In Praise of Simple Models

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Abstract. Simple models, in particular those based on Onsager’s point dipole in a spherical cavity embedded in a polarizable medium, played an important role in understanding equilibrium and dynamical interaction between solvent polarization and classical reaction kinetics. After a brief review of some crucial results, and an application to the interaction of fluctuating polarization field on a classical dipolar oscillator, I investigate the applicability of a similar simple model to quantum-classical interactions. Interesting differences with a fully classical system occur in equilibrium situations, and some fundamental problems with commonly used dynamical approaches are indicated.

1. The Onsager Model for an Oscillating Dipole.

Onsager’s model for a dipole in a spherical cavity[1], although originally developed to better understand the relation between molecular dipole moment and macroscopic dielectric constant\(^1\), also played an important role in understanding the role of solvents in chemical reaction kinetics. Both the theory of dielectrics and that of reaction rate constant made considerable initial steps in the 1930’s, and continued developing somewhat in parallel until the early 1980’s. An extremely brief history of the theory of reaction rates lets it start in the 1930’s with transition state theory[3], followed by the realization that solvent dynamics in the barrier region can play a crucial role by Kramers in 1941[4], and the understanding of dynamical interaction between solvent and reaction rates in the late 1970’s[5]. Marcus’ theory for electron transfer rates fits in this picture[6], since it emphasizes the fundamental role of polarization in creating the barrier for an electron transfer reaction taking place in a polarizable medium.

The model is shown in Fig. 1. A point dipole is located at the center of a spherical cavity of radius \(a\). For our purposes it is sufficient to take vacuum inside the cavity, whereas the dielectric can be described by the electric field \(E_o\), the displacement \(D_o\), and the polarization \(P_o\). Since, apart from the point dipole, there is vacuum inside the cavity, we only have to consider the inside electrical field \(E_i\). At the boundary these fields are related by boundary conditions

\[
\vec{n} \cdot \vec{E}_i = \vec{n} \cdot \vec{D}_o \quad \text{and} \quad \vec{n} \times \vec{E}_i = \vec{n} \times \vec{E}_o
\]

\(^1\) However, Onsager’s remark that Debye neglected to disregard the reaction field in his calculation is incorrect. Debye used the internal field calculated by Lorentz, who ignored the change in a dielectric due to a cavity. Onsager calculated the internal field by taking the boundary conditions at the cavity surface into account. It is the change in internal field, and not the reaction field that gives the Onsager relation between dielectric constant and molecular dipole moment. An interesting derivation of the Lorentz field can be found in Feynman [2]. The Lorentz field does not contain the reaction field.
Relations between the various fields, and the frequency dependent dielectric constant $\epsilon(\omega)$ are shown in the figure. We will denote the static dielectric constant by $\epsilon_s = \epsilon(0)$.

\[ \mathcal{E}_0(\omega) = \epsilon_0 \epsilon_s \mathcal{E}_0(\omega) \]

\[ E_0(t) \]

\[ D_0(t) \]

\[ E_{\text{int}}(t) \]

\[ \bar{\mu}(t) \]

\[ \mathcal{E}_0(\omega) = \epsilon_0 \mathcal{E}_0 + \mathcal{E}_R(\omega) \]

\[ \mathcal{E}_R(\omega) = \frac{1}{4\pi\epsilon_0 a^2} \frac{2(\epsilon(\omega) - 1)}{2\epsilon(\omega) + 1} \bar{\mu}(\omega) \equiv A(\omega)\bar{\mu}(\omega) \]

so that, at time $t$ the energy $U(t)$ of a dipole in its own reaction field can be written as

\[ U(t) = -\bar{\mu}(t) \cdot \mathcal{E}_R(t) \]
The time dependence of the reaction field is ultimately related to the dynamic equation satisfied by the polarization. Eq. (2) is only the simplest possible expression. More elaborate models have been considered within the context of reaction dynamics, such as the inclusion of inertial terms [8], or the possibility of non–local adjustment due to polarization diffusion [9]. These are all shown to lead to more or less complicated expressions for the function $A(\omega)$. The reaction field can be quite large. For a cavity of radius 0.5 nm, and a 5 D dipole (one electron charge displaced over 1 Å), it is already 1200 cm$^{-1}$ in equilibrium.

Next we consider the effect of the reaction field on a dipolar oscillator, depicted on the right hand side of Fig. 1. In the presence of a polarizable medium outside the cavity the oscillator satisfies the usual equation of motion:

\[ m \frac{d^2 x(t)}{dt^2} = -m\omega_0^2 x(t) + F(t) \]  

(6)

where $m$ is its reduced mass, and $\omega_0$ its frequency. $F(t)$ is the force acting on the dipole due to its own reaction field. An analysis closely resembling that of Nee and Zwanzig [7] leads to the following equation of motion for the extension $x(t)$ of the oscillator

\[ m \frac{d^2 x(t)}{dt^2} = -m\omega_0^2 x(t) + \mu^2 \int_{-\infty}^t d\tau A(t - \tau) x(\tau) \]  

(7)

This can be written in a more interesting way by first considering the Fourier transformed equation:

\[ -m\omega^2 x(\omega) = -m\omega_0^2 x(\omega) + \mu^2 A(\omega)x(\omega) = -m\omega_0^2 x(\omega) + \mu^2 \frac{A(\omega) - A_s}{-i\omega} (-i\omega x(\omega)) + A_s x(\omega) \]  

(8)

followed by inverse Fourier transformation, which leads to:

\[ m \frac{d^2 x(t)}{dt^2} = -(m\omega_0^2 - \mu^2 A_s)x(t) - \int_0^t d\tau \zeta_D(t - \tau) \frac{dx(\tau)}{d\tau} \]  

(9)

In these equations $A_s = A(\omega = 0)$, and $\zeta_D(t)$ is a friction kernel, defined by its Fourier transform

\[ \zeta_D(\omega) = \mu^2 \frac{A(\omega) - A_s}{-i\omega} \]  

(10)

Eq. (9) shows that the external polarization has two basic effects: it modifies the vibrational frequency, and it causes a friction on the oscillator, which will eventually bring it to rest. The modification of the frequency is usually not very large. In the case of an OH vibrational mode in a highly polarizable environment it can be a few tens of cm$^{-1}$, but OH modes in those circumstances are usually very broad peaks to begin with. Part of that linewidth could be due to polarizable solvent effects. For other vibrations the effect is usually much smaller, a few cm$^{-1}$ at most.

More interesting is considering this equation from a fundamental point of view. The oscillator at the center of the cavity is itself undamped, it will oscillate forever if there is no interaction with the external field. The polarization outside the cavity is damped — in fact for the case I considered here even overdamped — and only because of the coupling the oscillator becomes damped as well. In fact a much stronger statement can be made. If we add random polarization fields to Eq. (2), and assume a fluctuation dissipation theorem to be valid [10] it is a straightforward, albeit lengthy, exercise to prove that Eq. (9) is a suitable generalized Langevin equation. Which means that it also contains a random force term for which the
fluctuation dissipation theorem holds. This has the strong implication that the distribution of $x$–values decays to the correct equilibrium distribution. It can also be shown that $A_4$ is in fact the potential of mean force on the oscillator resulting from the equilibrium fluctuations of the outside polarization field.

Although calculations for systems based on this approach are simple, they contributed a lot to our understanding of processes occurring in solvents[8, 11, 12]. Many analytical results can be derived which help in understanding the various regimes in solvent reaction dynamics[13]. One serious drawback, however, is that the model is completely classical, whereas for many processes the quantum nature of the system can not be neglected. One would expect, or could hope, that a similar approach to mixed classical quantum systems — using simple but analyzable systems — would also help understanding classical–quantum interaction.

2. Equilibrium Interaction between Quantum Systems and Classical Fields.

Interaction between classical and quantum systems is usually described in the following way[14, 15]: the quantum system ‘feels’ a classical electric field due to polarization, and the classical system ‘sees’ the expectation value of some operator of the quantum system. For the latter usually the charge density is used. This is not according to the basic principles of quantum mechanics, which states that an observation leads to finding an eigenvalue of such an operator, upon which the quantum system collapses to an eigenstate. Unfortunately there are few papers in which this approach is used for simple models like the one described in the previous section, even though much could be learned from that.

**Figure 2.** A two–level system (2LS) in a cavity. The properties of the cavity and the polarizable medium are the same as for the classical case, but now we have a quantum system at the center. This quantum system can have a ground– and excited state dipole moment, as well as a transition moment $\vec{\mu}$. The transition moment is responsible for the polarization. On the right hand side free energy curves for various values of the interaction strength $A$ are drawn, for the case $\vec{\mu}_0 = \vec{\mu}_1 = 0$. For large enough values of $A$ the free energy has minima at finite values of the ground state dipole moment. On the right hand side free energy curves (see below Eq. (15)) for values below and above the splitting threshold. The ground state dipole moment at the minimum is 0.9 D. Input values were: $\epsilon = 12500 \text{ cm}^{-1}$, $\mu = 10 \text{ D}$.

The set–up is explained in Fig. 2. Mathematically it can be described by the Schrödinger equation

$$\mathcal{H} |\Psi\rangle = \lambda |\Psi\rangle \quad \text{with} \quad \mathcal{H} = \mathcal{H}_0 - \vec{\mu} E$$

(11)
where $H_0$ is the Hamiltonian of the unperturbed 2LS, $\hat{\mu}$ is the dipole operator, and $E$ is the electric field acting on the 2LS. This electric field should be a reaction field, which means that it is caused by the presence of a dipole in the cavity. In an equilibrium situation this means that

$$E = A_s \langle \hat{\mu} \rangle$$

(12)

where $A_s$ is the static reaction field factor introduced in the previous section. The two equations (11) and (12) need to be solved simultaneously. For the purpose of simplicity I take the simplest situation where there are no ground and excited state dipole moments, just a transition moment. The polarizability of such a quantum system is $\alpha = \frac{2\mu^2}{\Delta}$ where $\mu$ is the magnitude of the transition dipole moment and $\Delta$ the energy difference between ground and excited state. Both equations can be derived from a single Hamiltonian

$$H = H_0 - \hat{\mu}E + \frac{E^2}{2A_s}$$

(13)

where a variational principle for finding minima leads directly to Eqs. (11) and (12).

Using a representation of $|\Psi\rangle$ in terms of the original wavefunctions $|0\rangle$ and $|1\rangle$:

$$|\Psi\rangle = \frac{t}{\sqrt{t^2 + 1}} |0\rangle + \frac{te^{i\phi}}{\sqrt{1 + t^2}} |1\rangle$$

(14)

where $t$ can be chosen real. Finding the eigenstates of Eq. (13) is equivalent to finding the extrema of the function

$$G = \frac{\Delta t^2 - 2\mu E t}{t^2 + 1} + \frac{E^2}{2A_s}$$

(15)

both with respect to $E$ and $t$. This leads to solutions for $t$ given by

$$t = 0 \text{ and } t^2 = \frac{2A_s\mu^2 + \Delta}{2A_s\mu^2 - \Delta}$$

(16)

which shows that additional real solutions are possible when $2A_s\mu^2 > \Delta$. Those solutions give rise to a finite ground state dipole moment:

$$\mu_g = \pm \mu \sqrt{1 - \frac{\Delta}{2A_s\mu^2}}$$

(17)

This implies that the quantum system can acquire a ground state dipole moment if the interaction between the 2LS and polarizable solvent is large enough. This is not possible classically: the only solution of $\mu = aE$ together with $E = A_s\mu$ is $\mu = E = 0$. In Fig. 2 on the right I show the free energy curves based on minimizing $G$ with respect to $t$. For small values of $A_s$ there is only a minimum at $\mu_g = 0$, but for larger values of $A_s$ minima occur at the finite ground state dipole moments given by Eq. (17). For those values the higher energy of the ground state $|g\rangle$ is offset by the lower energy due to interaction with the environment $-\mu^2_g A_s$.

As far as I know, no theory of dielectrics was formulated on the basis of this model system.

3. Dynamics of Interaction between Quantum Systems and Classical Fields.

Although the description of the interaction between classical and quantum system does not lead to obvious problems or inconsistencies, the same is not true for its dynamical extension. As indicated in Sec. 1 classical interaction leads to a consistent picture for the dynamics of the subsystem: it experiences a potential of mean force due to equilibrium fluctuations, and friction
due to solvent relaxation. The interaction, as used for instance in QM/MM approaches to mixed
dynamics, is similar to the one described in the previous section. The quantum system ‘feels’
the electric field due to the classical environment, whereas the environment experiences the
expectation value of a quantum operator it is coupled to. Since the final equilibrium state
is a mixed quantum state, it is mandatory to use the density operator formalism for this
description[16], so we are led to the following equation for the density operator of the 2LS:

$$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar}[H_0, \rho] - \frac{i}{\hbar}[\hat{\mu}, \rho]E(t) \quad (18)$$

In this case I consider the electric field $E(t)$, due to the outside polarization to be overdamped,
so that it satisfies an equation similar to Eq. (2):

$$\frac{dE}{dt} = -E - A \langle \hat{\mu} \rangle \tau_D \quad (19)$$

where $\langle \hat{\mu} \rangle = \text{Tr}[\hat{\mu} \rho]$. This latter condition and the second term in Eq. (?? makes the equations
nonlinear in a rather complicated way. As in the classical situation, the equation of motion for
the density operator is undamped, and it can be hoped that coupling to the damped equation
of motion for the $E$–field would lead to decay of the density matrix to the ground state, or even
to the equilibrium state if random fields with the correct properties are added to Eq. (19). This
does not happen. Here just two numerically calculated traces for different initial conditions are
presented. These indicate that none of the expected behavior occurs, and in fact show behavior
seen in many non–linear systems.

![Figure 3](image)

**Figure 3.** Two simulations of Eqs. (18) and (19) above the bifurcation threshold (*cf.* Fig. 2),
with equal values of coupling– and dissipative constants, but with different initial conditions for
the coherence of the density matrix. On the left hand side the coherence starts out at a finite
value, and the ground state dipole moment (propoerntional to the real part of the coherence $\rho_{01}$)
and external field go to finite values. On the right hand side all initial conditions are the same,
except that we start the coherence at 0. In that case both external field and expectation value
of the dipole operator go to zero, which according to the results of the previous section should
be a maximum in the free energy.

The behavior of the solutions is sensitively dependent on the initial conditions, which is often
the case for non–linear equations[17], and also on parameter values. A full analysis of these,
and similar, equations will be submitted elsewhere. They show in general complicated behavior,
completely at variance with the similar simple classical models referred to in the first section. Since the methodology presented here is used in many QM/MM papers, where many other issues complicate the results — in particular the way classical and quantum systems are separated, and the presence of many simultaneously coupled modes of motion — so that the problems found in these simple models are obscured.

The equations of motion described above can be derived from a mixed classical–quantum mechanical Liouville equation[16], with the classical part extended to a Fokker–Planck equation[10] in the high friction limit[4]. It was pointed out that such a mixed description leads to fundamental problems and inconsistencies[18]. The example given here shows that these inconsistencies have unpredictable consequences for the solutions. The fundamental problem lies in the fact that classical phase space and quantum mechanical Hilbert spaces cannot be embedded in a single mathematical structure in which both can coexist, and where proper limits can be taken.

4. Concluding remarks.
Simple systems, in particular the ones based on Onsager’s dipole in a cavity model, played an important role in understanding the influence of solvent dynamics in solution reactions. The advantage of such a model is clear: in many cases analytical results are possible and fundamental properties can be derived that give fundamental insight in the behavior of systems embedded in a polarizable solvent. Unfortunately these results are restricted to classical interactions. No systematic study appears to have been made for mixed classical–quantum interaction for similar simple systems, and the results derived in this paper point to numerous fundamental problems with this approach. These problems are caused by an imperfect understanding of how a classical system interacts with a quantum system, and so far our simple models give a clear indication of limitations of common approaches used in quantum chemistry and QM/MM methodology.

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