Solvation dynamics in a Brownian dipole lattice: A comparison between theory and computer simulation

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Papazyan and Maroncelli [J. Chem. Phys. **95**, 9219 (1991)] recently reported computer simulations of solvation dynamics of an ion in a Brownian dipole lattice solvent. In the present article we compare these results to predictions of a number of theories of solvation dynamics in the diffusive limit. The frequency-dependent dielectric response functions needed as input to many of the theories are derived from further simulations of the lattice solvent [H. X. Zhou and B. Bagchi, J. Chem. Phys. **97**, 3610 (1992)]. When properly applied, all of the currently popular molecular theories yield reasonable predictions for the time scale of the solvation response. The dynamical MSA model [P. G. Wolynes, J. Chem. Phys. **86**, 5133 (1987)] and the memory function theory of Fried and Mukamel [J. Chem. Phys. **93**, 932 (1990)] both provide nearly quantitative agreement with all aspects of the solvation dynamics observed in these simulations.

I. INTRODUCTION

Considerable advances in our understanding of the dynamics of solvation in dense polar liquids have been made in recent years. Experiments, computer simulations, and theoretical studies have all played an important role in this advancement. Several reviews[1-6] provide an up-to-date summary of this and related research. Despite all of the recent progress, many aspects of solvation dynamics are still not fully understood. Theoretical treatment of dynamics in dense polar fluids is a formidable task and progress in this area therefore relies on approximate treatments of idealized model systems. The applicability of the theories developed in such a situation can only be tested through comparison to the results of experimental measurements and computer simulations. For example, both computer simulations[7] and the most recent experiments[8] have shown that solvation dynamics in a number of solvents is dominated by ultrafast inertial motions. Prior to the appearance of these results such underdamped motions had been neglected in theoretical treatments. More complete theories of solvation dynamics, capable of treating both the inertial and overdamped solvent motions, are only now being developed.[9,10] Due to the importance of the fastest parts of the solvation response to reaction dynamics, current attention has largely focused on the inertial aspect of the problem. However, our understanding of even the diffusive aspects of the dynamics has not been completely tested. Several alternative theories are presently available for predicting solvation in the overdamped limit. Although they have been compared to experimental results, intervention of possible effects due to inertial and translational dynamics make it difficult to use experiments to definitively choose between these theories.[1] Computer simulations of realistic fluids have also been of little help in this regard due to the prominence of the inertial component in all of the small-molecule solvents studied to date.

The objective of this paper is to present a comparison between computer simulations of solvation dynamics in a simple model dipolar "liquid" and predictions of current theories of ionic solvation in the overdamped limit. The solvent investigated here consists of an array of point dipoles fixed on the sites of a simple cubic lattice. Each dipole undergoes rotational Brownian motion in the force field of the rest of the lattice. Papazyan and Maroncelli[11] recently employed Brownian dynamics simulations to study the solvation of ionic solutes in this solvent and were able to obtain a rather complete characterization of the static and dynamic aspects of ionic solvation in these systems. However, comparison to theoretical predictions was limited by lack of knowledge of the dielectric response ($\epsilon(\omega)$) of the solvent, needed as input to many theories. The results of further simulations by Zhou and Bagchi[12] have provided $\epsilon(\omega)$ for these lattices so that a more detailed comparison with theory can now be undertaken. By virtue of the simplicity of the present solvent model, comparison to theoretical predictions provides a rather exacting test of the merits and deficiencies of currently available theories of solvation dynamics in the purely diffusive regime.

We include the following theories in the comparison: (a) The simple continuum (SC) model initially formulated by Bakshiev and co-workers[13] and later investigated by many authors.[14] In this model the solvent is assumed to be a homogeneous dielectric fluid so that the molecular nature of the solvent is completely neglected. Despite its obvious limitations, the continuum model has been shown to provide a good guide to experimentally determined solvation times in many liquids.[1,2] (b) The dynamical mean spherical approximation (DMSA) model introduced by Wolynes[15] and further developed by Rips, Klafter, and Jortner[16] and others.[17,18] (c) The Smoluchowski–Vlasov equation (SVE) theory first used by Calef and Wolynes[19]

and greatly extended by Chandra and Bagchi.[3,9,20] The latter authors reformulated the problem in the language of generalized hydrodynamics and time-dependent density functional theory. Here we investigate the predictions of the Markovian version of the Chandra–Bagchi theory as presented in Ref. 20, and refer to it as "SVE/CB." (d) The memory function theory of Fried and Mukamel[21] which, although in many respects is similar to the theory of Chandra and Bagchi, has certain advantages for practical purposes. We shall refer to this theory as "MF/FM." (e) Lastly, we consider the perturbative theory of solvation dynamics in the simple cubic lattice presented by Loring and Mukamel.[22] This theory is an extension of earlier work of Zwanzig[23] who developed the perturbation approach for dielectric relaxation in the Brownian dipolar lattice. Since it deals with precisely the system simulated, the comparison can provide a good test of the validity of the second order perturbation theory. We designate this theory "PE/LM."

All of the above theories along with their method of implementation will be discussed in more detail in Sec. III. For now it is useful to mention that they may be conceptually separated into two categories: the "ab initio" theories of Loring and Mukamel (PE/LM) and Chandra and Bagchi (SVE/CB) which are self-contained, and the "semiempirical" theories (SC, DMSA, and MF/FM) which require the frequency-dependent dielectric function $\epsilon(\omega)$ as input. In brief, the comparisons described herein yield the following results. As an ab initio theory, the SVE/CB theory does a remarkably good job of reproducing most aspects of the simulated dynamics at all polarities. In contrast, the PE/LM theory fares less favorably and is shown to have predictive value only at very low polarities. All of the semiempirical theories do a reasonable job of predicting the observed variation of solvation time scale with solvent polarity. The SC model predicts solvation times that are uniformly too fast and response functions that are closer to exponential than is the actual response. These shortcomings are remedied in the molecular DMSA and MF/FM theories, which reproduce the observed dynamics almost exactly.

The organization of the remainder of the paper is as follows. In the next section we briefly discuss the nature of the simulations involved. Both the simulations of ionic solvation[11] and the calculation of the frequency-dependent dielectric function[12] are discussed in more detail in separate publications, so that only the essentials required to make this article complete are included here. In Sec. III we collect the working expressions used to evaluate the predictions of all of the theories and also discuss the approximations that have been made in their implementation. In Sec. IV we present the comparison between the simulation results and the theoretical predictions. Finally, Sec. V contains a brief discussion of the conclusions possible from this study.

II. SIMULATION METHODS

A. Solvation dynamics

The systems studied by Papazyan and Maroncelli[11] consist of a single point charge (or hole) immersed in a lattice of point dipoles fixed to the sites of a simple cubic lattice. The dipoles undergo rotational Brownian motion in response to Markovian random forces (representing all nonelectrostatic interactions) and in response to forces due to electrostatic interactions among the dipoles and between the solvent dipoles and the solute charge. The time scale for the simulations is set by the free diffusion time, τ_0, defined by the single-particle reorientational time correlation function in the absence of electrostatic interactions,

$$\langle \boldsymbol{\mu}(0)\cdot\boldsymbol{\mu}(t)\rangle = \mu^2 \exp(-t/\tau_0), \tag{1}$$

where $\boldsymbol{\mu}$ is the dipole moment vector. When electrostatic interactions are turned on, the rotational dynamics become more complex than the exponential decay of Eq. (1). In general, the single particle reorientation becomes slower (and solvation faster) as the magnitude of the electrostatic coupling (solvent polarity) is increased. All properties of the pure lattice solvent are a function of a single dimensionless polarity parameter η defined by

$$\eta = \frac{\mu^2}{3k_B T a^3}. \tag{2}$$

In the above definition, $k_B T$ is Boltzmann's constant times the absolute temperature and a is the lattice constant.

The systems studied by Papazyan and Maroncelli[11] involve finite lattices of size $N = (2l+1)^3 = 27, 125, 343, 729,$ or 1331. A single solute with charge Q replaces the central dipole of the lattice. Papazyan and Maroncelli examined solvation as a function of all three variables η, Q, and N. In the present work we focus on the dependence of the solvation dynamics on solvent polarity and fix the other parameters at $Q=0$ and $N=343$. As discussed in Ref. 11 the solvation time does depend slightly on solute charge, becoming faster as Q increases. We chose $Q=0$ since this solute produces the least perturbation to the solvent and as such is the most directly comparable to the theories considered. The solvation dynamics was shown to have reached the $N \to \infty$ limit at a size of $N < 343$ so that it is appropriate to think of the simulated results as applying to bulk solvation.

The dynamics of interest is the change in solvation energy resulting from a step-function change in solute charge, $Q_i \to Q_f$. The time dependence of this process is conveniently expressed by the normalized response function,

$$S_{i\to f}(t) = \frac{\langle V(t)\rangle - \langle V(\infty)\rangle}{\langle V(0)\rangle - \langle V(\infty)\rangle}, \tag{3}$$

where $\langle V(t)\rangle$ is the average reaction potential (electrical potential at the solute charge site) at time t. (This response function can also be thought of as describing the relaxation of the solute–solvent interaction energy or the free energy difference between the two charge states.[1]) $S_{i\to f}(t)$ is a nonequilibrium response function. In computer simula-

tions, it is often more convenient to calculate the equilibrium time correlation function,

$$C_V(t) = \frac{\langle \delta V \delta V(t) \rangle_\alpha}{\langle \delta V^2 \rangle_\alpha}. \qquad (4)$$

In this expression δV is the fluctuation in reaction potential, $V - \langle V \rangle_\alpha$, and $\langle x \rangle_\alpha$ denotes the average value of x monitored in a system in equilibrium with a solute of charge Q_α. Under the assumption of a linear solvent response, applicable to the $\Delta Q \to 0$ limit, the equilibrium time correlation function derived from simulations of the two solute charge states $\alpha = i$ or f is identical to the nonequilibrium response function $S_{i \to f}(t)$. In this case the amplitude of the nonequilibrium response can also be calculated from $\langle \delta V^2 \rangle$ at either limit via

$$\langle \Delta V \rangle_{i \to f} \equiv [\langle V(0) \rangle - \langle V(\infty) \rangle]_{i \to f}$$

$$= (Q_f - Q_i) \frac{\langle \delta V^2 \rangle_\alpha}{k_B T}. \qquad (5)$$

Comparisons between $C_V(t)$ and $S_{i \to f}(t)$ for the dipole lattice show the linear response assumption to be a good approximation even up to $\Delta Q = 0.4e$.[11] In any event, the linear response assumption is inherent in all of the theories we consider. We therefore use Eqs. (4) and (5) and time correlation functions derived from simulations in the presence of an uncharged solute to make comparison to theory.

B. Dielectric response

The method employed for simulating the frequency-dependent dielectric function is based on the dielectric theory presented by McConnell.[24] We consider a spherical sample initially in equilibrium with a weak uniform electric field $\mathbf{E}$ that is suddenly switched off at time $t = 0$. Within the linear response regime, the decay of the total dipole moment of the spherical sample is related to the field by

$$\mathbf{M}(t) = b(t)\mathbf{E}(t=0). \qquad (6)$$

The coefficient $b(t)$ is called the after-effect function. Its Fourier transform defines the complex polarizability through the expression

$$\alpha(\omega) = -\int_0^\infty dt\, e^{i\omega t} \frac{db(t)}{dt}. \qquad (7)$$

For a uniformly polarized isotropic sphere, the frequency-dependent dielectric function $\epsilon(\omega)$ is related to the polarizability by the well-known relation

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{4\pi}{3V} \alpha(\omega), \qquad (8)$$

where V is the volume of the spherical sample.

Simulation of the dielectric function is accomplished through the following steps. We start with randomly oriented dipoles fixed at the lattice sites of a spherical sample of simple cubic lattice. Between 257 and 925 dipoles are included in the system depending on polarity. The dipoles are equilibrated to the presence of the uniform electric field and the other dipoles of the system. After equilibrium is reached the field is turned off and the subsequent decay of the total dipole moment in the direction of the external field recorded. The ratio between the dipole moment and the external field provides the after-effect function $b(t)$. Typically 60 independent starting points were used in generating averaged $b(t)$ functions. In addition, a difference technique similar to the suggestions of Ciccotti et al.[25] and Evans and Powles[26] was used. For each initial configuration, two independent simulations are carried out in which the strength of the external field is the same but its direction is reversed. The time dependence of the total dipole moment is found by subtracting the moment of the first simulation from that of the second. This difference technique significantly reduces the noise in the averaged $b(t)$ functions. More details of the simulation procedure can be found in Ref. 12.

At the lowest polarities studied ($\eta < 0.1$) the after effect functions are exponential, which translates into a Debye $\epsilon(\omega)$. However, for higher polarities $b(t)$ has a pronounced biexponential character. At all η the $b(t)$ functions yield dielectric response functions that are well described by a Davidson–Cole form,[27]

$$\epsilon(\omega) = 1 + \frac{\epsilon_0 - 1}{(1 + i\omega\tau_{DC})^\beta}, \qquad (9)$$

to within the uncertainties of the data.[28] The Davidson–Cole parameters best representing $\epsilon(\omega)$ as a function of η are collected in Table I. These fitted functions were used as input to the semiempirical theories in Sec. IV.

III. THEORETICAL PREDICTIONS

In this section we collect the predictions of the various theories of solvation dynamics that will be compared to the simulation results in the following section. Several recent reviews discuss these theories at length[1,2,4] so that we will only touch on the main points and give the working equations here. We express the results in terms of the reaction potential response $\langle V(t) \rangle$ to switching on a charge of magnitude Q; i.e., we examine the specific process $Q_i = 0 \to Q_f = Q$. In all cases the theories assume the solute to be an impenetrable sphere of radius r_u (here identified as half the lattice spacing, $a/2$). With the exception of the theory of Loring and Mukamel all deal with bulk solvation in an isotropic fluid. We will make some slight modifications where possible to the theories in order to partially account for the lattice structure of the simulated system (see below). However, it should be kept in mind that we are comparing liquid-state theories to simulated results on a solidlike lattice solvent. It is our contention that the translational order present in the lattice does not make the dynamics qualitatively (or even quantitatively) different from that which would be observed in a translationally disordered system. We therefore view these comparisons as providing appropriate tests for uncovering the strengths and weaknesses in the liquid-state theories. The validity of this point of view will be addressed later.

TABLE I. Dielectric dispersion parameters[a] of the dipole lattice from computer simulation and predicted by the PE/LM and SVE/CB theories.

	Simulation results					Theoretical predictions		
	Davidson–Cole fits			Debye fits		PE/LM[b]	SVE/CB[c]	
η	ϵ_0	τ_{DC}	β	ϵ_0	τ_D	ϵ_0	ϵ_0	τ_D
0.041	1.6	1.2	$(1.0)^d$	1.6	1.2	1.6	1.6	1.2
0.083	2.5	1.4	$(1.0)^d$	2.5	1.4	2.3	2.4	1.3
0.167	4.9	2.1	0.98	4.9	2.0	2.8	4.5	1.7
0.333	12.0	3.5	0.93	12.0	3.0	$\cdots$	10.0	2.2
0.500	19.0	4.7	0.89	19.0	3.7	$\cdots$	18.0	2.7

[a]These parameters are defined in Eqs. (9) and (24). Time constants are in units of τ_0.
[b]To the order of perturbation theory employed by the PE/LM treatment values of ϵ_0 are negative for $\eta > 0.2$ and so are not listed here.
[c]The SVE/CB theory predicts a Debye form dielectric function, with the dielectric constant ϵ_0 given by the MSA and the Debye relaxation time τ_0 related to ϵ_0 and τ_0 through $(\epsilon_0 - 1)\tau_0/4\pi\eta$.
[d]For $\eta = 0.041$ and 0.083 fits to a Davidson–Cole function were not noticeably better than fits to a Debye function. For these two cases we used the Debye fits $(\beta = 1)$ in making comparisons to solvation dynamics theories.

A. The simple continuum (SC) model

The most simplistic theory is the dynamical generalization of the venerable Born model of equilibrium solvation energetics.[29] The solvent is viewed as a homogeneous continuum fluid characterized solely by its dielectric response function $\epsilon(\omega)$. The reaction potential response may be calculated from a boundary value calculation as in the original static Born model with the result[14,16]

$$\langle V(t)\rangle - \langle V(\infty)\rangle = Q \mathscr{L}^{-1}\left\{\frac{1}{p}\,[\hat{\chi}_{cont}(0) - \hat{\chi}_{cont}(p)]\right\}, \tag{10}$$

where $\mathscr{L}^{-1}$ denotes an inverse Laplace transform:

$$\mathscr{L}^{-1}\{\hat{f}(p)\} = \frac{1}{2\pi i}\int_{\delta-i\infty}^{\delta+i\infty} dp\, e^{pt}\hat{f}(p) \tag{11}$$

and

$$\hat{\chi}_{cont}(p) = \frac{1}{r_u}\left\{1 - \frac{1}{\hat{\epsilon}(p)}\right\}. \tag{12}$$

B. The dynamical mean spherical approximation (DMSA)

The first molecular theory we will consider is the dynamical MSA model initially introduced by Wolynes[15] and further developed by several groups.[16–18] The essential idea in this approach is to assume that the frequency dependence of the solvation response can be obtained by merely substituting $\epsilon(\omega)$ for ϵ_0 in the functional relationship between the equilibrium solvation energy ($\langle V \rangle$ here) and ϵ_0 in any linear solvation theory. Thus in precisely the same way that the molecular nature of the solvent causes the equilibrium solvation energy to deviate from the simple Born relation, $\langle V \rangle \propto (1 - \epsilon_0^{-1})$, molecular effects also alter the dynamics. In practice, the only equilibrium solvation theory commonly employed has been the MSA solution for the solvation of an ion in a dipolar hard sphere fluid,[30] due to the fact that it yields simple analytical solutions. Using this model system, Rips and co-workers[16] showed that the solvation response can be written in the same form as in the simple continuum model,

$$\langle V(t)\rangle - \langle V(\infty)\rangle$$
$$= Q\mathscr{L}^{-1}\left\{\frac{1}{p}\,[\hat{\chi}_{DMSA}(0) - \hat{\chi}_{DMSA}(p)]\right\}, \tag{13}$$

except that the complex admittance,

$$\hat{\chi}_{DMSA}(p) = \frac{1}{r_u}\left\{1 - \frac{1}{\hat{\epsilon}(p)}\right\}\{1 + \hat{\Delta}(p)\}^{-1} \tag{14}$$

now contains a correction term,

$$\hat{\Delta}(p) \cong \frac{3\rho}{2}\{108^{1/3}[\hat{\epsilon}(p)^{1/6} - 2]^{-1}, \tag{15}$$

which accounts for solvent molecularity via the solute/solvent size ratio $\rho = 2r_u/\sigma$ (σ is the diameter of the dipolar hard sphere solvent, here identified with the lattice constant a). As in the simple continuum model, information about the solvent dynamics comes into the theory through use of the empirically determined dielectric function $\hat{\epsilon}(p = i\omega)$.

The remaining molecular theories to be considered incorporate molecular effects into the problem in a different manner from that used by the DMSA theory. They all express the solvation response in terms of an integral over the solute's electrostatic field times a function of the full wave vector- and frequency-dependent dielectric function of the pure solvent, $\epsilon_L(k,\omega)$. The solute's only role in determining how solvation in a molecular solvent differs from that in a continuum dielectric fluid is that it sets the k scale over which $\epsilon_L(k,\omega)$ is sensed. All of the intermolecular correlations and dynamics are those of the pure solvent and all of the effort in these theories rests in approximating the behavior of the function $\epsilon_L(k,\omega)$.

C. The Smoluchowski–Vlasov equation theory of Chandra and Bagchi (SVE/CB)

The Smoluchowski–Vlasov equation approach was first used in an early treatment of solvation dynamics by Calef and Wolynes.[19] It has more recently been employed by Chandra and Bagchi in an extensive series of studies.[3,9,20] Reference 3 provides a detailed exposition of this theory and its predictions. In the simplest version of the

theory considered here the coupled reorientational and translational dynamics involved in $\epsilon_L(k,\omega)$ are calculated using a mean-field density functional approach. The theory is what we will call an *ab initio* theory in the sense that no empirical information about $\epsilon_L(k,\omega)$ is used as input. The only solvent parameters required are the diameter, σ, and the rotational diffusion constant D_R arising from the short-range part of the intermolecular interaction, here assumed to be equal to $(2\tau_0)^{-1}$.[31] The solvation response is given in terms of the reduced wave vector $q=k\sigma$ by[20]

$$\langle V(t)\rangle - \langle V(\infty)\rangle = \frac{2Q}{\pi\sigma} \int_0^{q_{max}} dq \left\{ 1 - \frac{1}{\epsilon_L(q)} \right\}$$
$$\times \exp[-t/\tau_L(q)] \left\{ \frac{\sin(qr_c/\sigma)}{qr_c/\sigma} \right\}^2. \tag{16}$$

In this expression q_{max} is the maximum value of the wave vector, which can be either 2π or ∞ for reasons to be discussed later. The function $\sin(x)/x$, which also appears in all of the remaining theories, comes from writing the electrical field of an ion in a wave vector representation. The parameter r_c in its argument is a lower cutoff for the interaction between the solute and solvent, related to the solute radius by $r_c = r_u + \sigma/2$. We will also discuss the meaning of this choice of radius shortly. The solvent's dielectric response is here represented by the two functions $\epsilon_L(q) = \epsilon_L(k\sigma, \omega=0)$ and $\tau_L(q)$, given by[20]

$$1 - \frac{1}{\epsilon_L(q)} = 4\pi\eta \left[1 + \frac{1}{4\pi\sigma^3} h_{110}(q) \right] \tag{17}$$

and

$$\tau_L(q)^{-1} = 2D_R \left[1 - \frac{1}{4\pi\sigma^3} c_{110}(q) \right]. \tag{18}$$

In these expressions $h_{11m}(q)$ and $c_{11m}(q)$ are the $(11m)$ expansion coefficients of the distance and orientation dependent pair (h) and direct (c) correlation functions of the solvent. For these functions, which determine how translational and orientational correlations affect the dynamics, the MSA solutions for a dipolar hard sphere liquid are used.[32] Explicit expressions for these functions can be found in Ref. 33.

D. The memory function theory of Fried and Mukamel (MF/FM)

The theory proposed by Fried and Mukamel[21] is closely related to the Smoluchowski–Vlasov theory in spirit. Fried and Mukamel found that by a particular factorization of the memory function associated with $\epsilon_L(k,\omega)$ they could approximately separate the k and ω dependences in a manner similar to the decomposition expressed by Eq. (16). Their result can be written as[34]

$$\langle V(t)\rangle = \frac{8Q}{\sigma} \mathcal{L}^{-1} \left\{ \frac{1}{p} \int_0^{q_{max}} dq \, \hat{\alpha}_L(q,p) \left[\frac{\sin(qr_c/\sigma)}{qr_c/\sigma} \right]^2 \right\}, \tag{19}$$

where $\hat{\alpha}_L(q,p)$ is the longitudinal polarizability, which is given in terms of the dielectric function by[21]

$$\hat{\alpha}_L(q,p) = \frac{1}{4\pi} \left(1 - \frac{1}{\epsilon_0} \right) \left\{ \frac{1-c_{110}(q)}{1-c_{110}(0)} - \frac{[\hat{\epsilon}(p)-\epsilon_0]}{\epsilon_0[\hat{\epsilon}(p)-1]} \right\}^{-1}. \tag{20}$$

In this expression $c_{110}(q)$ is again the (110) component of the two-point direct correlation function and, as in the SVE/CB theory, this quantity is approximated using the analytic results of the MSA solution for the dipolar hard sphere liquid.[32,33] Although they take different approaches to the calculation of solvation dynamics, it turns out that the MF/FM and SVE/CB theories yield identical predictions in cases where the $\epsilon(\omega)$ functions involved are the same and of the Debye form assumed by the SVE/CB theory. In some sense, the MF/FM theory can be viewed as an extension of the SVE/CB theory that allows one to use any $\epsilon(\omega)$ function determined empirically to predict the solvation response of a system.

E. The perturbation expansion of Loring and Mukamel (PE/LM)

All of the previous theories were designed with liquid solvents in mind. The last theory, due to Loring and Mukamel,[22] was developed specifically for the cubic lattice solvent studied here (although it was in fact used as a simple model liquid solvent). Loring and Mukamel extended the perturbation expansion used by Zwanzig[23] to derive the dielectric properties of the Brownian dipole lattice relevant to the problem of solvation dynamics. Their expression for the solvation response can be written

$$\langle V(t)\rangle = \left(\frac{8\eta Q}{a} \right) \int_0^{q_{max}} dq \{1 - \eta T(q) + \eta^2 R\}^{-1} \widetilde{Z}(q,t)$$
$$\times \left[\frac{\sin(q)}{q} \right]^2. \tag{21}$$

The quantities R, $T(q)$, and $\widetilde{Z}(q,t)$ involve complicated lattice sums that will not be reproduced here. They can be found in Ref. 22. The theory involves expanding the properties of the system as a power series in the polarity parameter η about $\eta=0$ and so it is only expected to provide reasonable results for solvents with sufficiently small polarities. The range of applicability of this theory will be discussed in Sec. IV. We note that to obtain tractable final equations, Loring and Mukamel replaced some of the discrete sums in these terms by integrals in what they called an "Onsager liquid" approximation. Some of the information about the lattice structure is thereby lost and the theory is therefore not that far removed from the other theories we consider.

Two aspects of our implementation of the last three theories to the dipolar lattice solvent require comment. First, the limit q_{max} we have placed on the wave vector

integrations appearing in these theories differs from the value normally assumed. As originally formulated, the wave vector integrals in these theories extend to infinity. This choice is appropriate for liquids but not for a lattice system. Since there is no meaning to $q > 2\pi$ (or wavelengths shorter than the lattice spacing a) for the present application we limit integrations to $q_{max} = 2\pi$. In effect we thereby assume that the interdipolar correlations that define the lattice response via $\epsilon_L(k,\omega)$ are the same as in a dipolar liquid system except that all response at $k > 2\pi/a$ is absent. (We are also ignoring the fact that the true $\epsilon_L(\mathbf{k},\omega)$ of the lattice has cubic rather than spherical symmetry as in a liquid.) Because the difference between using the limits $q_{max} = \infty$ and $q_{max} = 2\pi$ is substantial, in the following section we will illustrate results obtained with both limits for one of the theories (MF/FM). We must also note that in the case of the DMSA theory, which is not written in terms of a wave vector integration, it is not obvious how to perform an equivalent treatment of the high k cutoff. We therefore leave it in the form initially developed for liquid systems keeping in mind that in so doing we are comparing it to the lattice simulation results on a slightly different footing than the other theories.

The second aspect of our application of the theories concerns the choice of solute size parameter. All of the liquid-based theories (and ultimately even the PE/LM theory) apply to a spherical solute of radius r_u. Here we assume this radius to be given by 1/2 of the lattice spacing, $r_u = a/2$. We have previously shown that such a choice leads to the expected relationship between total solvation energy and system size in finite lattices.[11] Related to the choice of r_u is the interaction cutoff r_c appearing in the $\sin(x)/x$ functions of the SVE/CB and MF/FM theories. In the original versions of the SVE/CB theory[20] and in the MF/FM theory[21] this radius was taken to be simply equal to the solute radius. In later work Chandra and Bagchi[3] proposed the use of $r_c = r_u + \sigma/2$ as a more appropriate alternative. Since the motivation behind this choice was not explicitly stated in Ref. 3 it is useful to do so here. As discussed in detail by Raineri *et al.*,[4] the $\sin(x)/x$ function arises when the solute's electric field is written in a k-space representation. Its argument reflects the lower limit of the spatial region where the solute field and the solvent polarization interact. The simplest choice, $r_c = r_u$, takes the interaction to begin at the solute boundary whereas the choice $r_c = r_u + \sigma/2$ recognizes that no solvent dipoles are closer to the solute than this pair distance. That the latter choice is more appropriate can be seen from results derived by Chandra and Bagchi[20(c)] in their discussion of solvation energetics. In that work they showed that theories of solvation that use $\epsilon_L(k,\omega)$ of the bulk solvent as described above are in essence approximating the solvent–solute radial distribution function by

$$g_{uv}(r) = \begin{cases} 1 & \text{for} \quad r > r_c \\ 0 & \text{for} \quad r \leqslant r_c \end{cases}. \tag{22}$$

Since in either the present lattice studies or in the treatment of hard-core liquids, the exact $g_{uv}(r)$ is zero for $r \leqslant r_u + \sigma/2$, choosing $r_c = r_u$ is not the optimum choice. Whereas
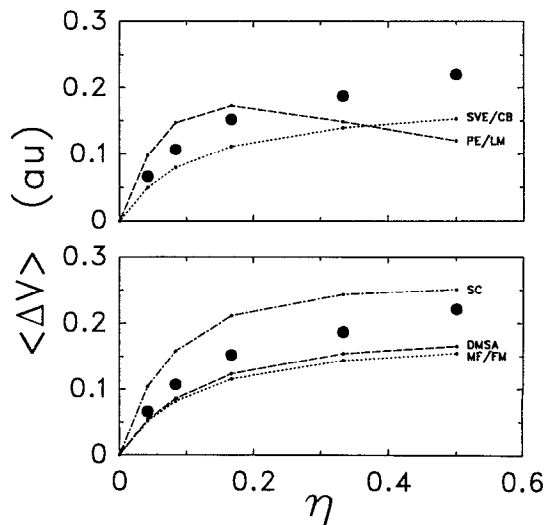

FIG. 1. Amplitudes of the response to a unit electronic charge jump as a function of solvent polarity η. The simulated values (large points) were calculated from measured values of $\langle \delta V^2 \rangle$ using Eq. (5). Theoretical predictions are shown as continuous curves but only the points at the simulated η values were determined.

a correct approximate $g_{uv}(r)$ is built into the DMSA treatment through its use of the MSA description of the solute–solvent radial structure, in the theories that focus on $\epsilon_L(k,\omega)$ of the pure solvent the only acknowledgment of solute-solvent structure comes from r_c. The use of $r_c = r_u + \sigma/2$ is an obvious way to incorporate the correct zeroth order description of $g_{uv}(r)$ into these theories. As with the q_{max} choice, the difference in results obtained using different cutoff radii is substantial and we will illustrate the effect of this choice using the MF/FM theory as an example in the following section.

IV. COMPARISON

In comparing the predictions of the above theories to the simulated solvation dynamics we will consider three aspects of the response and how these vary with the solvent polarity η. They are (i) the amplitude of the response, (ii) its time scale, and (iii) the functional form of its time dependence. For the simulated amplitude we make use of Eq. (5) to determine $\langle \Delta V \rangle$ corresponding to a 1 a.u. charge jump from simulated values of $\langle \delta V^2 \rangle_{Q=0}$. These values are compared to the theoretical predictions in Fig. 1. Figure 2 shows a representative $C_V(t)$ time correlation function observed from an equilibrium simulation and the corresponding $S_{i \to f}(t)$ response functions predicted for a lattice solvent with polarity $\eta = 0.33$. Since these functions are clearly nonexponential we characterize the time dependence by providing both the $1/e$ decay times in Fig. 3 and the exponent α obtained by fitting these functions to a stretched exponential form,

$$C_V(t), S_{i \to f}(t) = \exp\{-(t/\tau)^\alpha\}, \tag{23}$$

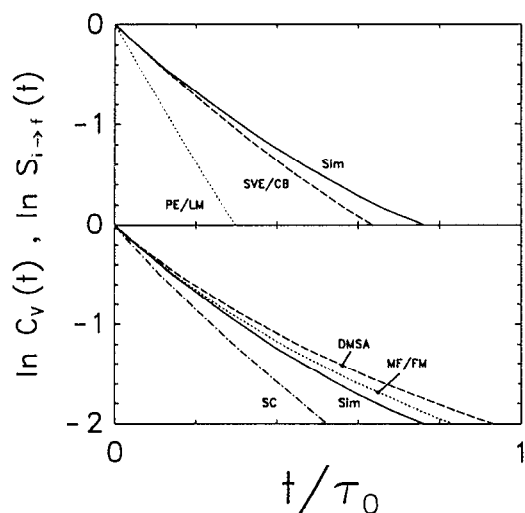in Fig. 4. The results shown in Figs. 1–4 contain theoretical predictions determined using the parameters $q_{max} = 2\pi$ and

FIG. 2. Simulated solvation time-correlation function $C_V(t)$ [solid curves; Eq. (4)] and predicted response functions $S_{i \to f}(t)$ for the $\eta = 0.33$ lattice.

FIG. 4. Exponents α obtained from stretched exponential fits [Eq. (23)] to the solvation response functions as a function of solvent polarity η.

$r_c = r_u + \sigma/2$. To see how these choices affect the predicted response we also plot the predictions of the MF/FM theory obtained with two alternative choices of these parameters in Fig. 5.

In Figs. 1–4 we have separated the theories into two categories, the ab initio theories SVE/CB and PE/LM in the top panels and the semiempirical theories, SC, DMSA, and MF/FM, in the bottom panels. The two groups differ in that the latter require the empirically determined $\epsilon(\omega)$ as input while the former theories compute these directly from η and τ_0. We will begin with the ab initio theories. In this case there are two aspects of the theories to be considered. The first is how accurately they predict the dielectric properties of the lattice system. After addressing this question we can then ask how well they relate these dielectric properties to the solvation dynamics. The first aspect of the
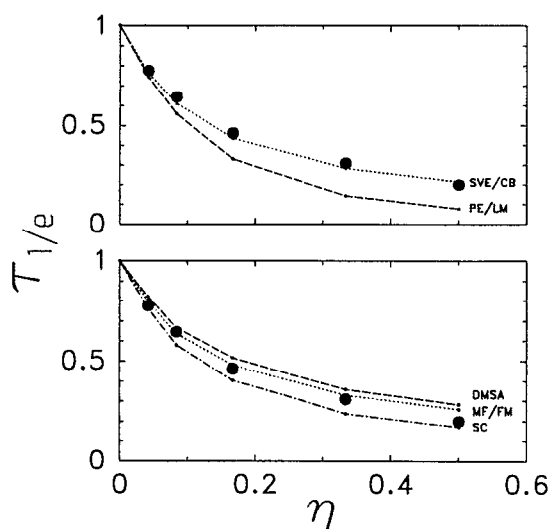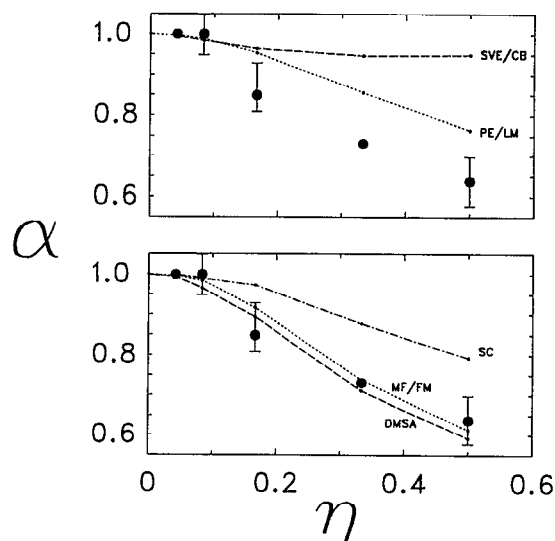
comparison between the ab initio theories and the simulation results is carried out in Table I. Here we compare the static dielectric constants ϵ_0 and the Debye relaxation times of the observed $\epsilon(\omega)$ with predictions of the PE/LM and the SVE/CB models.

As has been noted previously[11] the level of perturbation employed in the PE/LM theory only produces meaningful values of ϵ_0 for very low polarities, $\eta \leqslant 0.2$. At higher polarities the order of the perturbation expansion used is such as to predict unphysical, negative values of ϵ_0. Thus the PE/LM cannot adequately describe the dielectric properties of the solvent over the full range of polarities of interest here. It would therefore not be expected to yield accurate predictions for either the static or dynamic as-

FIG. 3. Solvation time constants ($1/e$ times) in units of τ_0 as a function of solvent polarity η.
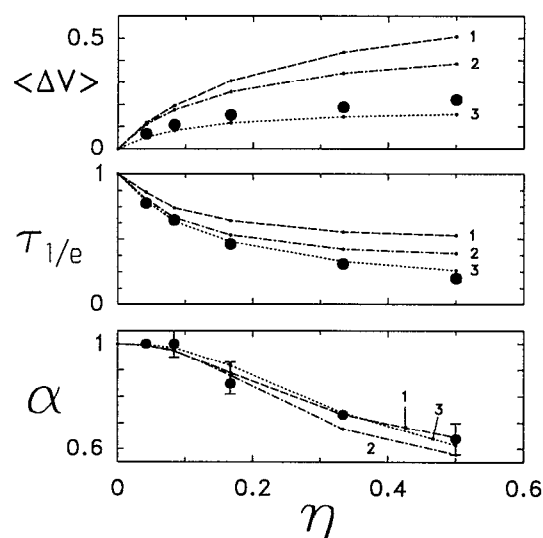

FIG. 5. Calculated properties (see Figs. 1, 3, and 4) of the solvation response predicted by the MF/FM theory for different choices of the parameters r_c and q_{max} (see the text). The curves are labeled according to (r_c, q_{max}) as $1 = (r_u, \infty)$, $2 = (r_u + \sigma/2, \infty)$, $3 = (r_u + \sigma/2, 2\pi)$.

pects of solvation at the higher polarities studied. This expectation is confirmed by the results shown in Figs. 1–4. The amplitude of the solvation response is reasonable for $\eta \leqslant 0.2$. In this region values of $\langle \Delta V \rangle$ are too high by 15%–50%. At higher values of η the amplitude of the solvation response *decreases* with increasing η, clearly a nonphysical result. The dynamical predictions of the PE/LM theory are also in poor agreement with simulation at the higher η values. At all η the predicted solvation times ($\tau_{1/e}$, Fig. 3) are too small such that by $\eta = 0.33$ the prediction differs from the observed time by as much as a factor of 2. The theory correctly predicts an increasingly nonexponential solvent response with increasing η but the exponents α (Fig. 4) are in general too large (i.e., the response is predicted to be too close to exponential). Essentially the same observations concerning the PE/LM theory were made in our earlier treatment work where we used $q_{max} = \infty$ instead of $q_{max} = 2\pi$ in theoretical calculations.

The SVE/CB theory is considerably more successful at reproducing the dielectric properties of the dipole lattice. As can be seen from Table I, the dielectric constants are within 15% of the observed values for all η studied. Since the SVE/CB theory [as employed here; but see Ref. 9(a)] is based on a Markovian description of the dielectric friction acting on solvent molecules it produces a dielectric response of Debye form,

$$\epsilon(\omega) = 1 + \frac{\epsilon_0 - 1}{1 + i\omega\tau_D}, \qquad (24)$$

having a single dielectric relaxation time, τ_D. Especially at the higher polarities studied, the true $\epsilon(\omega)$ of the lattice is best represented by a Davidson–Cole function [Eq. (9)], which implies the presence of a distribution of dielectric relaxation times. In order to compare some sort of overall dielectric time scale in the two cases we also present the results of a Debye fit (both ϵ_0 and τ_D varied) of the simulated $\epsilon(\omega)$ data in Table I. Comparison of these τ_D values with those predicted by the SVE/CB theory shows that although it does not correctly describe the nonexponentiality of the dielectric response, the theory does predict the correct time scale to within about 25%. Thus this *ab initio* theory is able to provide a reasonably good description of $\epsilon(\omega)$ in these lattices.

Figures 1–3 show that the SVE/CB theory is also able to do a rather good job of predicting the solvation behavior in these systems. For example, although the overall scale is wrong by ~25%, the η dependence of the solvation amplitudes (Fig. 1) is well reproduced. The solvation time scale, as measured by the 1/e times in Fig. 3, is predicted with remarkable accuracy. We note that much poorer agreement was reported in our past comparison to this theory[11] due to the use of $q_{max} = \infty$ and $r_c = r_u$ (see below). The main shortcoming of the SVE/CB theory is in predicting the degree of non-exponentiality of the solvation response. As seen in Figs. 2 and 4, the predicted response is much closer to exponential than is the observed response. The discrepancy can be mainly attributed to the fact that the theory predicts a single time scale for dielectric relax-

ation when in fact the true $\epsilon(\omega)$ contains a distribution of relaxation times.

We now turn to the semiempirical theories, beginning with the simple continuum model. The SC theory overestimates the solvation amplitude by 30%–40% and it tends to saturate too quickly with increasing η compared to the simulated results. Both of these features are well-known shortcomings of the continuum (Born) model for solvation energies.[35] The solvation response predicted by the SC model (Fig. 3) is uniformly too rapid, but the 1/e times do not deviate widely from the simulated values. The fact that the SC model predicts solvation times that are too fast faster than the predictions of molecular models (in the absence of translation) is well known.[1] Where the SC model fails most seriously is in predicting the nonexponentiality of the solvation response, which again is underestimated (Fig. 4). This feature of the SC model is also as expected.[1]

The two remaining semiempirical theories, the DMSA and MF/FM theories, perform equally well with respect to most comparisons to simulation. As with the SVE/CB theory, both of the latter theories underestimate the response amplitude by ~20%. The 1/e times are close to the simulated values, in this case being slightly high. In fact, the MF/FM theory yields times that agree with the simulated values to within the simulation uncertainties (roughly the size of the symbols in Fig. 3) except at the highest polarity, where the prediction is perhaps 20% high. In addition, these two semiempirical theories correct the error made by the SC and the SVE/CB theories with respect to the shape of $C_V(t)$. As shown in Fig. 4 the significant nonexponentiality observed in the simulated response functions is nicely reproduced by both of these theories. Thus both the DMSA and the MF/FM theories provide excellent overall representations of ionic solvation dynamics in these simple lattice solvents.

Before concluding this section it is useful to consider how the choices of q_{max} and r_c influence the predicted results. In Fig. 5 we illustrate their effect on the MF/FM theory. As can be seen from this figure, alternative choices for either of these parameters lead to substantially different predictions. Consider first the difference between $r_c = r_u$ and $r_c = r_u + \sigma/2$ (curves no. 1 and 2). We argued that the latter choice is more appropriate, independent of whether one is dealing with lattices or with real liquid solvents. Using the solute radius for this cutoff produces values of the solvation amplitudes [Fig. 5(a)] that are much larger than observed. The values obtained are even larger than predicted by the SC model, which also assumes that solvent interactions extend to r_u. Molecular theories such as the MF/FM theory predict enhanced intersolvent correlations near to the solute compared to a continuum fluid. Such correlations lead to solvation energies that are larger than the already excessive values of the SC model unless proper account is also made of the effect of solvent-excluded volume. The choice of r_c also has a marked effect on the time scale of the dynamics. At a polarity of $\eta = 0.5$ the solvation 1/e time differs by almost 40% between the two choices of r_c considered. Clearly one must be careful in

correctly choosing this parameter both in the present context and when comparing these theories to experimental measurements. Decreasing q_{max} has a similar effect to increasing r_c. For these lattice systems we argued that q_{max} is more appropriately chosen as 2π rather than the value $q_{max} = \infty$, correct for liquids. The use of 2π also reduces the solvation amplitude and the solvation time constant compared to the latter choice. Again, the changes are substantial. For example, $\tau_{1/e}$ changes by $\sim 35\%$ between cases 2 and 3. The effects produced by changing both q_{max} and r_c are readily understood as resulting from a reduced weighting of the high wave vector modes in $\epsilon_L(k,\omega)$ for the choices $q_{max} = 2\pi$ and $r_c = r_u + \sigma/2$. Since the high k modes have the slowest response, reducing the contribution of these modes in the overall response leads to faster dynamics. It is important to point out that making the alternate choices for either parameter would lead to considerably poorer agreement between the predictions of the SVE/CB and MF/FM theories and the simulated results as regards the solvation time scale. Finally, we note that we have made no correction to the DMSA theory equivalent to the 2π cutoff of the q integrations in the other molecular theories. Based on the results in Fig. 5 it is reasonable to suppose that if the DMSA theory could be reformulated so as to account for the periodicity of the lattice solvent the solvation times predicted would be slightly shorter and in even better agreement with the simulated results than is shown in Fig. 3.

V. CONCLUSIONS

The objective of the work reported here was to examine how well existing theories predict the dynamics of ion solvation in a simple model solvent. The solvent studied consists of a cubic array of point dipoles that undergo rotational Brownian motion in the force field produced by other dipoles in the system. Both translational and inertial motions of solvent molecules are absent in this simple model. Even so, the system exhibits rich dynamical behavior similar to that observed in more realistic solvents. Moreover, the simplicity of the present model helps to clearly expose one of the more fundamental aspects of the problem: the change in the dynamics as a function of the strength of intermolecular interactions, i.e., as a function of solvent polarity. The comparisons presented here allow us to judge how well current theories reproduce this essential feature of the solvation response.

The conclusions we draw must be viewed with one limitation in mind. Our simulated systems consist of a translationally ordered lattice rather than the isotropic, disordered liquids for which most molecular theories were designed. However, it is our belief that the differences caused by imposition of the lattice structure are modest. Assuming that the MSA solutions provide an accurate representation of the dipolar hard sphere liquid, Table I reveals that variation of the static dielectric constant with η is very nearly the same in these lattices as it is in the corresponding liquid. (The SVE/CB values of ϵ_0 in Table I are the MSA liquid values.) Thus the orientational correlations in our lattice solvents cannot be greatly affected

by the imposed translational order. We have also tailored the liquid theories slightly to account for a residual effect the lattice structure by properly truncating the wave vector integrations at wave vectors outside of the first Brillouin zone. The situation here is similar to approximations commonly employed in the theory of freezing.[36] With this choice of q_{max} we believe that the comparison between the simulations and the theoretical predictions should be quantitatively meaningful.

Given the above caveat, several general conclusions can be drawn from the comparisons of the last section. Of the *ab initio* theories, the perturbation treatment of dielectric relaxation by Zwanzig[23] and its extension to the solvation dynamics problem by Loring and Mukamel[22] is of limited utility. Even though this theory directly addresses the dipole lattice solvent, the perturbation expansion breaks down and provides poor predictions for $\epsilon(\omega)$ and the solvation response for polarities beyond $\eta = 0.2$ or for dielectric constants $\epsilon_0 > 5$. In contrast, the Smoluchowski-Vlasov equation approach of Chandra and Bagchi[20] does a remarkably good job of reproducing the solvation behavior in these systems at all polarities. The only failing of the SVE/CB theory is that the simple Markovian version of the theory used here predicts Debye dielectric response functions when in fact the observed $\epsilon(\omega)$ are non-Debye. For the same reason the theory fails to properly reproduce the nonexponential character observed in the solvation response.

Of the semiempirical theories, which require $\epsilon(\omega)$ as input, it should first be said that all of those studied do a reasonable job of predicting the correct time scale of the solvation response. Even the simple continuum model reproduces the η variation of $\tau_{1/e}$ to better than 20% except at the highest polarity. As expected, this zeroth-order theory predicts solvation times that are uniformly too short compared to the observed times. By virtue of the non-Debye $\epsilon(\omega)$ used as input, the response functions predicted by the SC theory are nonexponential as are those observed. However, the simulated response deviates from an exponential decay to a much greater extent than is predicted. These two shortcomings of the SC theory both result from its consideration of only the $k = 0$ limit, where the solvent response is fastest. The fact that the solute and solvent molecules are of comparable size requires that nonzero k portions of $\epsilon_L(k,\omega)$ must also contribute to the dynamics. Since the higher k components of $\epsilon_L(k,\omega)$ are in general slower than the $k = 0$ contribution, their inclusion results in a broadened distribution of relaxation times and an overall slower solvation response.

The two remaining theories, the dynamical MSA theory[15,16] and the memory function theory of Fried and Mukamel,[21] account for these finite-k contributions and thereby correct the deficiencies inherent in the SC model. Both semiempirical theories do an excellent job of predicting the observed solvation dynamics from a knowledge of the ($k = 0$) dielectric function $\epsilon(\omega)$. (While the MF/FM theory provides slightly better overall agreement with the simulated results the difference may only reflect our ne-

glect of the q_{max} correction in the DMSA model. We therefore take the view that these two theories provide equally good representations of the observed dynamics.) It is noteworthy that the two models behave as similarly as they do given that the molecular nature of the solvent is introduced in two very different ways. Whereas the DMSA model focuses on the effects of the solute–solvent ordering, the MF/FM theory considers only the solvent–solvent correlations reflected in $\epsilon_L(k,\omega)$ of the pure solvent. Based on the quantitative agreement with the simulated dynamics it appears that neglect of solute–solvent correlations does not seriously impair the accuracy of the MF/FM theory. This observation serves to validate the approach taken by many recent theories which assume that a knowledge of $\epsilon_L(k,\omega)$ of the pure solvent is sufficient to predict the dynamics of solvation of a molecular solute. We can therefore have some confidence that current efforts to model the effects of translational motions and inertial dynamics on $\epsilon_L(k,\omega)$ of the pure solvent will be a fruitful way to begin to understand solvation dynamics in more realistic systems.

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[35] Of course, if we had accounted for the excluded solvent volume by replacing r_u with $r_u + \sigma/2$ in the same way that we did with the SVE/CB and MF/FM theories the $\langle \Delta V \rangle$ values calculated by the SC theory would be much closer to those given by these latter theories and to the measured values.

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