the establishment of the nonequilibrium state, step A1 charges the solute to ρ_1 and Φ reaches equilibrium in the solvent of a static dielectric constant ϵ_s . In step A2, the solute is charged from ρ_1 to ρ_2 but only the electronic component of the solvent polarization, which corresponds to the optical dielectric constant ϵ_{op} of the solvent, responds. The system arrives a new state in which the electronic polarization of the solvent reaches equilibrium with ρ_2 but the orientational polarization does not. This state, denoted as $[\rho_2, \Phi_2^{\text{non}}]$, is referred to as the “nonequilibrium” state. The total potentials in both the equilibrium and nonequilibrium can be expressed as

$$\Phi_1^{\text{eq}} = \psi_1 + \varphi_1^{\text{eq}}, \Phi_2^{\text{non}} = \psi_2 + \varphi_2^{\text{non}} \quad (7)$$

If the electrical field is taken into account, beside the temperature and the pressure, the discussion can be made within the framework of thermodynamics. So the routine discussion on the solute-solvent system can be done with thermodynamics without any obstacle.

It is a common practice to integrate the work done in the charging process by the following equation,

$$\delta W = \int_V \Phi \delta \rho dV \quad (8)$$

The integration is over the whole space. If the penetration of ρ into the medium region is neglected, the integration will



be carried out only within the cavity occupied by the solute. Introducing a charging fraction α in step A1 of Eq. (6), the electrostatic free energy of the equilibrium state $[\rho_1, \Phi_1^{\text{eq}}]$ is obtained with the well-known form,

$$F_{\text{tot},1}^{\text{eq}} = W_{A1} = (1/2) \int_V \rho_1 \Phi_1^{\text{eq}} dV \quad (9)$$

On the basis of step A1, step A2 introduces an additional change, $\Delta\rho$, into the charge distribution, and the potential responds accordingly, so the charge distribution ρ^z and the total electric potential Φ^z in step A2 were written by Marcus as^[52]

$$\rho^z = \rho_1 + \alpha(\rho_2 - \rho_1) \text{ and } \Phi^z = \Phi_1^{\text{eq}} + \alpha(\Phi_2^{\text{non}} - \Phi_1^{\text{eq}}) (\alpha = 0 \sim 1) \quad (10)$$

Applying Eq. (8), Marcus gave the “reversible work” of step A2 as^[52,53]

$$W_{A2} = \frac{1}{2} \int_V (\rho_2 - \rho_1)(\Phi_2^{\text{non}} + \Phi_1^{\text{eq}}) dV \quad (11)$$

The sum of the “reversible work” done in steps A1 and A2 is thought just the electrostatic free energy for the nonequilibrium state {see Eq. (17) in Ref. [52]},

$$F_{\text{tot},2}^{\text{non}} = \frac{1}{2} \int_V (\rho_2 \Phi_2^{\text{non}} + \rho_2 \Phi_1^{\text{eq}} - \rho_1 \Phi_2^{\text{non}}) dV \quad (12)$$

By separating the self-energy of the solute charges from the total free energy, the free energy of the medium due to the polarization induced by an external field is of the form

$$F_2^{\text{non}} = \frac{1}{2} \int_V (\rho_2 \varphi_2^{\text{non}} + \rho_2 \varphi_1^{\text{eq}} - \rho_1 \varphi_2^{\text{non}}) dV \quad (13)$$

An alternative expression of Eq. (12) deduced by Marcus using the field-polarization notation is as follows {Eq. (25) in Ref. [52]}.

$$F_{\text{tot},2}^{\text{non}} = \frac{1}{2} \int_V \left[\frac{\mathbf{E}_{0,2} \cdot \mathbf{E}_{0,2}}{4\pi} - \mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{0,2} + \mathbf{P}_1^{\text{or}} \cdot \left(\frac{\mathbf{P}_1^{\text{or}}}{\chi_{\text{or}}} - \mathbf{E}_2^{\text{non}} \right) \right] dV \quad (14)$$

Similarly

$$F_2^{\text{non}} = \frac{1}{2} \int_V \left[-\mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{0,2} + \mathbf{P}_1^{\text{or}} \cdot \left(\frac{\mathbf{P}_1^{\text{or}}}{\chi_{\text{or}}} - \mathbf{E}_2^{\text{non}} \right) \right] dV \quad (15)$$

Here, \mathbf{E}_0 and $\mathbf{E}_2^{\text{non}}$ stands for the vacuum electric field due to the solute charge and the total field in the nonequilibrium state with a solute charge ρ_2 . Concerning the polarization \mathbf{P} , there have two partition schemes for the decomposition of fast and slow components of medium polarization.^[25] Throughout this review, we denote these two partition schemes as the “or-op” partition and “in-dyn” partition. As adopted by Marcus, Hynes, and other authors, in or-op partition, the fast polarization response is

assumed to be induced entirely by electronic degrees of freedom and we use “op” to refer to the electronic polarization, while the slow polarization response is attributed to nuclear or orientational motion of the medium, and we will use the index “or” to refer to the orientational polarization, that is,

$$\mathbf{P}^{\text{op}} = \chi_{\text{op}} \mathbf{E} \quad (16)$$

$$\mathbf{P}^{\text{or}} = \chi_{\text{or}} \mathbf{E} \quad (17)$$

with

$$\chi_{\text{op}} = \frac{\epsilon_{\text{op}} - 1}{4\pi} \text{ and } \chi_{\text{or}} = \frac{\epsilon_s - \epsilon_{\text{op}}}{4\pi} \quad (18)$$

Here, \mathbf{E} is the total electric field, including both the vacuum electric field and the polarization field. In contrast, another partition scheme, the “in-dyn” partition, does not specify physical degrees of freedom corresponding to electrons and nuclei, but instead uses the concept of a dynamic and an inertial polarization response to define the fast and slow polarizations, respectively, that is,

$$\mathbf{P}^{\text{dyn}} = \chi_{\text{op}} \mathbf{E}^{\text{dyn}} \text{ and } \mathbf{P}^{\text{in}} = \mathbf{P} - \mathbf{P}^{\text{dyn}} \quad (19)$$

Here, \mathbf{E}^{dyn} is the total electric field in the hypothetic medium with a dielectric constant ϵ_{op} . It is easy to prove that these two partitions yield the same total polarization free energy. In Nonequilibrium Solvation Theory Based on Constrained Equilibrium Principle, we prefer the “in-dyn” partition for the derivations of the theory.

The solvent reorganization energy was defined as the difference of the electrostatic free energies between the nonequilibrium and equilibrium states subject to the same solute charge distribution ρ_2 , that is,

$$\lambda = F_2^{\text{non}} - F_2^{\text{eq}} \quad (20)$$

with

$$F_2^{\text{eq}} = \frac{1}{2} \int_V \rho_2 \varphi_2^{\text{eq}} dV \quad (21)$$

Equation (20) indicates that solvent reorganization energy is defined as the negative value of the free energy change during the relaxation of $[\rho_2, \Phi_2^{\text{non}}] \rightarrow [\rho_2, \Phi_2^{\text{eq}}]$. Following Marcus expression of nonequilibrium free energy, the solvent reorganization energy is given by^[56,57]

$$\lambda = \frac{1}{2} \int_V \Delta\rho (\Delta\varphi^{\text{op}} - \Delta\varphi^s) dV \quad (22)$$

There are two parallel symbol notation systems for electrostatics. One is to use the potential and the free charge that we call the ρ - φ notation and the other is to use the electric field \mathbf{E} , the electric displacement \mathbf{D} , and the polarization \mathbf{P} with

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} \quad (23)$$

$$\Phi = a\rho + b \quad (27)$$

A parallel derivation led to an equivalent form for the Marcus expression of solvent reorganization energy, that is,^[56,57]

$$\lambda = \frac{1}{8\pi} \int (\Delta\mathbf{E}^{\text{op}} \cdot \Delta\mathbf{D}^{\text{op}} - \Delta\mathbf{E}^{\text{s}} \cdot \Delta\mathbf{D}^{\text{s}}) dV \quad (24)$$

where $\Delta\mathbf{E}^{\text{s}}$ and $\Delta\mathbf{D}^{\text{s}}$ are the equilibrium electric field and dielectric displacement caused by $\rho_2 - \rho_1$ in the realistic medium of dielectric constant ϵ_s , respectively, $\Delta\mathbf{E}^{\text{op}}$ and $\Delta\mathbf{D}^{\text{op}}$ have the similar meanings but in the hypothetical medium with a dielectric constant of ϵ_{op} . Introducing the two-sphere approximation, the famous Marcus two-sphere model was consequently developed and has been widely applied for decades, that is,^[51,53]

$$\lambda = \Delta q^2 \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{d} \right) \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \quad (25)$$

where Δq is the transferred point charge, r_D , r_A and d are the radii of the donor, the acceptor, and the distance between these two species.

Let us check the rationality of the above derivations. At first we recall the basic requirements of thermodynamics. It is well known that the reversible work as shown by Eq. (8) under the condition of Eq. (10) equals to the Helmholtz free energy change only if the process is reversible and isothermal. When we look at the realistic situation, however, the electronic transition in step A2 of Eq. (6) is so fast that the system has no time to reach the equilibrium. Therefore, the process is apparently irreversible. The concern in the Marcus treatment thus is the neglect of the irreversibility leading to the nonequilibrium state. This point will be further clarified in Nonequilibrium Solvation Theory Based on Constrained Equilibrium Principle.

Now let us consider an alternative path from the state $[\rho_1, \Phi_1^{\text{eq}}]$ to the nonequilibrium state $[\rho_2, \Phi_2^{\text{non}}]$, via an intermediate equilibrium state $[\rho_2, \Phi_2^{\text{eq}}]$ as

$$[\rho_1, \Phi_1^{\text{eq}}] \rightarrow [\rho_2, \Phi_2^{\text{eq}}] \rightarrow [\rho_2, \Phi_2^{\text{non}}]$$

If one abuses Eq. (8) with Eq. (10), disregarding the reversibility of the process, the free energy change in the second step will be zero as $\delta\rho=0$, and the free energy change for this path is entirely contributed from the first step $[\rho_1, \Phi_1^{\text{eq}}] \rightarrow [\rho_2, \Phi_2^{\text{eq}}]$, and it can be easily obtained as

$$W_{\text{II}} = \frac{1}{2} \int_V (\rho_2 \Phi_2^{\text{eq}} - \rho_1 \Phi_1^{\text{eq}}) dV \quad (26)$$

Comparing Eq. (26) with Eq. (11), one can immediately find the path-dependency of the free energy change which is against the fundamental thermodynamics principles as free energy is a state function and thus must be path-independent. Thus, we can conclude that Eq. (8) with Eq. (10) is not appropriate for a pathway linking an equilibrium state to a nonequilibrium one. In fact, if we change Eq. (10) to an alternative form,

with

$$a = \frac{\Phi_2^{\text{non}} - \Phi_1^{\text{eq}}}{\rho_2 - \rho_1} \text{ and } b = \Phi_1^{\text{eq}} - \rho_1 \frac{\Phi_2^{\text{non}} - \Phi_1^{\text{eq}}}{\rho_2 - \rho_1}$$

a feature of the concerted change of ρ and Φ becomes obvious, while the irreversible process from an equilibrium state to a nonequilibrium one is not the case.

To avoid the inconsistency in the traditional formulations of nonequilibrium solvation, we proposed a solution during the period from 2004 to 2008 for the free energy of nonequilibrium polarization by adopting the Jackson formula for the electrostatic energy increase integral, instead of Eq. (8), that is,^[58–63]

$$dF = \frac{1}{2} \int_V (\rho \delta\Phi + \Phi \delta\rho) dV \quad (28)$$

This integral is valid when the properties of the medium, for example, the dielectric constant, vary. Although Eq. (28) leads to a solvent reorganization energy which is just only one half of that by the Marcus model when an average value of the forward and backward processes is taken, later we found this manipulation is also invalid for nonequilibrium polarization. Eq. (28) is essentially an integral applicable for equilibrium polarization only. An alternative route which eventually leads to the solution for nonequilibrium solvation will be illustrated in Nonequilibrium Solvation Theory Based on Constrained Equilibrium Principle.

Originally, the Gibbs free energy was taken in the derivation by Marcus. However, for the condensed phase, the influences from the pressure and the volume can be ignored. In such cases, both Gibbs free energy and Helmholtz free energy coincide. In the matter of fact, these two quantities were indistinguishably called “free energy” in the literature of solvent effect. This will cause no problem for our definition and formulation, but in this review, we prefer Helmholtz free energy for our derivation, for the sake of the coherence of the thermodynamics.

Free energy functional approach

Based on the thermodynamic theory of fluctuations with electromagnetic fields and linear response theory, Felderhof^[64–66] proposed an equation describing the free energy due to medium polarization,

$$F = \frac{1}{2} \int_V \mathbf{P}^2 dV + \frac{1}{2} \iint \frac{\nabla \cdot \mathbf{P} \cdot \nabla' \cdot \mathbf{P}}{|\mathbf{r} - \mathbf{r}'|} dV dV' - \int \mathbf{P} \cdot \mathbf{E}_0 dV \quad (29)$$

with

$$\chi_s = \frac{\epsilon_s - 1}{4\pi} \quad (30)$$

Here, $-\nabla \cdot \mathbf{P}$ is the polarization charge distribution in the medium and χ_s is the dielectric susceptibility. Note that in Eq.

(29), the position coordinate \mathbf{r} is dropped. F is just the free energy change of the medium and it equals to the total electrostatic free energy of the field minus the self-energy of the solute charge. Considering that \mathbf{P} is a sum of partial polarization \mathbf{P}_j , and if all the components \mathbf{P}_j are proportional to a same electric field \mathbf{E} , that is,

$$\mathbf{P} = \sum_j \mathbf{P}_j \quad \text{and} \quad \mathbf{P}_j = \chi_j \mathbf{E} \quad (31)$$

the first term in the right-hand side of Eq. (29) can be easily decoupled and Eq. (29) becomes,^[66]

$$F = \frac{1}{2} \sum_j \int \frac{1}{\chi_j} \mathbf{P}_j^2 dV + \frac{1}{2} \iint \frac{\nabla \cdot \mathbf{P} \cdot \nabla' \cdot \mathbf{P}}{|\mathbf{r} - \mathbf{r}'|} dV dV' - \int \mathbf{P} \cdot \mathbf{E}_0 dV \quad (32)$$

When we separate the total polarization into \mathbf{P}^{or} and \mathbf{P}^{op} , that is,

$$\mathbf{P}^{\text{op}} = \chi_{\text{op}} \mathbf{E} \quad (33)$$

$$\mathbf{P}^{\text{or}} = \chi_{\text{or}} \mathbf{E} \quad (34)$$

it is easy to verify that

$$\begin{aligned} \int \frac{1}{\chi_{\text{op}}} (\mathbf{P}^{\text{op}})^2 dV + \int \frac{1}{\chi_{\text{or}}} (\mathbf{P}^{\text{or}})^2 dV &= \int \frac{1}{\chi_{\text{or}} + \chi_{\text{op}}} (\mathbf{P}^{\text{or}} + \mathbf{P}^{\text{op}})^2 dV \\ &= \int \frac{1}{\chi_s} \mathbf{P}^2 dV \end{aligned} \quad (35)$$

It should be emphasized again that the necessary condition for partition in the first term of Eq. (29) is that all the components are proportional to a same electric field. In other words, Eq. (31) implies an equilibrium state, and question does not arise in applying the following decomposition to the equilibrium states, that is,

$$\int \frac{1}{\chi_s} \mathbf{P}^2 dV = \sum_j \int \frac{1}{\chi_j} \mathbf{P}_j^2 dV \quad (36)$$

provided that Eq. (31) holds.

Equation (36) was introduced by Lee and Hynes to describe the solvation free energy of nonequilibrium.^[67] Considering the surface distribution of the polarization charge and dividing the polarization into electronic component \mathbf{P}^{op} and orientation component \mathbf{P}^{or} , Eq. (32) was extended to the nonequilibrium case. In 1990, Kim and Hynes proposed the following form by introducing the dipole tensor $\nabla \nabla' \cdot \frac{1}{|\mathbf{r} - \mathbf{r}'|}$ that is,^[68]

$$\begin{aligned} F_2^{\text{non}} &= \frac{1}{2} \int \left[\frac{1}{\chi_{\text{op}}} (\mathbf{P}_2^{\text{op}})^2 + \frac{1}{\chi_{\text{or}}} (\mathbf{P}_1^{\text{or}})^2 \right] dV \\ &+ \frac{1}{2} \iint_V \left(\mathbf{P}_2^{\text{op}} + \mathbf{P}_1^{\text{or}} \right) \cdot \nabla \nabla' \cdot \frac{1}{|\mathbf{r} - \mathbf{r}'|} \cdot \left(\mathbf{P}_2^{\text{op}} + \mathbf{P}_1^{\text{or}} \right) dV dV' \\ &- \int (\mathbf{P}_2^{\text{op}} + \mathbf{P}_1^{\text{or}}) \cdot \mathbf{E}_0 dV \end{aligned} \quad (37)$$

To be consistent with the notation in this review, we use the subscript "1" to denote the quantities due to the equilibrium solute charge distribution ρ_1 and "2" to the quantities

due to the final solute charge distribution ρ_2 . There is another expression that can be found in the work of Aguilar et al., that is,^[69]

$$\begin{aligned} F_2^{\text{non}} &= \frac{1}{2} \int \left[\frac{1}{\chi_{\text{op}}} (\mathbf{P}_2^{\text{op}})^2 + \frac{1}{\chi_{\text{or}}} (\mathbf{P}_1^{\text{or}})^2 \right] dV - \frac{1}{2} \int (\mathbf{P}_2^{\text{op}} + \mathbf{P}_1^{\text{or}}) \cdot \mathbf{E}_p dV \\ &- \int (\mathbf{P}_2^{\text{op}} + \mathbf{P}_1^{\text{or}}) \cdot \mathbf{E}_0 dV \end{aligned} \quad (38)$$

where \mathbf{E}_p denotes the electric field due to the polarization charge. Eq. (38) was further changed to the following form (see Eq. (31) in Ref. [69]),

$$F_2^{\text{non}} = -\frac{1}{2} \int (\mathbf{P}_2^{\text{op}} + \mathbf{P}_1^{\text{or}}) \cdot \mathbf{E}_{0,2} dV + \frac{1}{2} \int \mathbf{P}_1^{\text{or}} \cdot (\mathbf{E}_1^{\text{eq}} - \mathbf{E}_2^{\text{non}}) dV \quad (39)$$

A doubt arises in the free energy of nonequilibrium developed this way because it is factually a simple extension of the equilibrium solvation, without convincing deduction. We see that Eq. (31) is not satisfied any longer in the case of nonequilibrium polarization.

If one notes that

$$\mathbf{P}_2^{\text{op}} + \mathbf{P}_1^{\text{or}} = \mathbf{P}_2^{\text{non}} \quad (40)$$

$$\mathbf{E}_1^{\text{eq}} = \mathbf{P}_1^{\text{or}} / \chi_{\text{or}} \quad (41)$$

Equation (39) is reduced to Eq. (15). We can, therefore, conclude that the free energy functional method leads to the same expression for nonequilibrium free energy by Marcus. In the derivation above, the self-energy term of solute charge which is involved in the original expressions of the authors, is hid here for the convenience of comparative discussions with Felderhof equation.

Equations (37–39) are essentially the extension of the equilibrium solvation [Eq. (32)]. The similar treatment exists in derivation by Marcus. In fact, the integral by Eq. (8) associated with Eq. (10) along step A2 of Eq. (6) works only for the quasi-static processes linking two equilibrium states, and the last two terms in the right-hand side of Eq. (12) in such cases will cancel out. Unfortunately, this equilibrium expression was inappropriately applied to the nonequilibrium situation by optionally changing the equilibrium potential Φ_2 to Φ_2^{non} , without careful argumentation. In brief, the problems in both the reversible work integration by Marcus and the free energy functional approach are similar, and hence it is not surprising that these derivations lead to the same expression of nonequilibrium free energy.

Discretization and numerical solution

The discretization technique of polarization charge for arbitrary cavity surface has now become mature for equilibrium solvation. The self-consistent reaction field method has been widely used in the calculation of solvation energies for equilibrated solute-solvent systems, and the codes have been implemented in popular quantum chemistry software such as

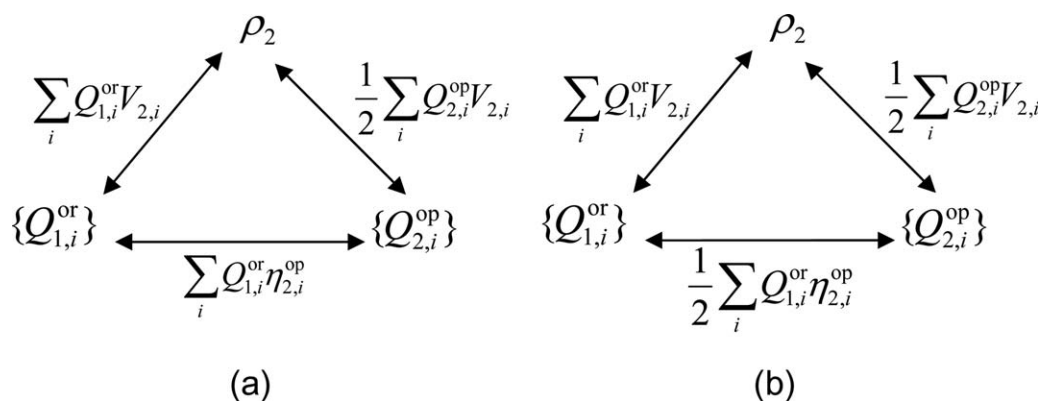


Figure 1. A diagram for the electrostatic interactions given in Ref. [70] a) and in Ref. [71] b). See text for the discussion on their differences.

Gaussian by combining the solvation models with the well-established quantum chemistry methods, for example, Hartree–Fock and density functional theory, and hence the so-called quantum-continuum models have been widely used in free energy calculations for electronically excited states in solution.

By discretizing the polarization charge on the solute cavity surface, Cossi and Barone^[70,71] developed a general formalism for nonequilibrium electrostatic free energy, which is applicable to all PCM versions, and implemented a procedure for the quantum-mechanical computation of nonequilibrium solvation. Here, we briefly depict the main points for the free energy. By splitting the polarization charge into electronic components $\{Q_i^{\text{op}}\}$ and orientational ones $\{Q_i^{\text{or}}\}$ on the i th tessera of the cavity occupied by the solute, that is,

$$Q_{1,i} = Q_{1,i}^{\text{or}} + Q_{1,i}^{\text{op}} \quad (42)$$

the electrostatic free energy of the initial equilibrium state 1 is given by the well-known form, that is,

$$F_1^{\text{eq}} = \frac{1}{2} \sum_i (Q_{1,i}^{\text{or}} + Q_{1,i}^{\text{op}}) V_i \quad (43)$$

where V_i is the electrostatic potential due to the solute charge density at the i th tessera.

In vertical excitation processes, only the electronic component of the polarization responsible for a polarization charge $Q_{2,i}^{\text{op}}$ is able to follow the instantaneous change in the solute wave function. To describe this phenomenon in the framework of a continuum model, one can split each polarization charge at tessera i into two distinct contributions from the solvent for the nonequilibrium excited state, that is,

$$Q_{2,i} = Q_{1,i}^{\text{or}} + Q_{2,i}^{\text{op}} \quad (44)$$

Up to this stage, how to express the free energy for the nonequilibrium solvation is the central problem. According to Cossi and Barone,^[70,71] there are three kinds of interactions in

the case of nonequilibrium polarization: the interaction between the solute charge and $Q_{1,i}^{\text{or}}$, the one between the solute charge and $Q_{2,i}^{\text{op}}$, and the one between $Q_{1,i}^{\text{or}}$ and $Q_{2,i}^{\text{op}}$. For clarity, we use Figure 1 to summarize the interactions between these three kinds of charges designated by Cossi and Barone. In choosing the energy term, Cossi and Barone claimed in Ref. [70] that there is a factor 1/2 for the interaction between the solute charge ρ_2 and the fast component $Q_{2,i}^{\text{op}}$ of the polarization charge, but this factor drops for the interactions between ρ_2 and $Q_{1,i}^{\text{or}}$ and between $Q_{1,i}^{\text{or}}$ and $Q_{2,i}^{\text{op}}$, as $Q_{1,i}^{\text{or}}$ keeps fixed during the establishment of ρ_2 and $Q_{2,i}^{\text{op}}$. Such a treatment sounds acceptable but the authors changed their original rational and a factor of 1/2 was pasted to the interaction between $Q_{1,i}^{\text{or}}$ and $Q_{2,i}^{\text{op}}$ in their final expression of nonequilibrium free energy (see the description below) without valid argument,^[71] and this is shown in Figure 1b. In this review, $\{\eta_i\}$ is used to denote the discrete form of the polarization potential φ , while $\{V_i\}$ for that of vacuum potential ψ . The symbol V_i defined here is expected not to cause confusion with the symbol V for volume. In this way the interaction energy form $\sum_{ij} Q_{1,i}^{\text{or}} Q_{2,i}^{\text{op}} / |\mathbf{r}_i - \mathbf{r}_j|$ is replaced by the more compact form $\sum_i Q_{1,i}^{\text{or}} \eta_{2,i}^{\text{op}}$ in Figure 1.

According to Cossi and Barone^[70,71] the nonequilibrium free energy for the excited state should involve the work done for the establishment of $Q_{1,i}^{\text{or}}$, that is, $\frac{1}{2} [\sum_i Q_{1,i}^{\text{or}} V_{1,i} + \sum_i Q_{1,i}^{\text{or}} \eta_{1,i}^{\text{op}}]$. Collecting all these terms, the nonequilibrium free energy was finally given^[71] (see also Table 2 in Ref. [18])

$$F_2^{\text{non}} = \sum_i Q_{1,i}^{\text{or}} V_{2,i} + \frac{1}{2} \sum_i Q_{2,i}^{\text{op}} V_{2,i} + \frac{1}{2} \sum_i Q_{1,i}^{\text{or}} \eta_{2,i}^{\text{op}} - \frac{1}{2} \left[\sum_i Q_{1,i}^{\text{or}} V_{1,i} + \sum_i Q_{1,i}^{\text{or}} \eta_{1,i}^{\text{op}} \right] \quad (45)$$

The expression given in Ref. [70] by the same authors is different from Eq. (45). The difference is just the factor 1/2 for the interaction between $\{Q_{1,i}^{\text{or}}\}$ and $\{Q_{2,i}^{\text{op}}\}$, in other words, the factor 1/2 of the third term in the right-hand side of Eq. (45)

was missing in Ref. [70]. Such an optional choice is not surprising since it is factually impossible for one to compose an free energy expression of a thermodynamically nonequilibrium state by intuitively collecting a series of interaction energy terms. A closer inspection can prove that Eq. (45) is exactly the result derived by Marcus. The proof for the identity of Eqs. (45) and (15) by Marcus is given in Appendix A.

By the free energy separation, Marenich et al.^[72] recently rewrote the free energy of a nonequilibrium excited state in solution as

$$F_2^{\text{non}} = F_2^{\text{op}} + F_2^{\text{or}} + F_2^{\text{op-or}} \quad (46)$$

where F_2^{op} is the electronic component, F_2^{or} the orientational component, and $F_2^{\text{op-or}}$ the electronic-orientational cross-term. A vertical excitation model, called VEM, was proposed, with the same expression as Eq. (45) for nonequilibrium solvation in the or-op partition. Besides, Marenich et al.^[72] reached a more compact form for the nonequilibrium free energy in in-dyn partition style, that is,

$$F_2^{\text{non}} = \frac{1}{2} \sum_i Q_{2,i}^{\text{dyn}} V_{2,i} + \sum_i (V_{2,i} - \frac{1}{2} V_{1,i}) Q_{1,i}^{\text{in}} \quad (47)$$

Cavity dependency of solvent reorganization energy

The cavity is a basic concept in all continuum solvent models. From the definition given in this review, the surface of the cavity is the physical boundary of the thermodynamic system. In performing the numerical solution of the solvation free energy for both the equilibrium and the nonequilibrium, the polarization surface charge is regarded as being spread on the cavity surface. The solvation free energy is sensitive to the cavity shape and cavity size,^[73] therefore, the cavity is always a hot topic for continuum models. In this aspect, several review papers have been devoted to the cavity construction,^[14,17,18] and further improvements are going on.^[74–78]

In PCM, the interlocking atom-centered (or functional-group-centered) spheres are usually used to construct the cavity, and the sphere radii could be related to atomic van der Waals (vdW)^[79] radii or be taken as empirical parameters. People defined various surface types to adapt the calculation of solvation free energy. It should be a difficult task to completely figure out all the cavity surface models and their modifications, and we do not try to illustrate the details of cavity surface but only takes some typical examples for the clarification of the nonequilibrium solvation theory. Owing to the surface dependency of the polarization charge distribution, the electrostatic interaction is highly sensitive to the cavity size. In the equilibrium solvation manipulation, for example, PCM, the solute cavity is constructed by taking the atomic sphere with vdW radii being scaled by a factor of about 1.2. Such a cavity size generally exhibits reasonable equilibrium solvation properties.

Concerning the nonequilibrium solvation, however, there exists a large and growing number of intermolecular ET proc-

esses that occur at second-order rates which are faster than can be accommodated by nonadiabatic (or weakly adiabatic) Marcus theory.^[80–82] In some cases, such discrepancies have been attributed to the participation of transient precursor complexes that are responsible for the significantly lower ET barriers.^[83,84] Formosinho et al.^[85] collected a number of examples on this issue, and claimed that Marcus ET theory severely underestimate by 3–8 orders of magnitude the analogues rate constants for nonadiabatic process and for $\text{Co}(\text{OH})_6^{2+/3+}$. Recently, Formosinho et al. reported new evidences that the solvent reorganization energy derived from free-energy dependence is much lower than that predicted by Marcus theory in long-rang photoinduced charge separations in polar media.^[86] There are also some perplexing results pointing to the overestimation of the solvent reorganization energy by the traditional theories.^[87,88]

Facing with the difficulties mentioned above in practice, people in general tend to adjust the cavity size to calibrate the theoretical results of solvent reorganization energy to the experimental observations. A larger solute cavities in general produce a smaller reorganization energy, and hence can balance the overestimation of theoretical models. Such a tradeoff often leads to the incongruous cavity size between the equilibrium and the nonequilibrium solvation. The following example better be used to clarify the above comments.

Closs and Miller carried out excellent experimental measurements in 1980's. Taking the biphenyl anion as the donor, they chose a series of acceptors to invoke changes in the driving force.^[89,90] However, accompanying the successful confirmation of the inverted region, doubts on the amount of the solvent reorganization energy arose. In 1989, Johnson and Miller tried to reevaluate this quantity for the biphenyl-bridge-naphthalene system with the Marcus two-sphere formula.^[91] From the experimentally fitted value of 0.75 eV of the solvent reorganization energy, a mean value of 5.07 Å for the cavity radii of biphenyl and naphthalene was deduced. Obviously, this value differs considerably from the available values of 3.9 Å for biphenyl and 3.7 Å for naphthalene derived from the structural data, and a satisfactory explanation for such a large discrepancy was not found.^[91] Further attempts using modified two-sphere models, which retain the dielectric continuum approximation but use elliptical cavities, did not significantly improve the result.^[91,92] Basilevsky et al.^[93,94] used a numerical scheme to evaluate the solvent reorganization energies for the Closs–Miller systems, but the calculated solvent reorganization energy for the biphenyl-androstane-acceptor system was overestimated by a factor of about 2 compared with that fitted from the experimental rate constants.^[89,90] If the torsion contribution of 0.13 eV^[95] is subtracted from the total value of 0.75 eV, the solvent reorganization energy due to the presence of polar solvent becomes even smaller, 0.62 eV, leading to an even larger mean value of 5.9 Å for the cavity radii. If one uses the same donor-acceptor distance (17.3 Å for the biphenyl-androstane-naphthalene system) and the mean radius value of 3.8 Å from the structural data, Marcus two-sphere model would predict a value for the solvent reorganization energy about twice the experimental fitting.

For the sake of obtaining acceptable value for the reorganization energy in comparison with experimental results, Newton et al.^[92] expanded the cavity radius by the so-called frequency-resolved cavity model (FRCM).^[92,94] That model assumes a solute surrounded by a medium with a dielectric constant ε that changes in stepwise fashion, hence assumes that around the cavity with $\varepsilon = 1$ there exists an intermediate layer with $\varepsilon = \varepsilon_{\text{op}}$, approximately being the first solvation shell of the solute. The medium part more remote from the solute was treated in terms of the static dielectric constant ε_s .

A careful investigation leads to doubts for FRCM. We consider a conductor in an electrical field. Because the medium in this case is an isopotential body, the polarization charge distribution inside the medium will not be permitted. In the usual Born model, the polarization charges spread on the boundary of the medium, and this is the widely accepted picture of continuum model. However, in FRCM, the fast and slow parts of the polarization charges are assumed to spread on different layers. Although such a two-layer distribution of polarization charge can lead to a smaller solvent reorganization energy that fits to the experimental value, theoretically it seems logically unreasonable from the viewpoint of continuum model.

Nonequilibrium Solvation Theory Based on Constrained Equilibrium Principle

Free energy of polarization

Following Landau and Lifshitz,^[96] we prefer the Helmholtz free energy for presentation in this review. By including the electrostatic free energy change of the solvent to the free energy change of the system, the nonequilibrium polarization of the solute-solvent system becomes simply a problem of thermodynamics. A rigorous deduction in the framework of thermodynamics should be the most efficient way to establish the expression of nonequilibrium solvation free energy or solvent reorganization energy. Thermodynamics concerns two kinds of states, namely the equilibrium ones (classical thermodynamics) and the nonequilibrium ones (nonequilibrium thermodynamics). The classical thermodynamics is an extremely important theory for macroscopic properties of systems at equilibrium, for example, the equilibrium solvation. Nevertheless, it is significant to explore a thermodynamic method to solve the problems in the nonequilibrium solvation.

For a thermodynamic system, the macroscopic properties which we call the state parameters (functions) can be classified into two types, that is, external and internal. The state parameters determined by the position of the object in the ambient are the external parameters, while those related to the thermal motion of the particles are referred to the internal parameters. All objects interacting with the system should be considered as the ambient. The distinction between external and internal parameters is not absolute, and it depends on the partition of the system and ambient. Note that whatever the division between system and ambient is, the system may do work to ambient only with the change of some external parameters.

Based on the thermodynamic equilibrium theory, the thermal homogeneous system at an equilibrium state can be uniquely defined with a set of external parameters $\{a_i\}$ and an internal parameter, the Kelvin temperature T , and its (internal) energy is given by the caloric equation of state, $U = U(a_i, T)$. Hence, one can choose either T or U as the internal parameter for the system. However, for a nonequilibrium state under the same external conditions, additional internal parameters are needed to characterize the nonequilibrium state of a thermal homogeneous system beside a set of external parameters $\{a_i\}$ and T . Those additional internal parameters are usually time-dependent.

In classical thermodynamics, the basic equation of thermodynamic functions is given by

$$dU = TdS - \sum_i A_i da_i \quad (48)$$

where S represents the entropy of the equilibrium system. a_i stands for the i th external parameter, and A_i is a generalized force which conjugates with a_i . The above equation can merely be integrated along a quasistatic path. Actually, TdS is the reversible heat δQ_r transferred between the system and the ambient in an infinitesimal change along a quasistatic path, dU is the energy change and $A_i da_i$ is the element work done by the system when external parameter a_i changes. The positions of any pair of A_i and a_i can interconvert through Legendre transformation. If we consider a system in which the gas is enclosed in a cylinder with constant temperature, there will be only one external parameter, that is, the gas volume V . The corresponding generalized force is the gas pressure p , and Eq. (48) can be simplified to the very familiar form

$$dU = TdS - pdV \quad (49)$$

The free energy in this case is given by

$$dF = -SdT - pdV \quad (50)$$

For a condensed solute-solvent system, we usually neglect the influence of pressure and volume and turn to consider the medium polarization resulted from an external electric field \mathbf{E}_0 in the space. As a thermodynamic manipulation, the system should be defined in advance. In the present case, the medium is defined as the system while the solute charges the ambient. In this way, we only need to focus on the polarization potential and such a definition makes the thermodynamic picture very clear. The energy and free energy changes of the medium are as follows^[96]

$$dU = TdS + \frac{1}{4\pi} \int (\mathbf{E} \cdot \delta \mathbf{D} - \mathbf{E}_0 \cdot \delta \mathbf{E}_0) dV \quad (51)$$

$$dF = -SdT + \frac{1}{4\pi} \int (\mathbf{E} \cdot \delta \mathbf{D} - \mathbf{E}_0 \cdot \delta \mathbf{E}_0) dV \quad (52)$$

where \mathbf{E} includes both the vacuum field \mathbf{E}_0 and the polarization field \mathbf{E}_p . The equivalent forms of Eqs. (51) and (52) can be given by

$$dU = TdS + \int (\Phi \delta \rho - \psi \delta \rho) dV \quad (53)$$

$$dF = -SdT + \int (\Phi \delta \rho - \psi \delta \rho) dV \quad (54)$$

In the isothermal case, Eq. (54) is reduced to

$$dF = \int \varphi \delta \rho dV \quad (55)$$

with

$$\varphi = \Phi - \psi \quad (56)$$

For a change between two equilibrium states, it is well known that the minus value of free energy change equals to the maximum isothermal work done by the system, that is,

$$-F = W_{\max} \quad (57)$$

Equation (57) indicates that if one tries to integrate the electric work done by Eq. (55) to gain free energy change between two states, one must design an isothermal reversible or quasi-static path between these two states. This is apparently infeasible for a process from an equilibrium state to a nonequilibrium state. Thus, Eq. (57) once again confirms that the concern in Marcus derivations is the incorrect application of Eqs. (8) or (55) associated with Eq. (10) to the fast process from the equilibrium polarization to the nonequilibrium one. To derive a correct expression of free energy for a nonequilibrium polarization state, we present a route that was explored recently by us to the correct terminal.

Nonequilibrium and constrained equilibrium

Even if we consider the influence from the electric field, we must strictly obey the thermodynamic principle in attempts to avoid any possible error. It is obviously a difficult task to efficiently extend the thermodynamic functions defined in the classical thermodynamics to the nonequilibrium polarization, whereas one feasible way is the method proposed by Leontovich.^[97,98] The key in Leontovich approach is to transform the nonequilibrium state to a constrained equilibrium one by imposing some additional external fields. The constrained equilibrium state retains the thermodynamic parameters except the imposing external fields. In other words, the constraint only freezes the time-dependent internal parameters of the nonequilibrium state, without doing any damage to the system. The constrained equilibrium becomes the nonequilibrium state immediately after the additional external fields are removed quickly. The removal of the additional external fields should be extremely fast so that the characteristic parameters of the system have no time to vary. Such a treatment will provide a way to thermodynamic functions of the nonequilibrium state from a constrained equilibrium state. Based on the relation between the constrained equilibrium state and the nonequilibrium one, the general idea of extending classical

thermodynamics to nonequilibrium systems can be summarized as follows:^[99,100]

1. By imposing suitable external fields, the nonequilibrium state of a system is transformed to a constrained equilibrium state so as to freeze the time-dependent internal parameters of the nonequilibrium state.
2. The change of a thermodynamic function from a constrained equilibrium state to another equilibrium (or constrained equilibrium) state can be computed simply by means of classical thermodynamics, say, reversible work technique.
3. The additional external fields can be suddenly removed without friction from the constrained equilibrium system so as to resume the nonequilibrium state, which will further relax irreversibly to the eventual equilibrium state.

Leontovich^[97,98] defined the entropy of a nonequilibrium state by a constrained equilibrium. In other words, the entropy of a constrained equilibrium and that of a nonequilibrium state exactly after the fast removal of the external field should be thought the same.

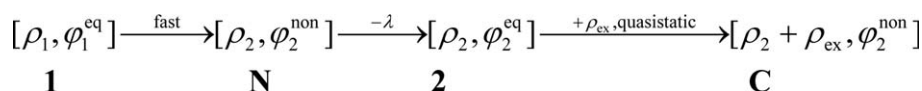
For a thermal homogeneous constrained equilibrium state, the external parameters can be classified into three kinds. The first class includes those original external parameters $\{a_i\}$ which have the conjugate generalized forces $\{A_i\}$. The second class involves the additional external parameters $\{x_k\}$ that are entirely different from the original ones. The generalized forces $\{\xi_k\}$ conjugate with $\{x_k\}$, and ξ_k acts as the internal parameter originated from the nonequilibrium state. If the introduced additional external parameter x_i superposes to an original external parameter a_i , a new external parameter $a'_i = a_i + x_i$ that conjugates with a generalized force A'_i will be formed and we call these external parameters the third class. By defining these three kinds of external parameters, $\{a_i\}$, $\{x_i\}$, and $\{a'_i\}$, the basic thermodynamic equation for a constrained equilibrium state can be expressed as

$$TdS^c = dU^c + \sum_i A_i da_i + \sum_k \xi_k dx_k + \sum_i A'_i da'_i \quad (58)$$

where S^c and U^c stand for entropy and energy of the constrained equilibrium state, respectively, and other terms are the work done by the system due to the changes of the external parameters. Because the removal of additional external fields $\{x_k\}$ are assumed extremely fast, the transformation from a constrained equilibrium to a nonequilibrium can be regarded adiabatic.^[97,98] A fast removal of the constraining forces $\{x_k\}$ from the system yields the expected nonequilibrium state. By this very construction, the constrained equilibrium and the nonequilibrium have the same internal variables. In particular, the nonequilibrium entropy S^{non} is equal to that of the constrained equilibrium, that is,^[97,98]

$$S^{\text{non}} = S^c \quad (59)$$

The energy change of the system in the fast process is as follows^[99–102]



Scheme 1. Nonequilibrium and constrained equilibrium states.

$$\begin{aligned}
 \Delta U = U^{\text{non}} - U^c = -W &= -\sum_k \xi_k \int_{x_k}^0 dx_k - \sum_l A_l' \int_{a_l + x_l}^{a_l} da_l' \\
 &= \sum_k \xi_k x_k + \sum_l A_l' x_l
 \end{aligned} \quad (60)$$

where $\sum_k \xi_k x_k$ and $\sum_l A_l' x_l$ are work done by getting rid of the second and the third kinds of additional external fields quickly.

If $A_l' = 0$, Eq. (60) is reduced to the Leontovich form, that is, (Eq. (3.5) in Ref. [98])

$$U^{\text{non}} = U^c + \sum_k \xi_k x_k \quad (61)$$

This means that Eq. (60) is an extension of Leontovich form of Eq. (61). If one notes that ξ_k and A_l' remain invariant during the fast removal of their conjugate parameters, the energy change by Eq. (61) is easy to understand.

For the constrained equilibrium, free energy is defined as

$$F^c = U^c - TS^c \quad (62)$$

Differentiating on both sides of Eq. (62) by substituting of Eq. (58), the free energy change of the constrained equilibrium state is given by

$$dF^c = -S^c dT - \sum_l A_l da_l - \sum_k \xi_k dx_k - \sum_l A_l' da_l' \quad (63)$$

Through the definition of the entropy for the nonequilibrium state as Eq. (59), the free energy of the nonequilibrium state F^{non} can be similarly defined as^[97,98]

$$F^{\text{non}} = U^{\text{non}} - TS^{\text{non}} \quad (64)$$

Subtracting Eq. (62) from Eq. (64), and by noticing Eq. (60), we have

$$F^{\text{non}} - F^c = \sum_k \xi_k x_k + \sum_l A_l' x_l \quad (65)$$

A particularly noteworthy point should be that A_l' and x_l are not a pair of conjugates, so the sum $\sum_l A_l' x_l$ in Eq. (65) does not satisfy the conditions of a state function. This leads to that the total differential of F^{non} does not exist. Adding the sum $\sum_l A_l' a_l$ to both sides of Eq. (65), the total differential can be obtained as

$$d(F^{\text{non}} + \sum_l A_l' a_l) = -S^{\text{non}} dT - \sum_l A_l da_l + \sum_k x_k d\xi_k + \sum_l a_l' dA_l' \quad (66)$$

Equation (66) shows that if there are external parameters of the third kind, the nonequilibrium free energy F^{non} which

comes from F^c of the constrained state does not possess a total differential. This is a new finding. However, it will not impede the use of Eq. (66) to obtain F^{non} , because with this method one can transform the nonequilibrium state to a constrained equilibrium state, and this approach can be called as state-to-state treatment. This treatment does not involve the state change with respect to time, so it can realize the extension of classical thermodynamics to nonequilibrium systems.

The thermodynamics principle introduced above can be adopted to obtain the free energy of a nonequilibrium polarization system, which is a critical problem in the description of fast processes in solution.

As shown in Scheme 1, for ET, or a photo absorption/emission process in solution, the system first stays at the initial equilibrium state 1 with a solute charge distribution ρ_1 and an equilibrium polarization potential φ_1^{eq} . Starting from the equilibrium polarization, the fast process occurs, and the solute charge suddenly changes from ρ_1 to ρ_2 . In this process, the fast part of the solvent polarization can adjust itself quickly and keep equilibrium with ρ_2 , while the slow part still keeps the value as that in the previous equilibrium. As a consequence, the system reaches the nonequilibrium polarization state N, $[\rho_2, \varphi_2^{\text{non}}]$, with φ_2^{non} being the nonequilibrium polarization potential. After a period of enough long time, the slow polarization will finally relax to equilibrate with the solute charge ρ_2 and the system arrives at another equilibrium state 2, $[\rho_2, \varphi_2^{\text{eq}}]$, which has the electrostatic free energy of

$$F_2^{\text{eq}} = \frac{1}{2} \int_V \rho_2 \varphi_2^{\text{eq}} dV \quad (67)$$

By introducing a proper distribution of the external free charge ρ_{ex} , which just produces a polarization electric potential φ' with

$$\varphi' = \varphi_2^{\text{non}} - \varphi_2^{\text{eq}} \quad (68)$$

and is called "residual" potential, one can define a constrained equilibrium state C, $[\rho_2 + \rho_{\text{ex}}, \varphi_2^{\text{non}}]$. We see that φ' measures the potential deviation of the nonequilibrium from the equilibrium with a same solute charge ρ_2 . It should be emphasized again here that we define the solvent as the "system," while both the solute charge and the constraining charges as the "ambient."

The constrained equilibrium state C with a total free change of $\rho_2 + \rho_{\text{ex}}$ and the corresponding polarization potential $\varphi^c = \varphi_2^{\text{non}}$, is constructed as a reference state for the gain of the electrostatic free energy of the true nonequilibrium state. This constrained equilibrium state can be prepared in a quasistatic manner, that is, based on the equilibrium state $[\rho_2, \varphi_2^{\text{eq}}]$,

we accumulate the external (constraining) charge ρ_{ex} in the ambient and correspondingly the solvent polarization potential of the system changes from φ_2^{eq} to φ_2^{non} . During this process, the solvent polarization keeps equilibrium with the sum of the solute charge and the external charge all the time, therefore, it can be regarded as a quasistatic pathway, and the work done to the system during the introduction of the external charge ρ_{ex} is given by

$$\delta W = \int_V \varphi^a \delta \rho^a dV \quad (69)$$

with

$$\begin{aligned} \varphi^a &= \varphi_2^{\text{eq}} + \alpha(\varphi_2^{\text{non}} - \varphi_2^{\text{eq}}) \\ \rho^a &= \rho_2 + \alpha \rho_{\text{ex}} \end{aligned} \quad \alpha = (0 \sim 1) \quad (70)$$

Please note that φ_2^{non} in the constrained equilibrium case is just the equilibrium polarization potential by $\rho_2 + \rho_{\text{ex}}$. As a result, the reversible work done from equilibrium $[\rho_2, \varphi_2^{\text{eq}}]$ to constrained equilibrium is obtained as

$$W_{2 \rightarrow C} = \int_V dV \int_0^1 \varphi^a \frac{\delta \rho^a}{\delta \alpha} d\alpha = \frac{1}{2} \int_V [(\rho_2 + \rho_{\text{ex}}) \varphi_2^{\text{non}} - \rho_2 \varphi_2^{\text{eq}}] dV \quad (71)$$

As an equilibrium state, the free energy of the constrained equilibrium F^C resulted from the polarization, is obtained as

$$F^C = \frac{1}{2} \int_V (\rho_2 + \rho_{\text{ex}}) \varphi_2^{\text{non}} dV \quad (72)$$

Equation (72) is well-known for an equilibrium polarization. Please note that the reversible charging process is considered isothermal.

Removing the external charge density ρ_{ex} suddenly ($Q = 0$), and assuming that the thermodynamic parameters of the solvent system have no time to vary, the polarization potential φ_2^{non} at the constrained equilibrium will keep unchanged. Hence, the work done by the system is given by

$$W_{C \rightarrow N} = -(U^{\text{non}} - U^C) = - \int_V dV \int_{\rho_{\text{ex}} + \rho_2}^{\rho_2} \varphi_2^{\text{non}} d\rho = \int_V \varphi_2^{\text{non}} \rho_{\text{ex}} dV \quad (73)$$

Therefore, the energy expression for the nonequilibrium state is written as

$$U^{\text{non}} = U^C - W_{C \rightarrow N} = \frac{1}{2} \int_V (\rho_2 + \rho_{\text{ex}}) \varphi_2^{\text{non}} dV - \int_V \rho_{\text{ex}} \varphi_2^{\text{non}} dV \quad (74)$$

and the free energy change during this fast process is

$$\Delta F = U^{\text{non}} - U^C - T(S^{\text{non}} - S^C) \quad (75)$$

Here, we ignore the temperature change in the fast process. This isothermal approximation in the fast process was also

implied in the theoretical treatments in the past. According to Leontovich,^[90,91] the following relation holds, that is,

$$S^{\text{non}} = S^C \quad (76)$$

This hypothesis is valid because the removal of the external charge does not change anything except the energy. The polarization will remain completely the same before and after the fast process, so the entropy will stay the same in both states N and C. Combining Eqs. (73), (75), and (76), one arrives the final expression of free energy of a state with a nonequilibrium polarization, that is,^[103]

$$F^{\text{non}} = F^C - W = \frac{1}{2} \int_V (\rho_2 + \rho_{\text{ex}}) \varphi_2^{\text{non}} dV - \int_V \rho_{\text{ex}} \varphi_2^{\text{non}} dV \quad (77)$$

Comparing Eq. (77) with the well-known form by Marcus, Eq. (13), one can find that the remarkable feature of Eq. (77) is that the variable, ρ_{ex} , which is used to equilibrate the "residual" polarization potential, $\varphi_2^{\text{non}} - \varphi_2^{\text{eq}}$, enters the free energy expression.

A parallel formulation can be made. We denote the vacuum and total electric fields of the constrained state C as

$$\mathbf{E}_0^C = \mathbf{E}_{0,2} + \mathbf{E}_{\text{ex}} \quad (78)$$

$$\mathbf{E}^C = \mathbf{E}_2^{\text{non}} + \mathbf{E}_{\text{ex}} \quad (79)$$

Here, $\mathbf{E}_{0,2}$ and \mathbf{E}_{ex} are the vacuum fields by ρ_2 and ρ_{ex} , respectively, and \mathbf{E}^C is the total field at the constrained equilibrium. For an equilibrium polarization, the electrostatic free energy is of the well-known form,^[58]

$$F^{\text{eq}} = \frac{1}{8\pi} \int_V \mathbf{E} \cdot \mathbf{D} dV - \frac{1}{8\pi} \int_V \mathbf{E}_0 \cdot \mathbf{E}_0 dV = -\frac{1}{2} \int_V \mathbf{P} \cdot \mathbf{E}_0 dV \quad (80)$$

So free energies for the constrained equilibrium C and the equilibrium state 2 can be expressed as

$$F^C = -\frac{1}{2} \int_V \mathbf{P}_2^{\text{non}} \cdot (\mathbf{E}_{0,2} + \mathbf{E}_{\text{ex}}) dV = -\frac{1}{2} \int_V (\mathbf{P}_2^{\text{eq}} + \mathbf{P}') \cdot (\mathbf{E}_{0,2} + \mathbf{E}_{\text{ex}}) dV \quad (81)$$

$$F_2^{\text{eq}} = -\frac{1}{2} \int_V \mathbf{P}_2^{\text{eq}} \cdot \mathbf{E}_{0,2} dV \quad (82)$$

\mathbf{P}' denotes the polarization difference between $\mathbf{P}_2^{\text{non}}$ and \mathbf{P}_2^{eq} which we call the "residual" polarization and it equilibrates with \mathbf{E}_{ex} in the medium of ϵ_s . With the similar treatment by the charge-potential notation, starting from the constrained equilibrium "C," we prepare the nonequilibrium state "N" by removing the \mathbf{E}_{ex} suddenly without friction, thus free energy of the nonequilibrium state N is readily established as the polarization-field form, that is,^[101,102]

$$F^{\text{non}} = F^C + \int_V (\mathbf{P}_2^{\text{eq}} + \mathbf{P}') \cdot \mathbf{E}_{\text{ex}} dV \quad (83)$$

Combining Eqs. (81) and (83), the electrostatic free energy of the medium for the nonequilibrium state "N" is given by

$$\begin{aligned}
 F^{\text{non}} &= -\frac{1}{2} \int (\mathbf{E}_{0,2} + \mathbf{E}_{\text{ex}}) \cdot (\mathbf{P}_2^{\text{eq}} + \mathbf{P}') dV + \int \mathbf{E}_{\text{ex}} \cdot (\mathbf{P}_2^{\text{eq}} + \mathbf{P}') dV \\
 &= \frac{1}{2} \int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}_2^{\text{eq}} dV - \frac{1}{2} \int \mathbf{E}_{0,2} \cdot \mathbf{P}' dV - \frac{1}{2} \int \mathbf{E}_{0,2} \cdot \mathbf{P}_2^{\text{eq}} dV \\
 &\quad + \frac{1}{2} \int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}' dV
 \end{aligned} \quad (84)$$

It is easy to prove that (see Appendix B)

$$\int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}_2^{\text{eq}} dV = \int \mathbf{E}_{0,2} \cdot \mathbf{P}' dV \quad (85)$$

thus Eq. (84) can be further simplified to the desired form, that is,

$$F^{\text{non}} = -\frac{1}{2} \int \mathbf{E}_{0,2} \cdot \mathbf{P}_2^{\text{eq}} dV + \frac{1}{2} \int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}' dV \quad (86)$$

If one makes a detailed analysis on the polarization compositions of the nonequilibrium state and the constrained equilibrium state, it can be seen that the total polarizations of the two states are the same, but the polarization components of the two states are different. In the real nonequilibrium, according to Marcus, the total polarization is decomposed to

$$\mathbf{P}_2^{\text{non}} = \mathbf{P}_1^{\text{in}} + \mathbf{P}_2^{\text{dyn}} \quad (87)$$

while in the constrained equilibrium state, the total polarization is just the superposition of the equilibrium polarization by $\rho_2 + \rho_{\text{ex}}$, that is,

$$\mathbf{P}^{\text{c}} = \mathbf{P}^{\text{non}} = \mathbf{P}_2^{\text{eq}} + \mathbf{P}' = \mathbf{P}_2^{\text{in}} + \mathbf{P}_2^{\text{dyn}} + \mathbf{P}_{\text{ex}}^{\text{in}} + \mathbf{P}_{\text{ex}}^{\text{dyn}} \quad (88)$$

In this manipulation, $\mathbf{P}^{\text{c}} = \mathbf{P}^{\text{non}}$ means that the identity of \mathbf{P}^{non} and \mathbf{P}^{c} is guaranteed but not for their components. Fortunately, the entropy depends only on the total polarization from the viewpoint of classical thermodynamics disregarding the microscopic information. So the different components of $\mathbf{P}_2^{\text{non}}$ and \mathbf{P}^{c} do not hurt the formulation above. Illustration here indicates it is taken for granted that the entropy change is zero from a nonequilibrium state with \mathbf{P}^{c} to another nonequilibrium state with $\mathbf{P}_2^{\text{non}}$. Even if there were an entropy change ΔS^* in the step from \mathbf{P}^{c} to $\mathbf{P}_2^{\text{non}}$ with all the other parameters fixed, one would only need to append a term $-T\Delta S^*$ to Eq. (77) [or Eq. (86)] to gain the quantity of F_2^{non} .

Solvent Reorganization Energy

General formulism

According to the definition, the solvent reorganization energy is given by Eq. (20). Substituting Eqs. (77) and (67) into Eq. (20), we have

$$\lambda = \frac{1}{2} \int (\rho_2 + \rho_{\text{ex}}) \varphi_2^{\text{non}} dV - \int \rho_{\text{ex}} \varphi_2^{\text{non}} dV - \frac{1}{2} \int \rho_2 \varphi_2^{\text{eq}} dV \quad (89)$$

Equation (89) can be further changed to

$$\lambda = \frac{1}{2} \int \rho_2 \varphi' dV - \frac{1}{2} \int \rho_{\text{ex}} \varphi_2^{\text{eq}} dV - \frac{1}{2} \int \rho_{\text{ex}} (\varphi_2^{\text{non}} - \varphi_2^{\text{eq}}) dV \quad (90)$$

where $\varphi' = \varphi_2^{\text{non}} - \varphi_2^{\text{eq}}$ is the equilibrium potential produced by ρ_{ex} in the medium of ϵ_s . So the first two integrals in Eq. (90) cancel out, that is,

$$\frac{1}{2} \int \rho_2 \varphi' dV - \frac{1}{2} \int \rho_{\text{ex}} \varphi_2^{\text{eq}} dV = 0 \quad (91)$$

and hence we obtain¹⁰³

$$\lambda = -\frac{1}{2} \int \rho_{\text{ex}} (\varphi_2^{\text{non}} - \varphi_2^{\text{eq}}) dV \quad (92)$$

The constrained equilibrium is just a superposition of two equilibrium polarizations; one is the final equilibrium with a free charge density of ρ_2 and its equilibrium polarization potential φ_2^{eq} , and the other is the equilibrium with constraining external charge ρ_{ex} and the residual potential φ' . It is well-known that the free energy of an equilibrium electric field $[\rho_{\text{ex}}, \varphi']$ is given by

$$F_{\text{ex}} = \frac{1}{2} \int \rho_{\text{ex}} \varphi' dV \quad (93)$$

In other word, as seen from Eq. (93), the solvent reorganization energy just measures the cost needed to maintain the "residual" polarization potential φ' . This cost is exactly equal to $-F_{\text{ex}}$, that is,

$$\lambda = -F_{\text{ex}} \quad (94)$$

If we alternatively make the discussion with the constraining external field \mathbf{E}_{ex} which is used to hold the equilibrium with the "residual" polarization $\mathbf{P}' = \mathbf{P}_2^{\text{non}} - \mathbf{P}_2^{\text{eq}}$, the solvent reorganization energy can be given in the parallel way, that is,^[99–102]

$$\lambda = \frac{1}{2} \int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}' dV \quad (95)$$

The physics of the solvent reorganization energy becomes very clear by conceiving Eq. (95). To maintain a nonequilibrium polarization vector \mathbf{P}' in the medium region which is defined as the thermodynamic system in this review, one can at first introduce an external field \mathbf{E}_{ex} to the medium consistently and the work done by the system to the environment is $\frac{1}{2} \int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}' dV$; subsequently one suddenly removes the external field from the system to produce the lonely polarization \mathbf{P}' , the work done by the environment to the system in this step is $\int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}' dV$. As a sum, the net value of work done by environment to system is $\frac{1}{2} \int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}' dV$ which is a positive value. Such a manipulation exactly causes an free energy increase of $\frac{1}{2} \int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}' dV$ in the medium. This quantity is defined as the solvent reorganization energy as given by Eq. (95).

According to the relationship of

$$\varphi_2^{\text{non}} = \varphi_1^{\text{eq}} + \Delta\varphi^{\text{dyn}} \quad (96)$$

Equation (91) can be changed to the following form

$$\lambda = \frac{1}{2} \int_V \rho_{\text{ex}} (\Delta\varphi^{\text{eq}} - \Delta\varphi^{\text{dyn}}) dV \quad (97)$$

where $\Delta\varphi^{\text{dyn}}$ stands for the solvent polarization potential produced by $\Delta\rho = \rho_2 - \rho_1$ in the medium with the optical dielectric constant ε_{op} , and $\Delta\varphi^{\text{eq}}$ is the solvent polarization potential produced by $\Delta\rho$ in the medium of ε_s .

A key step for us to evaluate the solvent reorganization energy is to determine constraining force ρ_{ex} or \mathbf{E}_{ex} . Considering the equilibrium feature between \mathbf{E}_{ex} and \mathbf{P}' in the medium of ε_s and taking the "in-dyn" partition, we have $\mathbf{P}' = \chi_s (\mathbf{E}_{\text{ex}} + \mathbf{E}'_{\text{p}})$, with \mathbf{E}'_{p} being the polarization field due to \mathbf{P}' . Thus the electric field \mathbf{E}' due to the constraining field in the medium of ε_s can be expressed as

$$\mathbf{E}' = \mathbf{E}_{\text{ex}} + \mathbf{E}'_{\text{p}} = \frac{\mathbf{P}'}{\chi_s} = \frac{\Delta\mathbf{P}^{\text{dyn}} - \Delta\mathbf{P}^{\text{eq}}}{\chi_s} = \frac{\chi_{\text{op}}}{\chi_s} \Delta\mathbf{E}^{\text{dyn}} - \Delta\mathbf{E}^{\text{eq}} \quad (98)$$

The quantity \mathbf{E}'_{p} , which will disappear after the relaxation from the nonequilibrium N to the final equilibrium 2, can be expressed as

$$\mathbf{E}'_{\text{p}} = \mathbf{E}_2^{\text{non}} - \mathbf{E}_2^{\text{eq}} = \Delta\mathbf{E}^{\text{dyn}} - \Delta\mathbf{E}^{\text{eq}} \quad (99)$$

Combining Eqs. (98) and (99), the constraining field strength is given by^[99–102]

$$\mathbf{E}_{\text{ex}} = \frac{\chi_{\text{op}} - \chi_s}{\chi_s} \Delta\mathbf{E}^{\text{dyn}} = \frac{\varepsilon_{\text{op}} - \varepsilon_s}{\varepsilon_s - 1} \Delta\mathbf{E}^{\text{dyn}} \quad (100)$$

and Eq. (95) becomes

$$\lambda = \frac{1}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_s - 1} \int_V \Delta\mathbf{E}^{\text{dyn}} \cdot (\Delta\mathbf{P}^{\text{eq}} - \Delta\mathbf{P}^{\text{dyn}}) dV$$

In the equilibrium case, the divergence of the medium polarization and polarization surface charge σ can be expressed as

$$\nabla \cdot \mathbf{P} = 0 \text{ and } \mathbf{n} \cdot \mathbf{P} = \sigma \quad (101)$$

Further using $\Delta\mathbf{E}^{\text{dyn}} = -\nabla(\Delta\Phi^{\text{dyn}})$, we have

$$\begin{aligned} \lambda &= \frac{1}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_s - 1} \int_V \nabla(\Delta\Phi^{\text{dyn}}) \cdot (\Delta\mathbf{P}^{\text{dyn}} - \Delta\mathbf{P}^{\text{eq}}) dV \\ &= \frac{1}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_s - 1} \oint_S \Delta\Phi^{\text{dyn}} (\Delta\mathbf{P}^{\text{dyn}} - \Delta\mathbf{P}^{\text{eq}}) \cdot \mathbf{n} dS \\ &= \frac{1}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_s - 1} \oint_S \Delta\Phi^{\text{dyn}} (\Delta\sigma^{\text{dyn}} - \Delta\sigma^{\text{eq}}) dS \end{aligned} \quad (102)$$

The final surface integral in Eq. (102) is particularly convenient for the numerical solution of λ for general cavity shapes and sizes.

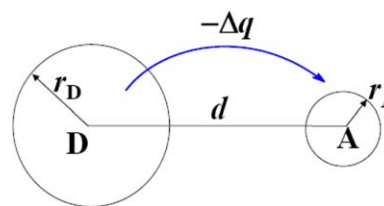


Figure 2. Two-sphere description of ET.

Two-sphere model for electron transfer

Two-sphere model is a simple and effective method to estimate the solvent reorganization energy. For an ET reaction between an electron donor D with a charge of q_D and an electron acceptor A with a charge q_A , the reaction process can be described by the following equation

$$D^{q_D} + A^{q_A} = D^{q_D + \Delta q} + A^{q_A - \Delta q} \quad (103)$$

where q_D and q_A are the charges brought by the donor and the acceptor, respectively, $-\Delta q$ is the charge transferred from D to A. It is assumed that all the point charges q_D , q_A , $q_D + \Delta q$, and $q_A - \Delta q$ locate at the centers of the two spheres as shown in Figure 2. The parameters r_D and r_A are the radii for donor and acceptor spheres, respectively. The spheres are surrounded by the medium with a dielectric constant of ε_s and the distance between the two spherical centers is d , which is assumed much larger than the radius r_D and r_A .

When the image charge effect due to the polarization surface charge is ignored, the polarization charge due to charge variation $\Delta q_D = \Delta q$ at the center of sphere D in the medium of ε_s and ε_{op} can be expressed as

$$Q_D^{\text{eq}} = \Delta q \left(\frac{1}{\varepsilon_s} - 1 \right), Q_D^{\text{dyn}} = \Delta q \left(\frac{1}{\varepsilon_{\text{op}}} - 1 \right) \quad (104)$$

Correspondingly, the charge variation $\Delta q_A = -\Delta q$ in sphere A induces the polarization charge on the surface of sphere A as

$$Q_A^{\text{eq}} = -\Delta q \left(\frac{1}{\varepsilon_s} - 1 \right), Q_A^{\text{dyn}} = -\Delta q \left(\frac{1}{\varepsilon_{\text{op}}} - 1 \right) \quad (105)$$

Thus, in the medium of ε_{op} , the polarization charge Q_D^{dyn} generates a polarization potential $\frac{\Delta q}{d} \left(\frac{1}{\varepsilon_{\text{op}}} - 1 \right)$ at the center of D, and similarly Q_A^{dyn} generates $-\frac{\Delta q}{d} \left(\frac{1}{\varepsilon_{\text{op}}} - 1 \right)$ at the center of D. Based on the principle of potential superposition, the total polarization potential at the center of D can be expressed as

$$\Delta\varphi_D^{\text{dyn}} = \left(\frac{\Delta q}{r_D} - \frac{\Delta q}{d} \right) \left(\frac{1}{\varepsilon_{\text{op}}} - 1 \right) \quad (106)$$

With the similar treatment, the total polarization potential at the center of A is

$$\Delta\varphi_A^{\text{dyn}} = -\left(\frac{\Delta q}{r_A} - \frac{\Delta q}{d} \right) \left(\frac{1}{\varepsilon_{\text{op}}} - 1 \right) \quad (107)$$

In the medium of ε_s , we have

$$\Delta\varphi_D^{\text{eq}} = \left(\frac{\Delta q}{r_D} - \frac{\Delta q}{d} \right) \left(\frac{1}{\varepsilon_s} - 1 \right) \quad (108)$$

$$\Delta\varphi_A^{\text{eq}} = - \left(\frac{\Delta q}{r_A} - \frac{\Delta q}{d} \right) \left(\frac{1}{\varepsilon_s} - 1 \right) \quad (109)$$

With the zeroth approximation of multiple expansions for the solute charge distribution, the constraining charges at the position of donor and acceptor can be derived as

$$q_{D,\text{ex}} = \frac{\varepsilon_{\text{op}} - \varepsilon_s}{(\varepsilon_s - 1)\varepsilon_{\text{op}}} \Delta q, q_{A,\text{ex}} = - \frac{\varepsilon_{\text{op}} - \varepsilon_s}{(\varepsilon_s - 1)\varepsilon_{\text{op}}} \Delta q \quad (110)$$

Here, the constraining charges can be thought to locate at the centers of spheres owing to the spherically symmetrical distribution. Substituting Eqs. (104)–(110) into Eq. (97), the solvent reorganization energy can be obtained as

$$\lambda_{\text{Li}} = \frac{(\Delta q)^2}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_{\text{op}}(\varepsilon_s - 1)} \left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{r_D} + \frac{1}{r_A} - \frac{2}{d} \right) \quad (111)$$

Note that Eq. (111) is different from the traditional Marcus equation^[56,57]

$$\lambda(\text{M}) = \frac{(\Delta q)^2}{2} \left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{r_D} + \frac{1}{r_A} - \frac{2}{d} \right) \quad (112)$$

It is clear that the two-sphere model Eq. (111) derived by us will predict a solvent reorganization energy smaller than the value from the Marcus formula Eq. (112) by a factor of k_{Li}

$$\lambda_{\text{Li}} = k_{\text{Li}} \lambda(\text{M}), k_{\text{Li}} = \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_{\text{op}}(\varepsilon_s - 1)} \quad (113)$$

The magnitude of the factor depends on the polarity of the solvent. For example, k_{Li} equals to 0.553 for water but becomes much smaller for nonpolar solvent. The scaling factor k_{Li} for some typical solvents has been given in Table 1, and k_{Li} falls into the region of 0.4–0.55 for the majority of polar solvents. In the cases of nonpolar solvents such as toluene, k_{Li} decreases to only ~ 0.05 . In fact, in nonpolar solvents, continuum model works poor since the electrostatic effect becomes negligible, and hence the predictions by both Eqs. (111) and (112) make little sense.

Spectral shift of point dipole in a spherical cavity

Spectral shifts for light absorption and emission are a crucial aspect of nonequilibrium solvation. Due to the Franck–Condon transition of the solute in medium, the solute-solvent system will experience the following processes. At first, the system undergoes a fast promotion from the equilibrium ground state to the nonequilibrium excited state, and then it relaxes to the equilibrium excited state, and finally goes back to the nonequilibrium ground state. Here, we use subscripts “1” and “2” to denote the different charge distributions at ground and excited states, respectively.

Table 1. The values of k_{Li} for different solvents.

Solvent	ε_s	ε_{op}	k_{Li}
Toluene	2.39	2.24	0.048
Diethyl ether	4.20	1.83	0.405
Tetrahydrofuran	7.52	1.97	0.432
Dichloromethane	9.08	2.03	0.430
Dimethylformamide	36.70	2.05	0.473
Acetonitril	37.50	1.81	0.540
Water	78.50	1.79	0.553

The spectral shift for the absorption spectrum is defined as the solvation free energy difference between nonequilibrium excited state “2” and equilibrium ground state “1,” that is,

$$\Delta(h\nu_{\text{ab}}) = F_2^{\text{non}} - F_1^{\text{eq}} \quad (114)$$

Correspondingly, for the inversed process, namely, emission (or fluorescence) spectrum, the spectral shift can be expressed as

$$\Delta(h\nu_{\text{em}}) = F_1^{\text{non}} - F_2^{\text{eq}} \quad (115)$$

Equations (114) and (115) imply that the positive value of $\Delta(h\nu)_{\text{ab}}$ corresponds to a blue shift; while the positive value of $\Delta(h\nu)_{\text{em}}$ to a red shift. According to the derivation above, we have^[100,104–106]

$$\begin{aligned} \Delta(h\nu_{\text{ab}}) &= \lambda + F_2^{\text{eq}} - F_1^{\text{eq}} \\ &= \frac{1}{2} \int_V (\rho_2 \varphi_2^{\text{eq}} - \rho_1 \varphi_1^{\text{eq}}) dV + \frac{1}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_s - 1} \oint_S \Delta\Phi^{\text{dyn}} (\Delta\sigma^{\text{dyn}} - \Delta\sigma^{\text{eq}}) dS \end{aligned} \quad (116)$$

$$\begin{aligned} \Delta(h\nu_{\text{em}}) &= \lambda + F_1^{\text{eq}} - F_2^{\text{eq}} \\ &= \frac{1}{2} \int_V (\rho_1 \varphi_1^{\text{eq}} - \rho_2 \varphi_2^{\text{eq}}) dV + \frac{1}{2} \frac{\varepsilon_s - \varepsilon_{\text{op}}}{\varepsilon_s - 1} \oint_S \Delta\Phi^{\text{dyn}} (\Delta\sigma^{\text{dyn}} - \Delta\sigma^{\text{eq}}) dS \end{aligned} \quad (117)$$

Here, the approximations of sphere cavity and point dipole used in the Onsager model^[48] are taken for the nonequilibrium polarization in spectrum. The solute charge distribution is considered as the point dipole, locating at the center of single vacuum sphere with a radius a , as shown in Figure 3. The solute cavity is surrounded by the solvent with a dielectric constant ε_s . The solute dipole will change from μ_1 to μ_2 due to the Franck–Condon transition in the light absorption process and the light emission will lead to the inversed change of the solute dipole.

Because ρ_i is treated as a point dipole located in a cavity with a radius of a , the total electric potential at position \mathbf{r} and the polarization surface charge density can be given by^[100,105,106]

$$\Phi_i^{\text{dyn}} = \frac{3\mu_i \cos \theta}{(1 + 2\varepsilon_{\text{op}})r^2}, \quad i = 1, 2 \quad (118)$$

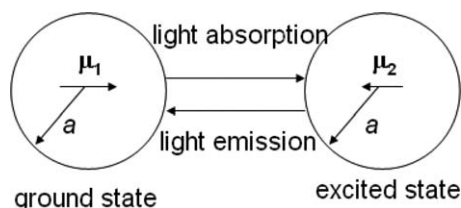


Figure 3. Solvation model for single sphere and point dipole.

$$\sigma_i^{\text{dyn}} = \frac{3(\epsilon_{\text{op}} - 1)}{4\pi(2\epsilon_{\text{op}} + 1)} \frac{\mu_i \cos \theta}{a^3}, \quad i=1, 2 \quad (119)$$

$$\sigma_i^{\text{eq}} = \frac{3(\epsilon_s - 1)}{4\pi(2\epsilon_s + 1)} \frac{\mu_i \cos \theta}{a^3}, \quad i=1, 2 \quad (120)$$

where θ is the angle between \mathbf{r} and the solute dipole.

The dipole moment can be expressed by

$$\boldsymbol{\mu} = \lim_{\substack{L \rightarrow 0 \\ q \rightarrow \infty}} q\mathbf{L} \quad (121)$$

where \mathbf{L} is the distance pointing from q_+ to q_- . Thus, we have

$$\int_V \rho \varphi dV = (q\varphi_+ - q\varphi_-) = \lim_{\substack{L \rightarrow 0 \\ q \rightarrow \infty}} q\mathbf{L} \cdot \nabla \varphi = -\boldsymbol{\mu} \cdot \mathbf{E}_p \quad (122)$$

where \mathbf{E}_p measures the polarization field, which is also called "reaction field," at the center of the sphere. For equilibrium solvation, the following equation holds

$$\frac{1}{V} \int_V \rho_i \varphi_i^{\text{eq}} dV = -\mu_i^2 \frac{(\epsilon_s - 1)}{a^3(2\epsilon_s + 1)}, \quad i=1, 2 \quad (123)$$

Combining Eqs. (116), (118), and (123), the final form for the absorption spectral shift with single sphere and point dipole approximation is given by^[100,105,106]

$$\Delta(h\nu_{\text{ab}}) = \frac{(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2}{a^3} \frac{9(\epsilon_s - \epsilon_{\text{op}})^2}{(\epsilon_s - 1)(2\epsilon_s + 1)(2\epsilon_{\text{op}} + 1)^2} + \frac{(\epsilon_s - 1)}{(2\epsilon_s + 1)} \frac{\mu_1^2 - \mu_2^2}{a^3} \quad (124)$$

A similar manipulation gives

$$\Delta(h\nu_{\text{em}}) = \frac{(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2}{a^3} \frac{9(\epsilon_s - \epsilon_{\text{op}})^2}{(\epsilon_s - 1)(2\epsilon_s + 1)(2\epsilon_{\text{op}} + 1)^2} - \frac{(\epsilon_s - 1)}{(2\epsilon_s + 1)} \frac{\mu_1^2 - \mu_2^2}{a^3} \quad (125)$$

From the derivations above, one can see that the solvent reorganization energy in photo absorption/emission is of the following form, that is,

$$\begin{aligned} \lambda &= \frac{(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2}{a^3} \frac{9(\epsilon_s - \epsilon_{\text{op}})^2}{(\epsilon_s - 1)(2\epsilon_s + 1)(2\epsilon_{\text{op}} + 1)^2} \\ &= \frac{3(\epsilon_s - \epsilon_{\text{op}})}{2(2\epsilon_{\text{op}} + 1)(\epsilon_s - 1)} (R_s - R_{\text{op}})(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2 \end{aligned} \quad (126)$$

The Stokes shift is thus given by Eq. (127 and 27) if only the solvent contribution is involved

$$\begin{aligned} \Delta(h\nu_{\text{sum}}) &= \Delta(h\nu_{\text{ab}}) + \Delta(h\nu_{\text{em}}) = 2\lambda \\ &= \frac{3(\epsilon_s - \epsilon_{\text{op}})}{(2\epsilon_{\text{op}} + 1)(\epsilon_s - 1)} (R_s - R_{\text{op}})(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2 \end{aligned} \quad (127)$$

Alternatively, using solvent reorganization energy obtained by the problematic way of Marcus reversible electric work, absorption and emission spectral shifts can be easily derived with the same approximations as follows^[53]

$$\Delta(h\nu_{\text{ab}})(M) = \frac{(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2}{a^3} \frac{3(\epsilon_s - \epsilon_{\text{op}})}{(2\epsilon_s + 1)(2\epsilon_{\text{op}} + 1)} + \frac{(\epsilon_s - 1)}{(2\epsilon_s + 1)} \frac{\mu_1^2 - \mu_2^2}{a^3} \quad (128)$$

$$\Delta(h\nu_{\text{em}})(M) = \frac{(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2}{a^3} \frac{3(\epsilon_s - \epsilon_{\text{op}})}{(2\epsilon_s + 1)(2\epsilon_{\text{op}} + 1)} - \frac{(\epsilon_s - 1)}{(2\epsilon_s + 1)} \frac{\mu_1^2 - \mu_2^2}{a^3} \quad (129)$$

The sum of Eqs. (128) and (129) gives the traditional form of the Stokes shift which is exactly the same as that by Lippert and Mataga^[49,50,53]

$$\begin{aligned} \Delta(h\nu)_{\text{sum}}(M) &= \frac{(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2}{a^3} \frac{6(\epsilon_s - \epsilon_{\text{op}})}{(2\epsilon_s + 1)(2\epsilon_{\text{op}} + 1)} \\ &= (R_s - R_{\text{op}})(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2 \end{aligned} \quad (130)$$

'Historically, people frequently applied Eq. (130) for the experimental fittings with the relationship of $\Delta(h\nu)_{\text{sum}} \sim (R_s - R_{\text{op}})$. From the updated theory introduced in this review, the orientational polarizability used for the linear fitting should be $\frac{3(\epsilon_s - \epsilon_{\text{op}})}{(2\epsilon_{\text{op}} + 1)(\epsilon_s - 1)} (R_s - R_{\text{op}})$, instead of the traditional one, $R_s - R_{\text{op}}$. Müller et al. most recently investigated the absorption and emission spectra for a series of compounds.^[107,108] Here, we take the compound quinoline 3c as an example (see Fig. 4 and Ref. [107] for details) to make a comparison between the linear fittings by Lippert–Mataga equation and the model by constrained equilibrium principle introduced above. From Eq. (5) or Eq. (130) the Stokes shift can be rewritten as

$$\Delta(h\nu_{\text{sum}})(M) = f_M \frac{2(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2}{a^3} \quad (131)$$

with

$$f_M = \frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{\epsilon_s - 1}{2\epsilon_s + 1} \quad (132)$$

However, the updated form, Eq. (127), can be changed to

$$\Delta(h\nu_{\text{sum}})(Li) = f_{Li} \frac{2(\boldsymbol{\mu}_2 - \boldsymbol{\mu}_1)^2}{a^3} \quad (133)$$

with

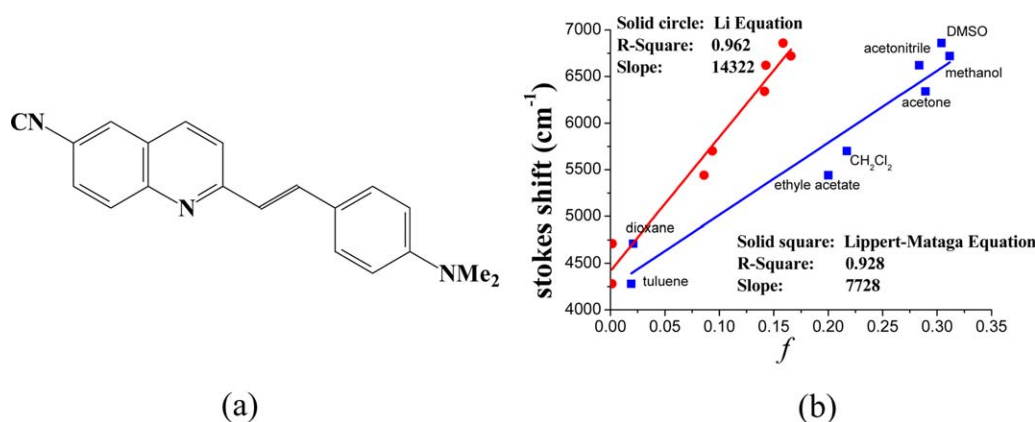


Figure 4. Compound quinoline 3c a) and the Stokes shift against the orientational polarizability f b). Experimental Stokes shifts are from Ref. [107].

$$f_{Li} = \frac{3(\epsilon_s - \epsilon_{op})}{(2\epsilon_{op} + 1)(\epsilon_s - 1)} \left(\frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{\epsilon_s - 1}{2\epsilon_s + 1} \right) \quad (134)$$

For different solvents given in Ref. [107], the dielectric constants, the coefficients f_M and f_{Li} have been given in Table 2. The linear fittings of $\Delta(h\nu_{sum})$ against f have been shown in Figure 4. It should be reminded that a linear fitting in this way ignores the mutual polarizations between the induced dipole and the solute dipole, and hence the solute dipoles for the ground state and the excited state are taken as a constant. From Figure 4, one can see both Eqs. (131) and (133) produce acceptable R-square coefficients: 0.928 from Lippert-Mataga equation (in Ref. [107], this value is 0.95) and 0.962 from the model by us. However, the significant difference lies in the slopes of the fitted lines, 7728 cm^{-1} vs. 14,332 cm^{-1} . This indicates that the values of $\frac{2(\mu_2 - \mu_1)^2}{a^3}$ will be considerably different. By taking a cavity radius of 8.6 Å,^[107] the linear fitting by Müller et al. produces a large dipole moment difference of 22 Debye that provides evidence for charge-transfer transition of this compound. From the ground state dipole moment μ_1 computed by geometry optimization, 13 Debye, μ_2 is estimated to be 35 Debye.^[107]

In fact, the spherical radius is an adjustable parameter and the optimal size of the cavity has thus been a subject of debate. Following Müller, we take the dipole moment difference of 22 Debye for the present case. From the slope of 14,332 cm^{-1} fitted by f_{Li} , the spherical radius is estimated to a reduced value, 7.0 Å. For the bar-like compound as given in Figure 4a, it is hard to say which size is more reliable, and this is possibly the reason that people use Lippert-Mataga equation for the Stokes fitting without suspicion in the past, although the basic model is problematic.

Matrix form of solvent reorganization energy

A matrix expression for solvent reorganization energy was recently developed by our group.^[109] Combining the numerical algorithm of the IEF-PCM, a corresponding program can be implemented. In this section, the author introduces the elegant matrix form of solvent reorganization energy.

For the purpose of numerical solution, Eq. (97) can be changed to the following matrix equation, that is,

$$\lambda = -\frac{1}{2} \mathbf{V}_{ex}^T (\Delta \mathbf{Q}^{dyn} - \Delta \mathbf{Q}^{eq}) \quad (135)$$

Here, the elements in the column matrix \mathbf{V}_{ex} are the electrostatic potential matrix by ρ_{ex} , and the superscript "T" indicates the transform matrix. The elements in the column matrix $\Delta \mathbf{Q}^{dyn}$ are the difference of polarization surface charges resulted from ρ_2 and ρ_1 in the medium of ϵ_{op} , and $\Delta \mathbf{Q}^{eq}$ has the similar definition but in the medium of ϵ_s . In PCM, the solute-solvent interactions are resorted to the polarization charge spreading on the cavity surface. By means of matrix equation of IEF-PCM,^[17,18] we have

$$\mathbf{DQ} = -\mathbf{V} \quad (136)$$

where \mathbf{D} is the interaction square matrix collecting elements related to the geometry of cavity and the dielectric constant ϵ_s or ϵ_{op} . The column vector \mathbf{Q} collects the polarization surface charges.

In the initial equilibrium state with the medium of ϵ_s , one can obtain \mathbf{Q}^{eq} by the matrix equation as follows,

Table 2. Linear fittings of solvent dependency of Stokes shift with Lippert-Mataga equation and with Eq. (127) by us

Solvent	ϵ_s	ϵ_{op}	f_M^a	f_{Li}^b	Stokes shift (cm^{-1}) ^c
DMSO	46.8	2.00	0.28932	0.1415	6340
Methanol	36.6	1.76	0.3116	0.1657	6720
Acetonitrile	35.9	1.81	0.3041	0.1585	6860
Acetone	20.1	1.85	0.2835	0.1427	6620
CH ₂ Cl ₂	8.93	2.03	0.2171	0.0936	5700
Ethyl acetate	6.02	1.88	0.2001	0.0859	5440
Dioxane	2.21	2.01	0.0219	0.0016	4710
Toluene	2.40	2.20	0.0192	0.0013	4280

[a] See Eq. (132) for the definition of f_M . [b] See Eq. (134) for the definition of f_{Li} . [c] Experimental values of Stokes shifts from Ref. 107.

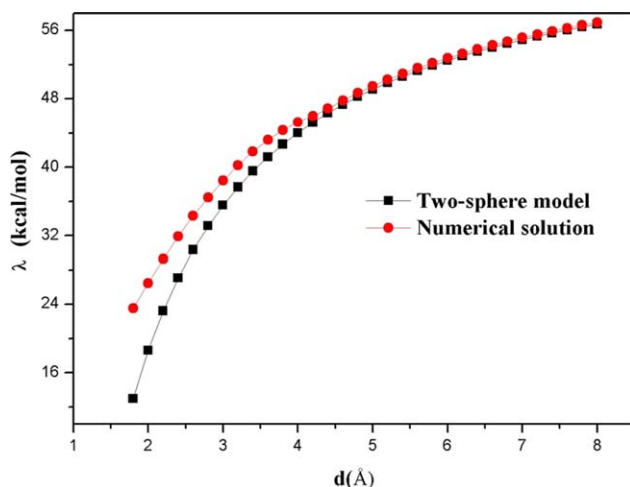


Figure 5. Distance dependency of the solvent reorganization energy (Reproduced with permission from Springer).^[109]

$$\mathbf{D}_s \mathbf{Q}^{\text{eq}} = -\mathbf{V} \quad (137)$$

Applying Eq. (137) to the two equilibrium states with respect to ρ_1 and ρ_2 , we have

$$\mathbf{Q}_1^{\text{eq}} = -\mathbf{D}_s^{-1} \mathbf{V}_1, \quad \mathbf{Q}_2^{\text{eq}} = -\mathbf{D}_s^{-1} \mathbf{V}_2, \quad (138)$$

Here, \mathbf{D}_s^{-1} is the reciprocal of \mathbf{D} . The difference matrix is of the following form,

$$\Delta \mathbf{Q}^{\text{eq}} = \mathbf{Q}_2^{\text{eq}} - \mathbf{Q}_1^{\text{eq}} = -\mathbf{D}_s^{-1} \Delta \mathbf{V} \quad (139)$$

with $\Delta \mathbf{V} = \mathbf{V}_2 - \mathbf{V}_1$. Similarly we have

$$\Delta \mathbf{Q}^{\text{dyn}} = -\mathbf{D}_{\text{op}}^{-1} \Delta \mathbf{V} \quad (140)$$

Please note that \mathbf{D}_s and \mathbf{D}_{op} are square matrixes that depends on the dielectric constants and geometrical parameters of the molecular cavity. For the constrained equilibrium, it holds

$$\mathbf{D}_s \mathbf{Q}_2^{\text{non}} = -(\mathbf{V}_2 + \mathbf{V}_{\text{ex}}) \quad (141)$$

with

$$\mathbf{Q}_2^{\text{non}} = \mathbf{Q}_2^{\text{dyn}} + \mathbf{Q}_1^{\text{in}} = \Delta \mathbf{Q}^{\text{dyn}} + \mathbf{Q}_1^{\text{eq}} \quad (142)$$

Following Eq. (137), \mathbf{V}_{ex} is given by

$$\mathbf{V}_{\text{ex}} = \mathbf{D}_s (\Delta \mathbf{Q}^{\text{eq}} - \Delta \mathbf{Q}^{\text{dyn}}) \quad (143)$$

Substituting Eqs. (139) and (140) into Eq. (143) yields

$$\mathbf{V}_{\text{ex}} = \mathbf{D}_s \cdot (\mathbf{D}_{\text{op}}^{-1} - \mathbf{D}_s^{-1}) \cdot \Delta \mathbf{V} \quad (144)$$

Combining Eqs. (139), (140), (143), and (135), the desired matrix equation for λ is given by

$$\lambda = \frac{1}{2} \mathbf{B}^T \cdot \mathbf{D}_s^{-1} \cdot \mathbf{B} \quad (145)$$

with

$$\mathbf{B} = (\mathbf{D}_s^{-1} - \mathbf{D}_{\text{op}}^{-1}) \cdot \Delta \mathbf{V}$$

If matrix \mathbf{D}_s is symmetric, Eq. (145) becomes^[109]

$$\lambda = \frac{1}{2} \mathbf{B}^T \cdot \mathbf{D}_s \cdot \mathbf{B} \quad (146)$$

Equation (145) shows that the solvent reorganization energy depends on the interaction matrix \mathbf{D} and the solute potential change $\Delta \mathbf{V}$.

By assuming a self-exchange ET with the same sphere radius of 1.464 Å, and considering the step $\text{A}^- + \text{A} = \text{A} + \text{A}^-$, we can get a numerical result for λ with Eq. (146), which can be compared with the value from the two-sphere model by Eq. (111). Since λ varies with the separation distance d , Figure 5 exhibits the correlation between λ and d . When d is large enough, the numerical solution and two-sphere model give comparable results. At the critical value of 2.928 Å of separation distance, that is, $d = r_A + r_D$, where the two cavities just contact with each other, the value of λ is 33.12 kcal/mol from the two-sphere model but 36.47 kcal/mol from our numerical solution. If the numerical solution is taken as accurate, it will be revealed that the two-sphere model underestimates λ by about 10%. This indicates that two-sphere approximation behaves quite well when the two spheres are far from each other. However, it behaves worse in the cases that the two spheres intersect ($d < r_A + r_D$). Caution is thus called for the limitation of the two-sphere model in applications.

Conclusions

In this review, the author outlines the traditional continuum medium theories and models on nonequilibrium solvation in fast processes such as ET and photon absorption/emission. In this field, Marcus theory takes the central position owing to the comprehensive formulation and the unambiguous definitions on nonequilibrium free energy, although Ooshika, Lippert, Mataga, and other people paved the way to the nonequilibrium solvation energy earlier. The problem in Marcus formulation has been paid particular attention to in this review. The failure of Eq. (8) with Eq. (10) for a nonquasistatic pathway has been proved by the rigorous thermodynamic analysis in this review. By comparing with Eq. (57) that is thermodynamic requirement for free energy change by integrating the nonvolume work, one will be aware that a concerted change between electrical potential and solute charge as shown by Eq. (27), which is just a substituent of Eq. (10), is apparently unreliable. Eq. (57) tells that Eq. (8) with Eq. (10) is valid only if the pathway is reversible, but definitely there is no possibility to find such a pathway linking the equilibrium and the nonequilibrium. The application of Eq. (8) associated with Eq. (10) or the substituent Eq. (27) is essentially a manipulation for equilibrium solvation, and hence Eq. (12) is an

equilibrium free energy with the self-energy of the solute charge included. If Φ_2^{non} was changed to Φ_2^{eq} in Eq. (12), the last two terms would cancel out, and that equation is just the free energy of equilibrium state 2. Unfortunately, this point was ignored. From the analysis presented in this review, one can see that Eq. (12) cannot be the correct form of nonequilibrium solvation free energy.

Various other expressions for nonequilibrium polarization using the free energy functional created by Felderhof have been put forward. By copying the terms $\frac{1}{2} \int (\frac{1}{\epsilon_{\text{or}}} (\mathbf{P}^{\text{or}})^2 + \frac{1}{\epsilon_{\text{op}}} (\mathbf{P}^{\text{op}})^2) dV$ of the equilibrium polarization to the nonequilibrium expression of free energy, Felderhof expression was simply extended to nonequilibrium states. The term holds true in the equilibrium case because $\frac{1}{2} \int (\frac{1}{\epsilon_{\text{or}}} (\mathbf{P}^{\text{or}})^2 + \frac{1}{\epsilon_{\text{op}}} (\mathbf{P}^{\text{op}})^2) dV = \frac{1}{2} \int \frac{1}{\epsilon_s} \mathbf{P}^2 dV$.

However, the situation is quite different and no evidence guarantees the feasibility of such an extension. It is possible that the defects in theory were concealed because free energy functional method gives a same expression of nonequilibrium solvation free energy as that by Marcus [see Eq. (15) and Eq. (39) and the discussions following the latter for the identity].

The central question is how to apply continuum models to the nonequilibrium cases. In the earlier efforts (before 2008) by our research group, another form of the free energy of nonequilibrium state was worked out using the Jackson formula Eq. (28) associated with Eq. (10). Such a manipulation gives average solvent reorganization energy of forward and backward ETs being exactly half of the Marcus result, but a closer inspection reveals that this treatment is still lack of solid thermodynamic foundation. From the efforts devoted in the past 60 years, it should be believed that the effective derivation for the free energy of nonequilibrium solvation is not an easy job, and an efficient tool is needed to bring us to the correct terminal for this issue.

Nonequilibrium solvation is a typical thermodynamic nonequilibrium state when we take the electric field as a thermodynamic variable. So a rigorous thermodynamic formulation is needed for the establishment of the free energy of nonequilibrium state. Fortunately, the constrained equilibrium principle provides the possibility for this purpose. The main goal of this review is to introduce the formulation of the free energy by this principle. From this completely different angle of view, one can see that the expression of the nonequilibrium free energy and the solvent reorganization energy should possess quite different forms. The most outstanding feature of the energy expression by constrained equilibrium principle is that a parameter which measures the strength of constraining force enters the free energy expression. The recent formulation by us gives the solvent reorganization energy with the compact form of $\lambda = \frac{1}{2} \int \mathbf{E}_{\text{ex}} \cdot \mathbf{P}' dV = -\frac{1}{2} \int \rho_{\text{ex}} \varphi' dV$, from which the "cost" for nonequilibrium polarization becomes unambiguous, as mentioned below Eq. (95).

From the analytical form for two-sphere model of ET, the expression of λ by the author differs from that by Marcus by a factor of $k_{\text{Li}} = \frac{\epsilon_s - \epsilon_{\text{op}}}{\epsilon_{\text{op}}(\epsilon_s - 1)}$ (see Eq. (113)). In the case of strong polar

solvent, $k_{\text{Li}} \approx 1/\epsilon_{\text{op}}$. This means that the theoretical prediction by the traditional model should overestimate the solvent reorganization energy by a factor of about 2. Thus, the discrepancies between the theoretical predictions and the experimental measurements that puzzled people for decades have found their answers finally.

Seen from Eqs.(137)-(146), we can write the matrix form for the relationships between the electric potentials due to the free charge and the polarization charge distribution, based on the well defined IEF-PCM technique and individual equilibrium features. Finally, the solvent reorganization energy can be given in an elegant matrix form of and the matrix form of $\lambda = \frac{1}{2} \mathbf{B}^T \cdot \mathbf{D}_s \cdot \mathbf{B}$, as shown by Eq. (146). This form is convenient for the development of codes for numerical solution.

It should emphasized that there is no conceptual difference between the theory by means of constrained equilibrium recommended in this review and those in the previous literatures by other groups on such as polarization potential, polarization charge, and partition style of the polarization, except some trivial terminological disparities. In fact, there are a number of numerical methods for the estimations of equilibrium solvation and nonequilibrium solvation so far, but this review concentrates only on the electrostatics of the nonequilibrium solvation theories. The solvation dynamics is also an important aspect of solvent effects by considering for example the time-dependency and temperature-dependency of the solvent effects. Although such a kind of topics have not been discussed here, the correct understandings at the level of electrostatics will certainly provide the solid foundation for further developments of solvation dynamics, for example, the expression of nonequilibrium time correlation functions^[18,110–112] and the time-dependent nonequilibrium dielectric response.^[113] So, how to deal with nonequilibrium dynamics of solvation accurately is still a challenging work.

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APPENDIX A

Proof for the identity of Marcus result and the ones by Cossi and Marenich
The expression by Marcus is as follows^[52]

$$\begin{aligned} F_2^{\text{non}} &= \frac{1}{2} \int \rho_2 \varphi_2^{\text{non}} dV + \frac{1}{2} \int \rho_2 \varphi_1^{\text{eq}} dV - \frac{1}{2} \int \rho_1 \varphi_2^{\text{non}} dV \\ &= \frac{1}{2} \int [(-\mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{0,2} - \mathbf{P}_1^{\text{eq}} \cdot \mathbf{E}_{0,2} + \mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{0,1}) dV \\ &= \frac{1}{2} \int \left[-\mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{0,2} + \mathbf{P}_1^{\text{or}} \cdot \left(\frac{\mathbf{P}_1^{\text{or}}}{\chi_{\text{or}}} - \mathbf{E}_2^{\text{non}} \right) \right] dV \end{aligned} \quad (\text{A1})$$

When we separate the polarized charge in the inertial-dynamic manner, Eq. (A1) becomes

$$\begin{aligned} F_2^{\text{non}} &= \frac{1}{2} \int [-\mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{0,2} - \mathbf{P}_1^{\text{eq}} \cdot \mathbf{E}_{0,2} + \mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{0,1}] dV \\ &= \frac{1}{2} \int [-(\mathbf{P}_1^{\text{in}} + \mathbf{P}_2^{\text{dyn}}) \cdot \mathbf{E}_{0,2} - (\mathbf{P}_1^{\text{in}} + \mathbf{P}_1^{\text{dyn}}) \cdot \mathbf{E}_{0,2} + (\mathbf{P}_1^{\text{in}} + \mathbf{P}_2^{\text{dyn}}) \cdot \mathbf{E}_{0,1}] dV \\ &= \frac{1}{2} \int [-(\mathbf{P}_1^{\text{in}} + \mathbf{P}_2^{\text{dyn}}) \cdot \mathbf{E}_{0,2} - (\mathbf{P}_1^{\text{in}} \cdot \mathbf{E}_{0,2} + \mathbf{P}_2^{\text{dyn}} \cdot \mathbf{E}_{0,1}) \\ &\quad + (\mathbf{P}_1^{\text{in}} + \mathbf{P}_2^{\text{dyn}}) \cdot \mathbf{E}_{0,1}] dV \\ &= -\frac{1}{2} \int \mathbf{E}_{0,2} \cdot \mathbf{P}_2^{\text{dyn}} dV - \int (\mathbf{E}_{0,2} - \frac{1}{2} \mathbf{E}_{0,1}) \cdot \mathbf{P}_1^{\text{in}} dV \\ &= \frac{1}{2} \int \rho_2 \varphi_2^{\text{dyn}} dV + \int (\rho_2 - \frac{1}{2} \rho_1) \varphi_1^{\text{in}} dV \end{aligned} \quad (\text{A2})$$

The discrete form is thus given by

$$F_2^{\text{non}} = \frac{1}{2} \sum_i Q_{2,i}^{\text{dyn}} V_{2,i} + \sum_i (V_{2,i} - \frac{1}{2} V_{1,i}) Q_{1,i}^{\text{in}} \quad (\text{A3})$$

This is Eq. (30) in the paper by Marenich et al.^[72] In the parallel way, the orientational-optical partition leads to the following equation, that is,

$$\begin{aligned} F_2^{\text{non}} &= \frac{1}{2} \int [-\mathbf{P}_2^{\text{non}} \cdot \mathbf{E}_{0,2} + \mathbf{P}_1^{\text{or}} \cdot (\frac{\mathbf{P}_1^{\text{or}}}{\chi_{\text{or}}} - \mathbf{E}_2^{\text{non}})] dV \\ &= \frac{1}{2} \int [-(\mathbf{P}_1^{\text{or}} + \mathbf{P}_2^{\text{op}}) \cdot \mathbf{E}_{0,2} + \mathbf{P}_1^{\text{or}} \cdot (\mathbf{E}_{0,1} - \mathbf{E}_{0,2}) + \mathbf{P}_1^{\text{or}} \cdot (\mathbf{E}_1^{\text{op}} - \mathbf{E}_2^{\text{op}})] dV \\ &= \int [-\frac{1}{2} \mathbf{P}_2^{\text{op}} \cdot \mathbf{E}_{0,2} + \mathbf{P}_1^{\text{or}} \cdot (\frac{1}{2} \mathbf{E}_{0,1} - \mathbf{E}_{0,2}) + \frac{1}{2} \mathbf{P}_1^{\text{or}} \cdot (\mathbf{E}_1^{\text{op}} - \mathbf{E}_2^{\text{op}})] dV \\ &= \frac{1}{2} \int \rho_2 \varphi_2^{\text{op}} dV + \int (\rho_2 - \frac{1}{2} \rho_1) \varphi_1^{\text{or}} dV + \frac{1}{2} \int \rho_1 (\varphi_2^{\text{op}} - \varphi_1^{\text{op}}) dV \end{aligned} \quad (\text{A4})$$

The discrete form is as follows

$$F_2^{\text{non}} = \frac{1}{2} \sum_i Q_{2,i}^{\text{op}} V_{2,i} + \sum_i Q_{1,i}^{\text{or}} (V_{2,i} - \frac{1}{2} V_{1,i}) + \frac{1}{2} \sum_i Q_{1,i}^{\text{or}} (\eta_{2,i}^{\text{op}} - \eta_{1,i}^{\text{op}}) \quad (\text{A5})$$

Eq. (A5) is just the one given by Cossi^[71] and by Marenich et al.^[72]

APPENDIX B

Proof of $\int_V \mathbf{E}_{0,2} \cdot \mathbf{P}' dV = \int_V \mathbf{E}_{\text{ex}} \cdot \mathbf{P}_2^{\text{eq}} dV$

As $\mathbf{P} = \chi_s \mathbf{E}$ for an equilibrium state, we have

$$\int_V \mathbf{E}_2^{\text{eq}} \cdot \mathbf{P}' dV = \int_V \mathbf{E}' \cdot \mathbf{P}_2^{\text{eq}} dV \quad (\text{B1})$$

Here, $\mathbf{E}' = \mathbf{E}_{\text{ex}} + \mathbf{E}_{\text{p}}$ with \mathbf{E}_{p} being the polarization field by \mathbf{P}' . Separating the electric field into vacuum and polarization parts, Eq. (B1) becomes

$$\int_V \mathbf{E}_{0,2} \cdot \mathbf{P}' dV + \int_V \mathbf{E}_{\text{p},2} \cdot \mathbf{P}' dV = \int_V \mathbf{E}_{\text{ex}} \cdot \mathbf{P}_2^{\text{eq}} dV + \int_V \mathbf{E}_{\text{p}} \cdot \mathbf{P}_2^{\text{eq}} dV \quad (\text{B2})$$

Here, $\mathbf{E}_{\text{p},2}$ is the polarization field due to $\mathbf{E}_{0,2}$. When the polarization potential and polarization surface charge are introduced,

$$\int_V \mathbf{E}_{\text{p},2} \cdot \mathbf{P}' dV = - \int_S \varphi_2^{\text{eq}} \sigma_{\text{ex}} dS = - \int_S \int_{S'} \frac{\sigma_2^{\text{eq}} \sigma_{\text{ex}}}{|\mathbf{r}_2 - \mathbf{r}_{\text{ex}}|} dS' dS = \int_V \mathbf{E}_{\text{p}} \cdot \mathbf{P}_2^{\text{eq}} dV \quad (\text{B3})$$

where σ_2^{eq} and σ_{ex} represent the polarization charges at the boundary by $\mathbf{E}_{0,2}$ and the field \mathbf{E}_{ex} , respectively, and $|\mathbf{r}_2 - \mathbf{r}_{\text{ex}}|$ denotes the distance between the polarization charges. Substituting Eq. (B3) into Eq. (B2), the desired relationship is obtained, that is,

$$\int_V \mathbf{E}_{0,2} \cdot \mathbf{P}' dV = \int_V \mathbf{E}_{\text{ex}} \cdot \mathbf{P}_2^{\text{eq}} dV \quad (\text{B5})$$

Keywords: nonequilibrium salvation • reversible work • constrained equilibrium • solvent reorganization energy

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