Quantum Theory of Solvation

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In the path integral representation of quantum theory, the behavior of quanatal degrees of freedom is isomorphic with the equilibrium statistical behavior of fluctuating classical species. Thus, the quantum theory of solvation is isomorphic with the classical theory of solvation for flexible compounds. This article reviews this powerful and unifying perspective. The principles of cavity distribution functions central to the classical theory are discussed, and the connection is described between these functions and influence functionals used in quantum theory to describe the effect of a surrounding medium on a quantum-mechanical system. Several applications both classical and quanatal are reviewed including conformational equilibria in liquids, quantum polarization fluctuations, tunneling in liquids, and the behavior of excess solvated electrons.

I. Introduction

The effects of liquid environments on the behavior of solute particles play a central role in chemical and biological phenomena. Examples include the conformational structures of flexible compounds such as biopolymers, the solvent shifts of chemical equilibria, and the states of solvated electrons. The first of these examples can often be analyzed in terms classical statistical mechanics while the third requires a quantum-mechanical treatment. During the past few years a unified theoretical approach has evolved with which all of these processes can be treated in a similar fashion. This article describes this approach.

The classical theory of conformational and chemical equilibria in condensed phases is based upon the observation that the solvent effects are properly described with a class of correlation functions called cavity distribution functions. The first formal derivation of this fact1 employed a cluster diagrammatic analysis. In section II, we review an alternative physical derivation drawing upon familiar reversible work principles of equilibrium statistical mechanics. The computation of cavity distribution functions, both with computer simulations and with analytical theory, has led to the first systematic treatments of fluctuating species in solution. Some examples of these applications are described in section II.

The classical theory provides necessary background for understanding the more general quantum-mechanical treatment discussed in section III. The treatment is based upon Feynman's path integral formulation of quantum theory.2 The formulation allows one to map the behavior of quanatal degrees of freedom onto the statistical mechanics of classical flexible compounds. As we will see, this result means that the same techniques developed to treat conformational equilibria in solution, such as the computational techniques for cavity distribution functions, can also be applied to treat quantum processes in solution.4 Indeed, the cavity distribution function is isomorphic to Feynman's influence functional, the object which describes the effect of a surrounding medium on quanatal degrees of freedom. The connection is discussed in section III, and examples are provided to illustrate the power of this approach. Included are descriptions of a quantum theory of polarization in fluids, a simulation of an excess electron dissolved in a fluid, and the qualitative effects of liquid environments on tunneling and localization. The discussion is a self-contained tutorial introducing the reader to a powerful methodology that I believe will soon become a ubiquitous theoretical tool in chemistry.


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II. Chemical Equilibria and the Internal Structures of Classical Molecules in Liquids

Reversible Work Theorem and the Cavity Particles. To begin our discussion, consider the reduced distribution function, $p_0(r_1, ..., r_n)$, for a few, $n$, degrees of freedom or particles in a classical many-body system. (We will often use the words "degrees of freedom" and "particles" interchangeably.) The reduced distribution function is obtained by integrating out all the degrees of freedom except those tagged by our considerations. With this definition and the canonical distribution law, it is easily established that

$$\frac{\partial}{\partial r_i} [k_B T \ln \rho_0(r_1, ..., r_n)] = F_i(r_1, ..., r_n) \quad (2.1)$$

where $k_B T$ is Boltzmann's constant times temperature and $F_i(r_1, ..., r_n)$ is the force on particle $i$ averaged over the configurations of all the particles except $1, ..., i, ..., n$, which are fixed at positions $r_1, ..., r_{i-1}, r_{i+1}, ..., r_n$, respectively. That is

$$F_i(r_1, ..., r_n) = -\frac{\partial}{\partial r_i} \ln \rho_0(r_1, ..., r_n) \quad (2.2)$$

where "PE" denotes the total potential energy of the system.

The most familiar example of this result is concerned with the radial distribution function, $g(r)$, for a pair of particles in a fluid. In the usual definition, $\rho g(r)$ is the average density of atoms at $r$ given another is at the origin and $\rho = (N)/V$ is the average number of particles per unit volume. According to (2.1)

$$\frac{\partial}{\partial r} k_B T \ln g(r) = \text{solvent-averaged force between a pair of tagged particles held fixed at a separation $r$} \quad (2.3)$$

The word "solvent" as used here means all the atoms in the liquid except those that are tagged.

We can integrate this equation using the boundary condition $g(r) = 1$ to obtain

$$-k_B T \ln g(r) = \text{reversible work required to bring a pair of particles from infinite separation in the solvent to a relative separation $r$} \quad (2.4)$$

When the thermodynamic variables $T$, $\rho$, and $V$ are used to characterize the state of the system, the reversible work is a change in Helmholtz free energy. Part of this energy is the direct potential of interaction, $w(r)$, between the pair of tagged particles. Let us factor this contribution out to form

$$w(r) = -k_B T \ln g(r) = u(r) + \Delta w(r) \quad (2.5)$$

The function $w(r)$ is often called the potential of mean force. The solvent contribution to it, $\Delta w(r)$, is the change in Helmholtz free energy of the solvent for a process in which a pair of atoms are initially far apart and are finally separated by a distance $r$. This identification is equivalent to saying that, within an additive constant, $\Delta w(r)$ is the chemical potential of a tagged pair of particles constrained in the fluid to a configuration with pair separation $r$.

The Boltzmann factor of $\Delta w(r)$

$$y(r) = \exp[+\beta \Delta w(r)] = \exp[-\beta \Delta w(r)] \quad (2.6)$$

is itself a distribution function. To understand this fact, it is necessary to introduce the concept of a cavity particle. These are hypothetical particles or degrees of freedom which are nearly identical with real particles or degrees of freedom. Cavities are distinguished solely by the fact that they do not interact with each other. However, cavities interact with real particles just as if cavities were real particles. Thus, the reversible work to bring two cavity particles to a relative separation of $r$ when they are initially infinitely far apart is entirely $\Delta w(r)$. As a result, the arguments which imply that $-k_B T \ln g(r) = w(r)$ lead to the conclusion that

The extension of these ideas to multicomponent systems is not difficult. For example

$$y_{AA}(r) = \exp[+\beta u_{AA}(r)] \quad g_{AA}(r) \quad (2.7)$$

is the pair distribution function for two cavity particles, one associated with a particle of type A and the other with a particle of type A', dissolved at infinite dilution in a liquid solvent. The solvent can be composed of many different types of species including A and A' particles (but not A and A' cavity particles).

As an illustrative example, let us compute $y_{AA}(r)$ for $r < (\sigma - \sigma')/2$ when particles A and A' are hard spheres of diameter $\sigma$ and $\sigma'$, respectively, and $\sigma > \sigma'$. Such small separations are possible because cavity particles do not interact with each other even though these particular cavities interact with neighboring particles with hard-sphere repulsions. At points $r < (\sigma - \sigma')/2$, the A cavity particle completely envelopes the smaller A' cavity. Hence, as far as the solvent medium is concerned, the difference between configurations for which A and A' are separated by a large distance and those for which $r < (\sigma - \sigma')/2$ is that, in the former, both an A particle and an A' particle are dissolved in the liquid, while in the latter, the A' has disappeared. Thus, the reversible work in going from one configuration to the other is

$$\Delta w_{AA}(r) = -\Delta u_{AA}, \quad r < (\sigma - \sigma')/2 \quad (2.9)$$

where $\Delta u_{AA}$ is the excess chemical potential for a hard-sphere A' particle (not necessarily at infinite dilution) in the liquid solvent.

Thus

$$y_{AA}(r) = \exp[\beta \Delta u_{AA}], \quad r < (\sigma - \sigma')/2 \quad (2.10)$$

which is a result discussed by many authors.

Association and Conformational Equilibria. The real importance of these concepts to chemical phenomena becomes apparent when we consider a hypothetical association reaction

$$A + B \rightleftharpoons AB \quad (2.11)$$

where A and B are structureless spherical groups (or atoms). The reaction can occur in a gas or liquid solvent, and the concentration of reactants and products need not be very small. But to simplify our considerations, assume that once an A–B pair is chemically bound, these particular groups cannot bind to other A or B particles. They can only interact via intermolecular forces. In other words, the chemical bonding saturates at the dimer level.

In the dilute-gas phase, the equilibrium constant for the association reaction and the intramolecular distribution for the AB molecule are determined straightforwardly from the A–B chemical bond energy. The intramolecular potential $w_{AB}^{(0)}(r)$ denotes this energy as a function of the A–B separation, $r$, with $w_{AB}^{(0)}(r)$ taken as the zero of energy. The equilibrium constant we consider is defined as

$$K = \frac{\rho_{AB}}{\rho_A \rho_B} \quad (2.11)$$

where $\rho_M$ is the concentration or number density of species M. The gas-phase value for $K$ is the Boltzmann weighted sum over configurational states for the AB molecule. That is

$$K^{(0)} = \sum_{\alpha} \rho_{AB} H_{AB}^{(0)}(r) \exp[-\beta \Delta w_{AB}(r)] \quad (2.12)$$

where $\rho_{AB}$ is the symmetry number of the AB molecule and $H_{AB}(r)$ is the characteristic function for the AB molecule. In particular, $H_{AB}(r)$ is unity for those $r$ values which correspond to configurations we call an AB molecule; for other values of $r$, $H_{AB}(r)$ is zero.

The superscript "0" labeling $K$ in eq 2.12 indicates that the expression is appropriate to the dilute (ideal) gas. Similar considerations provide a formula for the gas-phase intramolecular distribution function of an AB molecule. In general, it is defined as


\[ s_{\text{AB}}(r) = \langle \delta(r - r_{\text{AB}}^0) + r_{\text{AB}}^0 \rangle \]

where the pointed brackets indicate the equilibrium ensemble average and \( r_{\text{AB}}^0 \) is the location of atom \( a \) in the tagged AB molecule. In the gas phase, the equilibrium average yields

\[ s_{\text{AB}}^0(r) = H_{\text{AB}}(r) \exp[-\beta W_{\text{AB}}(r)] / \int dx H_{\text{AB}}(x) \exp[-\beta W_{\text{AB}}(x)] \]

(2.13)

When the association reaction occurs in a dense medium, both the equilibrium constant and the intramolecular distribution function differ from those in the dilute gas. As far as the surrounding solvent molecule is concerned, an AB molecule can be regarded as two overlapping cavities, one of type \( \text{A}_a \) and the other of type \( \text{B}_b \), held together at a distance corresponding to a chemically bonded configuration. The reversible work (at constant concentration, volume, and temperature) to move cavity particles around in a solvent should then determine the effect of a condensed-phase environment on the intramolecular distribution. The work is \( \Delta w_{\text{AB}}(r) = -k_BT \ln y_{\text{AB}}(r) \), the potential of mean force between an \( \text{A}_a \) cavity and a \( \text{B}_b \) cavity immersed in infinite dilution in the actual system of interest. The total Helmholtz free energy change acquired by altering the separation of the A and B groups in a single AB molecule is the change in \( \Delta w_{\text{AB}}(r) \). Accordingly, \( s_{\text{AB}}(r) \) should be proportional to the Boltzmann factor for \( \Delta w_{\text{AB}}(r) \) or equivalently

\[ s_{\text{AB}}(r) = c s_{\text{AB}}^0(\tau) S_{\text{AB}}(r) \]  

(2.14)

where \( c \) is the normalization constant.

A similar reversible work argument can provide a relationship between \( \Delta w_{\text{A}}^0 \). To begin, assume that the A and B molecules are separated by a large distance. No change in energy is incurred by switching these particles into \( \text{A}_a \) and \( \text{B}_b \) cavities, respectively, since the cavities are separated by a great distance and they interact with the surrounding particles as if they are real particles. Now imagine converting these separated cavities into \( \text{A}_a \) and \( \text{B}_b \) cavities, respectively. The energy for this conversion will be negligibly because if the A and B groups appear to be the same (as far as intermolecular forces are concerned) whether they are bound in an AB molecule or exist as separated species. However, there are many conceivable systems where the similarity does not hold, and the reversible work for the conversion is

\[ (\Delta w_{\text{A}}^0 - \Delta w_{\text{A}}[\text{A}]) + (\Delta w_{\text{B}}^0 - \Delta w_{\text{B}}[\text{B}]) = k_BT \ln \left( \frac{Q_{\text{A}} Q_{\text{B}}}{Q_{\text{A}}[\text{A}] Q_{\text{B}}[\text{B}]} \right) \]

(2.15)

where \( \Delta w_{\text{A}}^0 \) is the interaction or excess chemical potential for a cavity particle of type \( \text{A}_a \) immersed at infinite dilution in the condensed medium which contains A, B, AB, and solvent molecules and \( Q_{\text{A}} Q_{\text{B}} \) is the Boltzmann factor for the change in these chemical potentials. Incidentally, the appearance of these \( Q \) factors is a consequence of our modeling the A and B particles as structureless species. When all relevant degrees of freedom are included explicitly in a model, all solvation energies are fully described by the potentials of mean force, and the \( Q \) factors will be unity.

Having created the \( \text{A}_a \) and \( \text{B}_b \) cavities, one may now imagine bringing these particles to a mutual separation \( r \) corresponding to a bonding configuration. The free energy change of the solvent due to this process is \( w_{\text{AB}}(r) \). Thus, the total reversible work to form the AB molecule from separated A and B particles is

\[ -k_BT \ln \left( \frac{Q_{\text{A}} Q_{\text{B}}}{Q_{\text{A}}[\text{A}] Q_{\text{B}}[\text{B}]} \right) + \Delta w_{\text{AB}}(r) + w_{\text{AB}}(r) \]

The Boltzmann factor for this energy can then be summed over bonding configurations to give the equilibrium constant. That is

\[ \tilde{K} = \text{FA}_a \int dr H_{\text{AB}}(r) \tilde{q}_{\text{A}}(r) \tilde{q}_{\text{B}}(r) \exp[-\beta \Delta w_{\text{AB}}(r)] = \tilde{K}_0 \tilde{q}_{\text{A}}(r) \tilde{q}_{\text{B}}(r) \int dr y_{\text{AB}}(r) s_{\text{AB}}(r) \]

(2.16)

Equations 2.14 and 2.16 show that the cavity distribution function, \( y_{\text{AB}}(r) \), plays the central role in determining the condensed-phase effects on chemical equilibria and intramolecular structures. As we have discussed, a cavity distribution function corresponds to the radial distribution, \( g(r) \), after the direct Boltzmann factor containing the pair interaction, \( w(r) \), has been removed from it. Direct (intramolecular) interactions are not present in \( y_{\text{AB}}(r) \) since intramolecular energetics are properly accounted for with \( s_{\text{AB}}^0(r) \) and \( K_0^0 \).

**Equivalent Mixture Model.** These results lead to an alternative, though necessarily equivalent, perspective. In particular, the solution containing the solutes A, B, and AB can be conceived of as an infinite-component mixture with A and B species and AB compounds for each value of AB separation, \( r \). The concentration of one of the latter is \( \rho_{\text{AB}} S_{\text{AB}}(r) \). Furthermore, it has been shown by Onsager's trick \( \text{(1)} \) where one may regard molecules of different orientations as being different species of a mixture. Hoyer and Still have successfully applied the mixture approach to a number of problems involving fluctuating species in condensed phases, \( \text{(2-3)} \) and one should bear in mind that, for the special cases they consider, their theory is fully equivalent to the treatment described herein.

**Generalizations.** The general results for both the equilibrium constant and the intramolecular distribution functions for arbitrarily complex species have the same form as eq 2.14 and 2.16. In these results, first derived by Pratt and this author, \( \text{(4)} \) an ideal-gas function (which contains all the information concerning the chemistry of the isolated species) is multiplied by a solvent term which is determined by the free energy changes incurred by rearranging cavity particles. For example, a flexible molecule with \( n \) particles or degrees of freedom has the intramolecular distribution

\[ s(r_1, \ldots, r_n) \leq s_{\text{AB}}(r_1, \ldots, r_n) y(r_1, \ldots, r_n) \]

(2.17)

where \(-k_BT \ln y(r_1, \ldots, r_n) = \Delta w(r_1, \ldots, r_n)\) is the excess chemical potential for the molecule when it is constrained to configuration \( r_1, \ldots, r_n \) and dissolved at infinite dilution in the liquid. When considering a molecule composed of only two spherical groups, the cavity distribution function appearing in the formulas is a pair (i.e., a two-point) correlation function. For more complete molecules, however, one must deal with multipoint functions as indicated in (2.17).

One might expect that the superposition approximation, \( \Delta w(r_1, \ldots, r_n) = \sum_j \Delta w(r_j) \), would provide a good estimate. If correct, the approximation reduces the calculation \( y(r_1, \ldots, r_n) \) to that of a pair correlation function—something for which reliable analytical theories are readily available. However, the superposition approximation is often not useful. The reason is that, for many configurations of a polyatomic compound, certain groups will shield others from the solvent. In such a configuration, the reversible work associated with changing the separation of a shielded pair will be different from that associated with a pair exposed to the solvent. In other words, the solvent-induced reversible work function for a given pair of groups in the compound depends upon the configuration of many other groups; that is, \( \Delta w(r_1, \ldots, r_n) \) is not pair decomposable.

This issue can be more than just a quantitative detail since the nonsuperimposability can account for several \( k_BT \) in free energies.\( \text{(7)} \) Fortunately, a practical method based upon the RISM


\( \text{(9)} \) Errors in the superposition approximation are largest when cavity particles are very close together. Such configurations are common when considering conformational equilibria since covalent radii are much smaller than van der Waals radii. A feeling for the typical size of errors is obtained by considering the example of three hard-sphere cavities in a configuration where two of them, say particles 2 and 3, are concentric. In the superposition approximation, \( \Delta w(r_1, r_2, r_3) \approx \Delta w[r_1, r_2] + \Delta w(r_2, r_3) \), whereas the exact expression (derived from the type of arguments which led us to (2.10)) is \( \Delta w[r_1, r_2, r_3] \approx \Delta w[r_1, r_2] + \Delta w[r_2, r_3] \). The error in \( \ln y(r_1, r_2, r_3) \) for this case is therefore \( -\beta \Delta w[r_1, r_2] \), and the value of \( -\beta \Delta w(r) \) can be several \( k_BT \) in a dense fluid where \( r \) corresponds to a covalent bond length.
theory\textsuperscript{10} has been devised for estimating multipoint correlation function.\textsuperscript{11,12} This procedure should play a useful role in analytical theories for cavity distribution functions.

Another complication should also be noted. The cavity distribution function, \( s_{AB}(r) \), is a functional of \( s_{AB}(r) \) (unless the system contains the species A, B, and AB only at very low concentrations). As a result, eq. 2.14 and its generalizations to more complex systems are actually a self-consistent equation. This important feature of the theory will be illustrated in the discussion of liquid polarization given in one of the examples below.

**Example: n-Butane in a Liquid.** The trans-gauche equilibrium of the \( n \)-butane molecule pictured in Figure 1 provides an example of the ideas we have been describing. By neglecting small-amplitude vibrations, we can assume that the dihedral angle \( \phi \) is the only appreciable internal degree of freedom. As a result

\[
\phi = \phi_0(\phi) + \gamma(\phi) \quad (2.18)
\]

where \( \gamma(\phi) \) is the cavity distribution function associated with reversibly changing the \( \phi \) of a single \( n \)-butane molecule in a solvent. One may compute this function from computer simulations since according to its definition

\[
\gamma(\phi) = (\delta(\phi - \phi_0))' \quad (2.19)
\]

where \( \phi \) is the instantaneous dihedral angle (a function of the atomic coordinates) of the tagged molecule and \( (...)' \) denotes the ensemble average performed with the intramolecular potential \( V(\phi) \) absent from the tagged molecule. A simulation of this sort was reported by Jorgensen\textsuperscript{13} for the case of \( n \)-butane dissolved in water. These results are shown in Figure 2. It is seen that the aqueous solvent shifts the equilibrium toward the gauche conformation, confirming the predictions of the Pratt–Chandler theory of the hydrophobic effect.\textsuperscript{12b}

The removal of the potential \( V(\phi) \) in the simulation calculation of \( \gamma(\phi) \) allows the trajectory to sample all values of \( \phi \) relatively freely, unhindered by the potential barriers which separate the trans and gauche conformers in the actual system of interest. Simulations in which potentials involving only tagged degrees of freedom are removed (or more generally, altered) are called simulations with umbrella sampling.\textsuperscript{13} While citing these interesting calculations, a word of caution is in order. Proper statistical sampling of all \( \phi \) values with umbrella sampling requires very long trajectories. This point seems well appreciated by Berne and co-workers,\textsuperscript{14} who performed the first computer simulation determinations of \( \gamma(\phi) \). Others\textsuperscript{15,16} have returned to the simple model system studied by the Berne group, and in one case,\textsuperscript{17} presumably poor statistics inhibited verification of the Berne results, while in the other,\textsuperscript{18} long runs and additional umbrella sampling tricks gave results in accord with Berne’s.

**Example: Polarization in Liquids.** The polarizability of an atom is a manifestation of the internal structure of an atom, in particular the fluctuations in the charge distribution. The effect of a liquid environment on the polarizability of an atom provides another helpful illustration of the ideas we have described above.

For the time being, we will persist with a classical description even though we know that the charge fluctuations within an atom are surely quantum mechanical in nature.

The model we adopt for the intramolecular charge distribution is the often-used Drude oscillator for which the dipole of the \( i \)th atom, \( m_i = e \zeta_i \cdot B_i \), is harmonically and isotropically bounded to the center of the \( \delta \)th atom, and the linear restoring force constant is \( \omega_0^{-1} \), where \( \omega_0 \) is the polarizability of the unperturbed atom. One may compute the polarizability by monitoring the average induced dipole as a function of an applied electric field or equivalently (from linear response theory) by computing \( \langle m_i^2 \rangle \). Indeed, in the classical case

\[
\langle m_i^2 \rangle = 3 \alpha / \beta \quad (2.20)
\]

While eq. 2.20 is a general result, the reader may find it instructive to check this result in the ideal-gas (unperturbed atom) limit where

\[
\langle m_i^2 \rangle = \int \frac{\sin^2 \theta}{\theta^2} d\theta \quad (2.21)
\]

To assess the role of a condensed phase, we assume that the interactions in the system are given by

\[
U = U_0 - \sum_{\delta \neq \delta'} m_{\delta}(T_{\delta}(R_{\delta}) \cdot R_{\delta'}) \quad (2.22)
\]

where \( T(R) \) is the dipole tensor, \( \nabla \cdot (1/R) \), \( R_i \) is the location of atom \( i \), and \( U_0 = U_0(R_{\delta}, \ldots, R_{\delta'}) \) is a sum of short-ranged interactions, perhaps hard-sphere repulsions. In this model, the instantaneous charge distributions within each atom couple to all the others through dipole–dipole interactions.

The effect of this coupling on the internal structure of a tagged atom is determined by the cavity distribution function, \( \gamma(m) \), through

\[
\gamma(m) = \int \frac{e^{-\delta m^2 / 2 \omega_0}}{\sqrt{2\pi \omega_0}} dm \quad (2.23)
\]

The quantity \( -\delta^{-1} \ln \gamma(m) \) is the chemical potential for one of the atoms when it is constrained, in the fluctuating equilibrium fluid, to have a dipole moment of magnitude \( m \). Mean-field theories and many integral equation theories predict that the chemical potential for such a species is proportional to \( m^2 \). The basis of this prediction is that the dipole \( m \) induces a polarization field proportional to \( m \), and this field couples with the dipole leading


to a solvation energy proportional to the field times the dipole. Thus, we write

$$y(m) = e^{\beta\beta_m}$$  (2.24)

where $E$ depends upon the average properties of the solvent, indeed upon $(m^2)$. One may show that the quantity $-m^1E(m^2)$ is the dipolar part of the internal energy per particle of a one-component classical system composed of nonpolarizable molecules with permanent dipole moment $m$. By combining eq 2.20, 2.22, and 2.24, we obtain a formula expressing the solvent renormalization of the atomic polarizability:

$$\alpha = \alpha_0/[1 - 2\alpha_0E(3\alpha/\beta)]$$  (2.25)

This result, first obtained by Pratt on the basis of the theory outlined here, is closely related to Wertheim's renormalized theory of polarizable fluids. Pratt used his theory to successfully interpret the electric field near a polar species dissolved in a polarizable fluid. These specific numerical results could equally well have been obtained with Wertheim's theory employing his “single-supercellen” approximation. The advantage of the Pratt theory, however, is that it is generalizable, leading naturally to a quantum theory of polarization. The Wertheim theory, on the other hand, is based upon the traditional Kirkwood–Yvon model of polarization which avoids any statements concerning the molecular origin of polarizability—the intramolecular charge fluctuations. Without any such statements, there is no way the fluctuations can be quantized.

III. Quantum Processes in Liquids

We now consider the treatment of quantal degrees of freedom in liquids exploiting the isomorphism between quantum theory and classical chemical equilibrium. This isomorphism is based upon Feynman's path integral formulation of quantum mechanics. A most useful introduction is given in Chapter 3 of Feynman's "Statistical Mechanics" (but look out for typographical errors).

**Isomorphism.** By suitable differentiations, all observable properties can be obtained from the partition function

$$Q = Tr e^{\beta H} = \int dx\, (x|e^{-\beta H}\rangle x) \quad \beta^{-1} = k_B T$$  (3.1)

where $H$ is the Hamiltonian operator, and in the second equality, we have chosen the configurational representation of states (x denotes a point in configuration space). The Hamiltonian has an unperturbed part, $H_0$, and a potential energy interaction part, $V$.

We may factor this trace of the Boltzmann operator as follows:

$$Q = |\langle x^{(0)}|\cdots|x^{(N)}\rangle|^2$$

$$\int dx^{(1)} dx^{(2)} dx^{(3)} dx^{(4)} \cdots dx^{(N)}\langle x^{(1)}|e^{-\beta H_0}\rangle \langle x^{(2)}|e^{-\beta H_0}\rangle \cdots \langle x^{(N)}|e^{-\beta H_0}\rangle$$  (3.2)

where $\epsilon = \beta/P$. For small enough values of $\epsilon$ (i.e., large enough $P$)

$$e^{i\epsilon(H_+e)} = e^{-\epsilon H_0}e^{\Delta P} [1 + O(\epsilon^2)]$$

Hence

$$\langle x|e^{-\beta H}|x\rangle \sim \rho_0(x,x';\epsilon)e^{-i\epsilon V(x)} \quad \text{small}$$  (3.3)

where $\rho_0(x,x';\epsilon)$ is the unperturbed density matrix, $\langle x|\exp(-\epsilon H_0)|x\rangle$. As a result

$$Q = \int dx^{(1)} \cdots dx^{(N)} \prod_{i=1}^{N} \rho_0(x^{(i)},x^{(i+1)};\epsilon)e^{-iV(x^{(i)})}$$  (3.4)

with $x^{(N+1)} = x^{(1)}$. Equation 3.4 for the quantum partition function looks very similar to a classical partition function for cyclic polymers.

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The radial distribution function between the electron and the positive ion in molten KCl at $T = 1400$ K. The points are from a molecular dynamics simulation employing the isomorphic polymer to represent the electron (ref 19), and a smooth line is drawn through the points as a visual aid. The electron interacts with the K$^+$ particles with a Shaw pseudopotential, a Coulomb repulsion is used for the interaction between the electron and the Cl$^-$ ion, and the ion–ion interactions are of the usual Born–Mayer type. Calculations with $P = 100$ or 200 agree for this system within statistical uncertainties.

In Figure 4. At the temperature of 1400 K, the unperturbed electron polymer forms a region of diameter $(\beta h/\vert m\vert)^{1/2} = 10$ Å. In the liquid, however, it becomes localized, taking on a size of between 2 and 3 Å, the diameter of a negative solvent ion in this system. This observation was readily established with a modest simulation. Consistency checks showed that only $P = 100$ or 200 is required to properly model the $P \to \infty$ limit in this system. Hence, the simulation required only a few hundred particles, total, to describe the entire electron plus liquid system. If the system was at a lower temperature or if the electron was delocalized or extended (as does happen in some fluids), the simulation would become much more time-consuming than it is for this case. Nevertheless, this simulation documents the outstanding power of the isomorphism. A statistically meaningful calculation of a solvated electron by more traditional methods such as the Schrödinger algorithm would be impossibly time-consuming even on the most powerful computers.

Influencing Functionals and Cavity Distribution Functions. Let us now consider the nature by which a solvent influences a quantum-mechanical solute from a less computationally intensive perspective. The isomorphism between the behavior of a quantal degree of freedom and that of a classical flexible polymer allows us to treat the effects of a solvent environment with the cavity distribution functions. Each different possible path of the quantal degree of freedom corresponds to a different instantaneous structure of the isomorphic classical compound. The different structures or configurations perturb the surrounding solvent in different ways. In the isomorphism, we know from the previous section that the Boltzmann factor for the reversible work done on the solvent to accommodate each different configuration will determine the statistical weight of the quantal degree of freedom. That is

$$s^{(1)}(r^{(1)}...r^{(P)}) = s^0\{s^{(1)}(r^{(1)}...r^{(P)}) \exp[-(1/P)\Delta\omega(r^{(1)}...r^{(P)})]\}$$  

(3.7)

where $s^0$ is the position of the ath site for the tagged isomorphic polymer, $s^{(1)}(r^{(1)}...r^{(P)})$ and $s^0$ refer to the probabilities of a path interacting and not interacting with the solvent, respectively, and $\Delta\omega(r^{(1)}...r^{(P)})$ is the reversible work of which the Boltzmann factor is the cavity distribution function. This cavity distribution function is also known as the influence functional since it describes the influence of the environment on the tagged degrees of freedom. Notice that it depends only on the solvent and the interactions between the tagged solute and the solvent. The cavity distribution function or influence functional is independent, however, of the internal structure of the isomorphic polymer (i.e., the quantum dynamics of the solute). Thus, the cavity distribution function is to a significant extent transferable from one system to another. Statistical-mechanical problems still remain due to the many-body nature of the isomorphic polymer, but these problems are often of a traditional statistical-mechanical nature and can be treated by standard techniques. Cavity distribution functions by themselves can be obtained via integral equation theories (as illustrated below) and by simulations. They can also be estimated with the aid of empirical information about the solvent. The first discussion of the isomorphism between influence functionals and cavity distribution functions was given in ref 4, and more details can be found there.

Time Dependence and Correlation Functions. The Boltzmann factor, $\exp[-\beta\Delta H]$, differs from the propagator $\exp[-i\Delta t/H]$ only inasmuch as temperature is usually regarded as a real number. The factor $\exp[-\beta\Delta H]$ propagates states in the imaginary-time interval between 0 and $\beta\Delta t$. Thus, each site on the isomorphic polymer represents the quantum particle at a particular (imaginary) time. The pair correlations between different sites on a targeted polymer are therefore correlations between a particle and itself at other points in (imaginary) time. The nature of these correlations for imaginary time tells us about the role of quantum dispersion. A disturbance at one point on the polymer affects another section of the polymer. In the ordinary Schrödinger view of quantum mechanics, this occurs because an external disturbance impinging on one point in space affects the particle at other points since the Schrödinger wave functions have finite widths.

If we are sufficiently bold, and it can be shown that it is proper to be so, we can analytically continue these imaginary-time correlation functions to real times. When this is done, we learn how to study real-time dynamical phenomena from the isomorphism with classical equilibrium statistical mechanics of polymers. Examples are mentioned later.

Exchange. For the sake of simplicity, we have not discussed the nature of particle indistinguishability. An analysis has been carried out, however, which shows the indistinguishability of particles is manifest in the isomorphism by the existence of ring dimers, trimers, etc. Exchange processes are isomorphic to classical association equilibria and obey a law of mass action identical with the equations governing the principles of classical chemical equilibrium.

Example: Quantized Polarizable Solvent. As a concrete illustration of these ideas, we return to the Drude model of a polarizable liquid discussed in section II, and we generalize Pratt’s classical theory to describe the quantization of this model. To begin, we express the unperturbed dipole path distribution function, $s^0(m(t)...m(t))$, in the $P \to \infty$ limit. Since $P_0 = \beta$ remains finite, the discrete points on the polymer form a continuum in the $P \to \infty$ limit, and one can show that

$$\langle m(t) \rangle = \exp(-1/\hbar) \int_0^{\hbar t} dt \{ m(t')/(2\alpha t') + m(t)/(2\alpha) \}$$  

(3.8)

where the function $m(t)$ for $0 < t < \beta$ describes the continuum of points on the polymer. Because the isomorphic polymer is cyclic, i.e., $m(t)$ is periodic with period $\beta$, $m(t)$ can be represented in a discrete Fourier series:

$$m(t) = \sum_{n=-\infty}^{\infty} A_n e^{i\Omega_n t}, \quad \Omega_n = 2\pi n/\beta\hbar$$  

(3.9)

This representation of $m(t)$ diagonalizes the functional in (3.8), and thus each Fourier component is statistically independent. The integral equation or reaction field theories leading to eq 2.24 in the classical case will produce a quadratic functional for $\Delta\omega(m(t))$. That is, the response of the solvent is treated as if it were linear. As we did in the classical theory, we shall adopt this approximation for the quantum-mechanical theory too. Thus, the influence functional, $\exp[-\beta\Delta\omega(m(t))]$, is then a Gaussian in $m(t)$ which is diagonalized with the Fourier components $A_n$. These components are therefore independent modes in the theory, and the cavity distribution function for $A_n$ can be calculated as in the classical case. It is

$$y(A_n) = \exp[\beta A_n^2 E_n]$$  

(3.10)

where $E_n = E[2A_n(\Omega_n)/\beta]$, defined in the previous section, gives the reaction field exerted by the solvent on a dipole when the
solvent is made up of classical Drude oscillators with polarizability \( \alpha(\Omega) \). Here, \( \alpha(\Omega) \) is determined self-consistently (see eq 2.25)

\[
\alpha(\Omega) = \frac{\alpha_0(\Omega)}{1 - 2\sigma_0(\Omega)E_0} = \frac{\beta}{3} (\Delta \mu(0))^{2}
\]

(3.11)

where \( \Delta \mu(0) \) refers to the root-mean-square value of the \( n \)th Fourier component of an atomic dipole in the fluid. Unlike traditional continuum reaction field theories, eq 3.11 accounts for solvent structure through the use of integral equation estimates of \( 2E(\Omega) \).

The analysis sketched above can also be applied to calculate the excess chemical potential (i.e., solvation free energy):

\[
\beta \Delta \mu = \beta \Delta \mu_{\text{classical}} + \sum_{\alpha=1}^{N} \ln \left(1 - 2\sigma_0(\Omega)E_0\right)
\]

(3.12)

See ref 21 for details. Expansion of the logarithm in (3.12) shows that this result is closely approximated by the pairwise sum of London dispersion forces provided the polarizability is small. For highly polarizable species, however, eq 3.12 can differ substantially from this perturbation theory result, and nonpairwise additivity is evident.

Because of the decomposition of modes in this theory for the Drude oscillator, the interactions of the quanl Drude solvent with a sluggish polarizable solute (i.e., one with small \( \omega_m \)) through a classical dipole or a classical charged solute would all be the same as it would be if the Drude solvent were classical.

As mentioned earlier, the similarity of the time propagator and the Boltzmann factor makes it possible also to obtain dynamic properties by analytic continuation. This has been done for this model by analytic continuation. In particular, \( \alpha(\Omega) \) is the Fourier transform of the dipole response function in imaginary time. The Fourier transform of the real-time response function corresponds to \( \alpha(z) \), where \( z = \omega + i\epsilon \) and \( \epsilon \to 0^+ \). (Some care must be taken in identifying the unique physically appropriate choice in this continuation.) The real-time response function determines time convolution functions and absorption spectra through the fluctuation–dissipation theorem. Thus, the condensed-phase alteration of spectra can be determined. Such an analysis and comparison with experiment have been carried out for the quantized Drude model solvent.

Example: Solvation of Tunneling Systems. The theory of tunneling in condensed phases is important as the passage of an electron or proton between two potential wells is an essential feature of many chemical phenomena. As a concrete example, one might consider the electronic states of a mixed-valence compound. The behavior of the classically isomorphic polymer in such a system is illustrated in Figure 5. Configurations corresponding to paths with tunnelling are configurations which possess kinks passing from one well to the other. If the barrier between the wells is high, the kinks (i.e., the crossing events) will be nearly statistically independent, and one can think of the problem in terms of a gas of these objects. The quantum-mechanical matrix element that gives the probability amplitude for tunneling is then the fugacity for forming a kink.

When immersed in a solvent, the behavior of the tunneling system is altered. The cavity distribution function or influence functional which describes this alteration introduces nonnearest-neighbor long-range bonds between the particles on the isomorphic polymer. To model the influence functional, note that the dipole of the tunneling system fluctuates and changes sign as the quanl particle moves from one well to the other. Thus, if we use an influence functional appropriate to a dielectric solvent, such as the Drude model above, the solvent-induced-long-ranged bonds will tend to stabilize localized configurations since these have larger dipole moments than those that are delocalized corresponding to tunneling or resonance configurations.

Several groups have considered a simple two-state model to study this phenomena—the promotion of intramolecular localization and the inhibition of tunneling or resonance configurations by a fluctuating bath. In the model, the configurational state of an electron in any time interval is specified by whether the electron is in the left or right well. The configurational states then differ only by the sign of their dipoles, \( \Delta \mu \). It is an analogue of the tight-binding or LCAO model used in quantum chemistry. The instantaneous dipoles are then coupled to the electric field of the bath, \( \delta \), with the standard interaction \( -\mu \delta \). The field fluctuates and is specified statistically by Gaussian distribution with a given (time-dependent) variance.

Remarkably, this model—a two-state system linearly coupled to a Gaussian bath—is isomorphic to a one-dimensional Ising magnet with long-range interactions (26) The analyses of the model, employing a variety of different techniques including Monte Carlo and renormalization group, have shown that tunneling and solvation are competing effects for quantum systems in condensed phases. Indeed, under certain circumstances, the tendency of a fluctuating (i.e., polarizable) medium to locate the electron (i.e., stabilize the dipole) can lead to phase transition behavior isomorphic to the ordering of spins by long-ranged interactions in the Ising system.

Summary. The isomorphism between quantum theory and classical equilibrium statistical mechanics has led to new perspectives and new computational procedures for analyzing these phenomena.

Feynman introduced the ideas of path integrals and influence functionals more than 30 years ago, and he used the ideas to solve several important problems including his successful treatment of quantum electrodynamics, his theory of slow electrons in solids (the polaron problem), and his analysis of quantized liquid helium. The approach fell from popularity, however, resurfacing on occasion, for example, in the development of semiclassical theories of scattering. But these applications were limited by severe constraints on the homogeneity and simplicity of the systems.


approximations, and the true renaissance did not begin until the mid 1970s. Naturally, it coincided with the modern revolution in statistical mechanics—the discovery of the renormalization group procedure, the development of efficient Monte Carlo schemes, and the wide availability of computers with which to perform these calculations. These techniques provide a variety of methods by which one can for the first time successfully treat nonlinear classical statistical-mechanics problems. By exploiting the isomorphism which arises from the path integral formulation, the new techniques provide methods for approaching classes of quantum phenomena that could not be treated before.

Physicists have begun applying the path integral methods with Monte Carlo and renormalization group calculations to solve a number of problems in particle physics. Progressing in a different direction, the recent research reviewed herein has exploited the advances in the modern statistical-mechanical theories of the liquid state and has extended Feynman’s classical isomorphism in ways which make the methodology particularly useful to chemistry. Along with the work we have explicitly reviewed, the recent literature contains many more applications, and we list here a few of them: Thirumalai and Berne have described the analytic continuation of Monte Carlo simulation results to obtain time correlation functions, and they have tested it on some simple one-dimensional systems. Behrman et al. have presented a method for direct Monte Carlo evaluation of time correlation functions, and they have applied it to the simple two-state tunneling model described above. This application attempts to grapple with the fact that the weight functionals are not always positive for paths in real time (as opposed to the imaginary time 1/s encountered in equilibrium calculations). The feature of nonpositive weights is frequently referred to as the “alternating-weights problem”, which is also a stumbling block in treating by these methods many-body systems composed of fermions. This problem is thus present when considering condensed-phase effects on chemical bonding of many-electron molecules. A Monte Carlo method for handling such phenomena has been proposed by Chiles et al. and they illustrated their method with a primitive model for an influence functional. It remains to be seen whether their particular scheme will be useful with more realistic and quantitative treatments of the solvent and solvent-solute interactions.

Finally, we note that Logan has extended the quantum theory of the Drude oscillator solvent to include quadrupoles as well as dipoles. The extension provides a theory for collisional-induced dipolar spectra, but no test of the theory has yet been made. Thus, the applications are still at an early stage, but it is already clear that in the hands of an experienced practitioner of classical equilibrium statistical mechanics, the isomorphism provides a powerful tool for solving condensed-matter quantum problems. We may also anticipate that the isomorphism coupled with renormalization group–Monte Carlo techniques will soon alter the way we think about the electronic structure of molecules and provide sorely needed insights into the nature of chemical bonding.

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