

Free Energy of Nonequilibrium Polarization Systems. 4. A Formalism Based on the Nonequilibrium Dielectric Displacement

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An expression for the free energy of nonequilibrium polarization systems, valid in the presence or absence of dielectric images, is derived using the nonequilibrium dielectric displacement and electric field vectors. The results are compared with those based on the nonequilibrium polarization vector (Part I). For the case of longitudinal polarization they are equivalent. However, the present expression is simpler and more compact. The results are compared with others in the literature.

I. Introduction

In some systems, such as in electron-transfer reactions or for a polaron, i.e., a trapped electron in a polar medium, the dielectric polarization $\mathbf{P}(\mathbf{r})$ of the solvent at each point $\mathbf{r}$ is not that which is given by the usual equilibrium electrostatic field. In electron-transfer reactions the reaction is typically preceded (and later followed) by fluctuations in $\mathbf{P}(\mathbf{r})$ from the value dictated by the ionic reactants' charges. Again, in the polaron system the electron is distributed over the nearby solvent molecules and the slow part of $\mathbf{P}(\mathbf{r})$ cannot be in equilibrium everywhere with the instantaneous charge distribution of the electron.

In treatments of these systems a nonequilibrium dielectric polarization $\mathbf{P}(\mathbf{r})$ is frequently introduced,^{1,2} together with an electric field $\mathbf{D}_0(\mathbf{r})$ due to the bare charges and a field $\mathbf{E}(\mathbf{r})$ due to the latter and to the polarized dielectric medium, treated frequently as a dielectric continuum.^{1,3}

When there are no cavities in the continuum, e.g., no discontinuous changes of dielectric constant, the treatment is relatively straightforward. Such a situation occurs in the case of some polarons, but not when the system consists of an ion or ions in solution. In the case of two ionic or molecular reactants in solution dielectric image effects occur, so as to satisfy the boundary conditions at the discontinuities (e.g., at the boundaries of the cavities) in the system. The effect of the latter is to introduce relatively complicated expressions¹ for the electrostatic properties, which contain the $\mathbf{P}(\mathbf{r})$, $\mathbf{D}_0(\mathbf{r})$, and $\mathbf{E}(\mathbf{r})$ mentioned above.

In the present article we use instead a nonequilibrium dielectric displacement $\mathbf{D}(\mathbf{r})$ and an electric field $\mathbf{E}(\mathbf{r})$. This type of approach is useful pedagogically, as we have found in teaching a course on electron-transfer reactions during the past two years. The derivation itself is much simpler than that in part I, and the resulting equation, eq 2.17, is more compact, though equivalent (for longitudinal $\mathbf{D}(\mathbf{r})$) to the previous one. The results also have a usefulness in research, as Liu and Newton, who arrived at it independently,⁴ have shown.

A method used in part II,³ based on charges and potentials instead of on their counterparts $\mathbf{D}$ and $\mathbf{E}$, is even simpler than the $\mathbf{D}$ and $\mathbf{E}$ approach and yields the same compact form for ΔG , the free energy of formation of the nonequilibrium system. Indeed, the present final equation, eq 2.17, can be immediately obtained from equations in part II, by relating the charges to $\mathbf{D}(\mathbf{r})$ and the potentials to $\mathbf{E}(\mathbf{r})$ in the standard way. Moreover, the expression based on charges and potentials is simpler to use in applications (e.g., as in the cited articles in ref 3) than that based on vectors, in part because of the availability of literature expressions for the potentials of various systems. Indeed, even more generally, in

problems in electrodynamics, potentials (now both scalar and vector) are frequently introduced to replace the original vectors. Although the $\mathbf{D}$ and $\mathbf{E}$ approach is not as simple as the charges-potential one, the present article is written, in part, to relate this ($\mathbf{D}$, $\mathbf{E}$) approach to those based on the widespread use of $\mathbf{P}$, $\mathbf{D}_0$, and $\mathbf{E}$ in the dielectric literature.

The expression for ΔG is obtained in section II, its use in electron transfers by minimizing ΔG subject to a constraint is given in section III, and a comparison with the results in parts II and III, with an expression of Felderhof, and with an extension of the latter is given in section IV.

II. Free Energy of Fluctuations

As in part I, the free energy of a system composed of reactants in a nonequilibrium-polarized dielectric medium is calculated by finding a reversible path for forming that system. As before, the path consists of two steps. The first step now is to change the charges until the desired but unknown nonequilibrium dielectric displacement function $\mathbf{D}(\mathbf{r})$, denoted by $\mathbf{D}^*(\mathbf{r})$, is produced. The next step is to change $\mathbf{D}^*(\mathbf{r})$ to a value appropriate to the original charges, but holding the orientational and vibrational dielectric polarization fixed.

During each of the two steps of the charging process the reversible work done, w , is given by

$$w = \int_{\lambda=0}^1 \left(\int_V \psi^\lambda \frac{d\rho^\lambda}{d\lambda} d\mathbf{r} + \int_S \psi^\lambda \frac{d\sigma^\lambda}{d\lambda} d\mathbf{S} \right) d\lambda \quad (2.1)$$

where $\rho^\lambda(\mathbf{r})$ is any bulk charge density, $\sigma^\lambda(\mathbf{r})$ any surface charge density, and $\psi^\lambda(\mathbf{r})$ the electrostatic potential at $\mathbf{r}$, all at the stage λ in this charging step. The charges in the system may be bulk, surface, or both. Boundaries occur at each interface, e.g., at each reactant's interface with the surrounding medium. The integral over $d\mathbf{r}$ denotes an integral over the volume V of the entire large system, and the integral over $d\mathbf{S}$ denotes the integral over all surfaces S (including interfaces).

The usual electrostatic relations obtain

$$-\nabla\psi^\lambda = \mathbf{E}^\lambda, \quad 4\pi\rho^\lambda = \nabla \cdot \mathbf{D}^\lambda, \quad 4\pi\sigma^\lambda = \text{Div } \mathbf{D}^\lambda \quad (2.2)$$

during the charging step. $\mathbf{E}(\mathbf{r})$ denotes the electric field at $\mathbf{r}$, and Div is a standard symbol for the surface divergence. Equations 2.1 and 2.2 yield the standard result:

$$w = \frac{1}{4\pi} \int_{\lambda=0}^1 \left(\int_V \mathbf{E}^\lambda \cdot \frac{d\mathbf{D}}{d\lambda} d\mathbf{r} \right) d\lambda \quad (2.3)$$

We consider next the two charging steps. The symbols used are summarized in Table 1.

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TABLE 1: Quantities at the Start and End of the Charging Steps

	start	end
step I	$\mathbf{D}^r, \mathbf{E}^r$	$\mathbf{D}^*, \mathbf{E}^*$
step II	$\mathbf{D}^*, \mathbf{E}^*$	$\mathbf{D}_n^r, \mathbf{E}_n^r$
relations	$\nabla \cdot \mathbf{D}^r - \nabla \cdot \mathbf{D}_n^r = \nabla \cdot \mathbf{D}_0^r$ $\mathbf{D}^* - \mathbf{D}^r = \epsilon_s(\mathbf{E}^* - \mathbf{E}^r), \mathbf{D}^* = \epsilon_s \mathbf{E}^*$ (or nonlocal form) $\mathbf{D}_n^r - \mathbf{D}^* = \epsilon_{op}(\mathbf{E}_n^r - \mathbf{E}^*)$ (or nonlocal form)	

Step I. The initial value of $\mathbf{D}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$, denoted by $\mathbf{D}^r(\mathbf{r})$ and $\mathbf{E}^r(\mathbf{r})$, is the equilibrium value for the reactants. The value of $\mathbf{D}$ and $\mathbf{E}$ at the end of this step is denoted by $\mathbf{D}^*$ and $\mathbf{E}^*$. In one application, for example, this $\mathbf{D}^*$ will denote a hypothetical $\mathbf{D}$ which would produce the orientational-vibrational dielectric polarization occurring in the transition state of an electron-transfer reaction.

We have

$$\mathbf{D}^\lambda = \mathbf{D}^r + \lambda(\mathbf{D}^* - \mathbf{D}^r) \quad (2.4a)$$

$$\mathbf{E}^\lambda = \mathbf{E}^r + \lambda(\mathbf{E}^* - \mathbf{E}^r) \quad (2.4b)$$

The relation between $\mathbf{D}^\lambda$ and $\mathbf{E}^\lambda$ during this step is the usual equilibrium one, which for a local response model is

$$\mathbf{D}^\lambda(\mathbf{r}) = \epsilon_s(\mathbf{r}) \mathbf{E}^\lambda(\mathbf{r}) \quad (2.5a)$$

or, for a nonlocal model,

$$\mathbf{D}^\lambda(\mathbf{r}) = \int \epsilon_s(\mathbf{r}, \mathbf{r}') \mathbf{E}^\lambda(\mathbf{r}') d\mathbf{r}' \quad (2.5b)$$

In eq 2.5a $\epsilon_s(\mathbf{r})$ is the static dielectric constant of the system at the point $\mathbf{r}$, regarded as piecewise continuous. In part I ϵ_s was taken as piecewise constant. Actually, the results in part II (and the present results) show that the final result also applies to nonlocal dielectrics, the main assumption being one of linearity, as in eq 2.5b, rather than in a specific functional form such as eq 2.5a. For the local case, $\epsilon_s(\mathbf{r}, \mathbf{r}') = \epsilon_s(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$.

Equations 2.3 and 2.4 yield

$$w_I = \frac{1}{8\pi} \int (\mathbf{E}^* \cdot \mathbf{D}^* - \mathbf{E}^r \cdot \mathbf{D}^r) d\mathbf{r} \quad (2.6)$$

where the integral is over the volume V of the entire system, cavities included. Equation 2.6 is valid regardless of whether or not interfaces are present.

Step II. In this step the orientational-vibrational polarization is held fixed at the value it had at the end of step I, and the change in $\mathbf{E}$ now responds to a change $\delta\mathbf{D}(\mathbf{r})$ in $\mathbf{D}$ only via the electronic contribution to the dielectric polarization of the medium. The dielectric constant at $\mathbf{r}$ describing that response is denoted, in the local model, by $\epsilon_{op}(\mathbf{r})$; that is, we have $\delta\mathbf{D}(\mathbf{r}) = \epsilon_{op}(\mathbf{r}) \delta\mathbf{E}(\mathbf{r})$. Accordingly, during the charging process in step II we have, in the case of a local model,

$$\mathbf{D}^\lambda - \mathbf{D}^* = \epsilon_{op}(\mathbf{E}^\lambda - \mathbf{E}^*) \quad (2.7)$$

For a nonlocal model an $\epsilon_{op}(\mathbf{r}, \mathbf{r}')$ is introduced instead, and the right-hand side then involves an integral over $\mathbf{r}'$.

The final value of $\mathbf{D}^\lambda$ in step II, denoted by $\mathbf{D}_n^r$, is chosen to be the $\mathbf{D}$ appropriate to the initial charges. It differs, however, from $\mathbf{D}^r$, since the polarization field at the beginning of step I differs from that at the end of step II, even though the ionic charges are the same. In a medium with interfaces there are usually dielectric image effects, which cause $\mathbf{D}_n^r$ and $\mathbf{D}^r$ to differ.

On the other hand $\mathbf{D}_n^r$ and $\mathbf{D}^r$ have the same divergence:

$$\nabla \cdot \mathbf{D}_n^r = \nabla \cdot \mathbf{D}^r = 4\pi\rho^r \quad (2.8)$$

The value of $\mathbf{E}$ at the end of step II is denoted by $\mathbf{E}_n^r$.

During step II using the linear relation between $\delta\mathbf{D}$ and $\delta\mathbf{E}$, and not necessarily a local one, we have

$$\mathbf{D}^\lambda - \mathbf{D}^* = \lambda(\mathbf{D}_n^r - \mathbf{D}^*) \quad (2.9a)$$

and

$$\mathbf{E}^\lambda - \mathbf{E}^* = \lambda(\mathbf{E}_n^r - \mathbf{E}^*) \quad (2.9b)$$

Introduction of these results into eq 2.3 yields the work done,

$$w_{II} = \frac{1}{4\pi} \int \left[\mathbf{E}^* + \frac{1}{2}(\mathbf{E}_n^r - \mathbf{E}^*) \right] \cdot (\mathbf{D}_n^r - \mathbf{D}^*) d\mathbf{r} \quad (2.10)$$

The sum of w_I and w_{II} gives the reversible work w needed to form a system with the as yet unknown $\mathbf{D}^*$ and so gives the free energy ΔG^* of formation of this fluctuation:

$$\Delta G^* = w = w_I + w_{II} = \frac{1}{2} \int [(\mathbf{E}_n^r - \mathbf{E}^*) \cdot (\mathbf{D}_n^r - \mathbf{D}^*) - (\mathbf{E}^* - \mathbf{E}^r) \cdot (\mathbf{D}^* - \mathbf{D}^r)] d\mathbf{r} \quad (2.11)$$

where a term that would have been present on the right-hand side of eq 2.11 can be shown⁵ to vanish:

$$\int (\mathbf{D}_n^r - \mathbf{D}^r) \cdot \mathbf{E}^* d\mathbf{r} = 0 \quad (2.12)$$

It was not assumed in the derivation of eq 2.11 that the $(\mathbf{E}, \mathbf{D})$ relationship is a local one.

Equation 2.11, which is more symmetric than the result in part I, can be written still more compactly by introducing the two hypothetical systems introduced in part II. They each have a charge density $\rho^* - \rho^r$, namely, the change in charge density in step I. The linear relations

$$\nabla \cdot (\mathbf{D}^* - \mathbf{D}^r) = 4\pi(\rho^* - \rho^r) \quad (2.13)$$

and

$$\mathbf{D}^* - \mathbf{D}^r = \epsilon_s(\mathbf{E}^* - \mathbf{E}^r) \quad (\text{local}) \quad (2.14a)$$

or

$$\mathbf{D}^* - \mathbf{D}^r = \int \epsilon_s(\mathbf{r}, \mathbf{r}') (\mathbf{E}^*(\mathbf{r}') - \mathbf{E}^r(\mathbf{r}')) d\mathbf{r}' \quad (\text{nonlocal}) \quad (2.14b)$$

show that a hypothetical system with a charge density $\rho^* - \rho^r$, denoted by ρ^{*-r} , produces an equilibrium electric field $\mathbf{E}^* - \mathbf{E}^r$, denoted below by $\mathbf{E}_s^{*-r}$, in a medium of a piecewise continuous static electric constant $\epsilon_s(\mathbf{r})$ (or having the nonlocal parameter $\epsilon_s(\mathbf{r}, \mathbf{r}')$ for the static system), and an equilibrium dielectric displacement, $\mathbf{D}^* - \mathbf{D}^r$, denoted below by $\mathbf{D}_s^{*-r}$.

Similarly, from the relations

$$\nabla \cdot (\mathbf{D}_n^r - \mathbf{D}^*) = 4\pi(\rho^r - \rho^*) \quad (2.15)$$

$$\mathbf{D}_n^r - \mathbf{D}^* = \epsilon_{op}(\mathbf{E}_n^r - \mathbf{E}^*) \quad (2.16)$$

(noting that ρ_n^r is ρ^r), it is seen that $\rho^r - \rho^*$ produces an equilibrium dielectric displacement $\mathbf{D}_n^r - \mathbf{D}^*$ and electric field $\mathbf{E}_n^r - \mathbf{E}^*$ in a medium of piecewise continuous dielectric constant $\epsilon_{op}(\mathbf{r})$ (or equivalent nonlocal parameter $\epsilon_{op}(\mathbf{r}, \mathbf{r}')$ for the electronically responding system), and so the latter will be denoted by $\mathbf{D}_{op}^{r-*}$ and $\mathbf{E}_{op}^{r-*}$, respectively.

Equation 2.11 may then be rewritten as

$$\Delta G^* = \frac{1}{8\pi} \int (\mathbf{E}_{op}^{*-r} \cdot \mathbf{D}_{op}^{*-r} - \mathbf{E}_s^{*-r} \cdot \mathbf{D}_s^{*-r}) d\mathbf{r} \quad (2.17)$$

Inasmuch as the first term is the equilibrium electrostatic free energy of a system with charge density $\rho^* - \rho^r$ and piecewise continuous dielectric constant $\epsilon_{op}(\mathbf{r})$, or an $\epsilon_{op}(\mathbf{r}, \mathbf{r}')$, while the second term is the corresponding quantity for a system with piecewise continuous dielectric constant $\epsilon_s(\mathbf{r})$, or an $\epsilon_s(\mathbf{r}, \mathbf{r}')$, eq 2.17 represents a simple form for the free energy ΔG^* of the fluctuation. It is seen to be identical to the result obtained in eq 2.3 of part II when the $\rho\psi$'s in eqs 17 and 18 there are converted to the $\mathbf{E} \cdot \mathbf{D}$'s here, using the standard relations (eq 2.2).

III. Minimization of ΔG^*

Taking variations in eq 2.17, noting that each $\int \delta \mathbf{E} \cdot \mathbf{D} d\mathbf{r}$ equals $\int \mathbf{E} \cdot \delta \mathbf{D} d\mathbf{r}$, since $\mathbf{D}$ is proportional to each $\mathbf{E}$ (with $\epsilon_s(\mathbf{r}, \mathbf{r}') = \epsilon_s(\mathbf{r}', \mathbf{r})$), we have

$$\delta \Delta G^* = \frac{1}{4\pi} \int (\mathbf{E}_{op}^{*-r} \cdot \delta \mathbf{D}_{op}^{*-r} - \mathbf{E}_s^{*-r} \cdot \delta \mathbf{D}_s^{*-r}) d\mathbf{r} \quad (3.1)$$

Inasmuch as the $\mathbf{E}_{op}^{*-r}$ and $\mathbf{E}_s^{*-r}$ are gradients of potentials in the present (electrostatic) case, it can readily be shown⁶ that the $\delta \mathbf{D}_{op}^{*-r}$ and $\delta \mathbf{D}_s^{*-r}$ in eq 3.1 can be replaced by $\delta \mathbf{D}_0^{*-r}$, where the $\mathbf{D}_0$ refers to the bare charges, i.e., charges in a vacuum. In turn, since $\delta \mathbf{D}_0^{*-r}$ equals $\delta \mathbf{D}_0^* - \delta \mathbf{D}_0^r$ and since $\mathbf{D}_0^r$ is not varied, we have

$$\delta \Delta G^* = \frac{1}{4\pi} \int (\mathbf{E}_{op}^{*-r} - \mathbf{E}_s^{*-r}) \cdot \delta \mathbf{D}_0^* d\mathbf{r} \quad (3.2)$$

Since $\delta \mathbf{D}_0^*$ is arbitrary, $\mathbf{E}_{op}^{*-r} - \mathbf{E}_s^{*-r}$ vanishes, and since $\epsilon_s \neq \epsilon_{op}$, $\mathbf{E}_{op}^{*-r}$ and $\mathbf{E}_s^{*-r}$ must vanish separately. Thereby, the nonequilibrium field $\mathbf{E}^*$ reduces to the equilibrium field $\mathbf{E}^r$, when the variation of ΔG^* to find a minimum is unconstrained.

In the case of an application to electron-transfer reactions there is a constraint: If ΔG_R^* denotes the standard free energy of reaction at a typical separation distance R in the transition state, we have^{1,3}

$$\Delta G_R^* = \Delta G^* - \Delta G_p^* \quad (3.3)$$

where ΔG_p^* is the free energy of formation of the transition state from the products at that R . Similarly to eq 3.2 one can write

$$\delta \Delta G_p^* = \frac{1}{4\pi} \int (\mathbf{E}_{op}^{*-p} - \mathbf{E}_s^{*-p}) \cdot \delta \mathbf{D}_0^* d\mathbf{r} \quad (3.4)$$

the $* - p$ signifying a charge density $\rho^* - \rho^p$.

We note that in the transition state the free energy G^* for the reactants has been shown to equal G_p^* for the products.¹ Thus, eqs 3.2–3.4 yield

$$0 = \frac{1}{4\pi} \int [(\mathbf{E}_{op}^{*-r} - \mathbf{E}_s^{*-r}) - (\mathbf{E}_{op}^{*-p} - \mathbf{E}_s^{*-p})] \cdot \delta \mathbf{D}_0^* d\mathbf{r} \quad (3.5)$$

Multiplying eq 3.5 by a Lagrangian multiplier m and adding to eq 3.2, we have

$$[(m+1)\mathbf{E}_{op}^{*-r} - m\mathbf{E}_{op}^{*-p}] - [(m+1)\mathbf{E}_s^{*-r} - m\mathbf{E}_s^{*-p}] = 0 \quad (3.6)$$

since $\delta \mathbf{D}_0^*$ is arbitrary. Since $\epsilon_s \neq \epsilon_{op}$, each of the terms in square brackets must vanish, and it follows that $(m+1)(\rho^* - \rho^r) - m(\rho^* - \rho^p) = 0$. That is,

$$\rho^* = (m+1)\rho^r - m\rho^p \quad (3.7)$$

This result for the "apparent charge density" ρ^* in the transition

state is the same as that obtained in the earlier papers of this series. This ρ^* is the hypothetical ρ which produces the orientational–vibrational polarization of the transition state.

We note that in electron-transfer reactions the charge density ρ^{*-r} giving rise to the $\mathbf{E}^{*-r}$ and $\mathbf{D}^{*-r}$'s in eq 2.17 is obtained from

$$\rho^{*-r} = \rho^* - \rho^r = m(\rho^r - \rho^p) \quad (3.8)$$

Thereby, ΔG^* for forming the transition state becomes

$$\Delta G^* = m^2 \lambda_0 \quad (3.9)$$

where

$$\lambda_0 = \frac{1}{8\pi} \int (\mathbf{E}_{op}^{r-p} \cdot \mathbf{D}_{op}^{r-p} - \mathbf{E}_s^{r-p} \cdot \mathbf{D}_s^{r-p}) d\mathbf{r} \quad (3.10)$$

and the fact that each $\mathbf{E} \cdot \mathbf{D}$ varies as the square of the charge density has been used. Since $\rho^* - \rho_p = (m+1)(\rho_r - \rho_p)$, it is also seen from eq 3.8 that

$$\Delta G_p^* = (m+1)^2 \lambda_0 \quad (3.11)$$

and so eqs 3.3, 3.9, and 3.11 yield the value of the Lagrangian multiplier m :

$$\Delta G_R^* = -(2m+1)\lambda_0 \quad (3.12)$$

As in earlier work,⁷ it is straightforward to add to the calculation of ΔG^* the classical contribution λ_l from the vibrations, eq 3.9 then becoming, instead,

$$\Delta G^* = m^2(\lambda_0 + \lambda_l) \quad (3.13)$$

where λ_l has its usual value. Similarly ΔG_p^* and ΔG_R^* are given by eqs 3.11 and 3.12 but with λ_0 replaced by $\lambda_0 + \lambda_l$.

If in eq 3.10 for λ_0 the reacting systems were treated as a pair of spheres, with radius a_i for reactant i ($i = 1, 2$), with a center-to-center separation distance of R , and with Δe denoting the magnitude of the change in charge of each reactant, eq 3.10 would yield the usual value,

$$\lambda_0 = (\Delta e)^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \quad (3.14)$$

when dielectric image effects are neglected.

IV. Comparison with Earlier Results

It is useful to compare eq 2.11 with some results given earlier in the literature. In part I ΔG^* is obtained from eq 25 there, which, rewritten in the present notation, yields

$$\Delta G^* = \frac{1}{2} \int \left[(\mathbf{P}^r - \mathbf{P}_n^r) \cdot \mathbf{D}_0^r + \mathbf{P}_u^* \cdot \left(\frac{\mathbf{P}_u^*}{\alpha_u} - \mathbf{E}_n^r \right) \right] d\mathbf{r} \quad (4.1)$$

where $\mathbf{P}^r(\mathbf{r})$ is the equilibrium polarization in the initial reactants' system and $\mathbf{P}_u^*(\mathbf{r})$ is a function of the orientation–vibrational polarization of the solvent in the nonequilibrium system. All of the quantities in eq 4.1 are functions of $\mathbf{r}$. $\mathbf{P}_u^*(\mathbf{r})$ is related in eq 4.2 below to the electric field $\mathbf{E}^*$ at the end of step I. $\mathbf{E}_n^r(\mathbf{r})$ and $\mathbf{P}_n^r$ are the electric field and the polarization for the nonequilibrium system, respectively, at the end of step II. We have, thereby,

$$\mathbf{P}_u^* = \alpha_u \mathbf{E}^*, \quad \mathbf{P}_n^r = \mathbf{P}_u^* + \alpha_e \mathbf{E}_n^r \quad (4.2)$$

where

$$4\pi\alpha_e = (\epsilon_{op} - 1) \quad (4.3)$$

$$4\pi\alpha_u = (\epsilon_s - \epsilon_{op}) \quad (4.4)$$

To relate eq 4.1 to 2.11 we first note from eqs 4.2–4.4 that

$$4\pi(\mathbf{P}^r - \mathbf{P}_n^r) = 4\pi(\mathbf{P}^r - \mathbf{P}^* + \mathbf{P}^* - \mathbf{P}_n^r) = (\epsilon_s - 1)(\mathbf{E}^r - \mathbf{E}^*) + (\epsilon_{op} - 1)(\mathbf{E}^* - \mathbf{E}_n^r) \quad (4.5)$$

Equation 4.1 then becomes

$$\Delta G^* = \frac{1}{8\pi} \int [(\mathbf{D}^* - \mathbf{D}_0^r) \cdot (\mathbf{D}^* - \mathbf{D}_n^r) \frac{1}{\epsilon_{op}} + (\mathbf{D}^r - \mathbf{D}_n^r) \cdot \mathbf{D}_0^r - [\mathbf{D}^* \cdot (\mathbf{D}^* - \mathbf{D}_n^r) + \mathbf{D}_0^r \cdot (\mathbf{D}^r - \mathbf{D}^*)] \frac{1}{\epsilon_s}] \mathbf{dr} \quad (4.6)$$

Using the fact that $\mathbf{D}^r$, $\mathbf{D}_n^r$, and $\mathbf{D}_0^r$ have a common divergence, $4\pi\rho^r$, it can be shown that eq 4.6 reduces to⁸

$$\Delta G^* = \frac{1}{8\pi} \int [(\mathbf{D}^* - \mathbf{D}_n^r)^2 / \epsilon_{op} - (\mathbf{D}^* - \mathbf{D}_n^r)^2 / \epsilon_s] \mathbf{dr} \quad (4.7)$$

which is the same as the local response case of eq 2.11. We note that the ϵ_s and ϵ_{op} in eq 4.7 are piecewise continuous and are typically specialized to be piecewise constant. Equation 4.7 corresponds to the result given by Liu and Newton.⁴

Another expression in the literature for the free energy G of a system with an arbitrary polarization $\mathbf{P}(\mathbf{r})$ for the static case has been given by Felderhof (among other properties given there for the dynamic case).⁹ In the present notation, it can be written as

$$G = \frac{1}{2} \int \alpha^{-1} \mathbf{P}(\mathbf{r}) \cdot \mathbf{P}(\mathbf{r}) \mathbf{dr} - \int \psi_0^r \nabla \cdot \mathbf{P}(\mathbf{r}) \mathbf{dr} + \frac{1}{2} \int \int \frac{(\nabla \cdot \mathbf{P}(\mathbf{r}))(\nabla \cdot \mathbf{P}(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} \mathbf{dr} \mathbf{dr}' \quad (4.8)$$

when magnetic effects are omitted. Here, ψ_0^r is the potential due to the bare charges ($\mathbf{D}_0^r = -\nabla\psi_0^r$). The static susceptibility α is $(\epsilon_s - 1)/4\pi$.

The first term on the right-hand side of eq 4.8 is the energy stored up in the polarized volume elements,¹ the second is the interaction of the polarized volume elements with the field due to the bare charges,¹ and the third is the interaction of the polarized volume elements with each other ($-\nabla \cdot \mathbf{P}(\mathbf{r})$ is equivalent to a charge density at $\mathbf{r}$ arising from the polarized volume element there). A self-energy term for the charges, $(1/2) \int \mathbf{D}_0^r \cdot \mathbf{D}_0^r \mathbf{dr}$, is not included in eq 4.8.

To compare with expressions in this paper, eq 4.8 can be rewritten as follows: the second term on the right side of eq 4.8 can be rewritten¹⁰ as $-\int \mathbf{P} \cdot \mathbf{D}_0^r \mathbf{dr}$. The last term in eq 4.8 is similarly rewritten¹⁰ as $(1/2) \int \mathbf{P} \cdot (\mathbf{D}_0^r - \mathbf{E}) \mathbf{dr}$, upon using eq 4.9 for $\mathbf{E}$ (e.g., Part I or ref 11).

$$\mathbf{E} = \mathbf{D}_0^r - \nabla \int \mathbf{P}(\mathbf{r}') \cdot \nabla \frac{1}{|\mathbf{r} - \mathbf{r}'|} \mathbf{dr}' \quad (4.9)$$

We then have

$$G = \frac{1}{2} \int [-\mathbf{P} \cdot \mathbf{D}_0^r + \mathbf{P} \cdot \left(\frac{\mathbf{P}}{\alpha} - \mathbf{E}\right)] \mathbf{dr} \quad (4.10)$$

The corresponding electrostatic free energy of the equilibrium system is $-(1/2) \int \mathbf{P}^* \cdot \mathbf{D}_0^r \mathbf{dr}$, and the ΔG associated with the fluctuation $\mathbf{P} - \mathbf{P}^r$ then becomes

$$\Delta G^* = \frac{1}{2} \int [(\mathbf{P}^r - \mathbf{P}) \cdot \mathbf{D}_0^r + \mathbf{P} \cdot \left(\frac{\mathbf{P}}{\alpha} - \mathbf{E}\right)] \mathbf{dr} \quad (4.11)$$

In eq 4.8, and thereby in eq 4.11, $\mathbf{P}$ is arbitrary. If eq 4.11 were valid for general $\mathbf{P}$, it would apply to the $\mathbf{P}$ given by the $\mathbf{P}_n^r$ in eq 4.1. If eqs 4.1 and 4.8 are equated, one finds that either α_e

= 0 or $\int \alpha_u (\mathbf{E}^* - \mathbf{E}_n^r)^2 \mathbf{dr}$ vanishes. But $\mathbf{E}^* \neq \mathbf{E}_n^r$ unless the polarization $\mathbf{P}_n^r$ is an equilibrium one. Thus for the class of $\mathbf{P}$'s in eq 4.2, eq 4.11, and thereby eq 4.8, is valid only when $\alpha_e = 0$. This result could probably have been anticipated from the discussion given in Appendix IV of part I, since eq 4.8 here contains only one explicit susceptibility α , while that appendix contains two.

In some recent discussions of free energy functionals^{12,13} the one-susceptibility form of eq 4.1 has been used (i.e., $\alpha_e = 0$). Indeed, a common model in computer simulations for the solvent in the literature has been one which neglects the electronic polarizability of the solvent, i.e., sets $\alpha_e = 0$. There is, of course, a need for simulations which avoid that approximation. We next compare eq 4.1 with eq 4.11 (and hence eq 4.8), for the special case for which eq 4.8 is valid, namely, for $\alpha_e = 0$. In this particular case the $\mathbf{P}_u^*$ in eq 4.1 is $\mathbf{P}$, the $\mathbf{E}_n^r$ is $\mathbf{E}$, and eq 4.11 is, at first glance, now more general than eq 4.1, in that the $\mathbf{P}$ in eq 4.11 is arbitrary but the one in the derivation of eq 4.1 in the body of the text of part I is restricted to being longitudinal.¹⁴ ($\mathbf{P}_u^*$ is assumed to be derivable from a potential in the electrostatic case (eq 4.2) and hence to be longitudinal.)¹⁴ Various authors^{12,13,15} have noted this relationship between eqs 4.1 and 4.8, although not necessarily explicitly noting the restriction on eq 4.11 that $\alpha_e = 0$. Lee and Hynes¹⁵ extended Felderhof's equation, eq 4.8, by not requiring that $\alpha_e = 0$. As they and others have noted, a case of particular interest for electron transfers is that actually given in eq 4.2, namely, where $\mathbf{P}_u^*$ is longitudinal.^{12–15} Chandra and Bagchi¹² have given, for $\alpha_e = 0$ and for general k , a more general expression for the free energy functional.

While the derivation of eq 4.1 given in the body of the text of part I does assume a longitudinal $\mathbf{P}_u^*$, it is interesting to note that the one given in Appendix IV of part I does not. Thereby, eq 4.1 is actually more general than is implied by the derivation in the body of the text of part I. It is actually equivalent to that in the work of Lee and Hynes,¹⁵ which did not require $\mathbf{P}_u^*$ to be longitudinal. The equivalence of this result in ref 15 and that in Appendix IV of part I, which led to eq 4.1, is seen by noting that the $\int \mathbf{P} \cdot \mathbf{E} \mathbf{dr}$ term in eq 4.1 ($\mathbf{P}$ denotes $\mathbf{P}_u^*$) can be rewritten using eq 4.9 as $\int \mathbf{P} \cdot \mathbf{D}_0^r \mathbf{dr} - \int \mathbf{P}(\mathbf{r}) \cdot \nabla \int \mathbf{P}(\mathbf{r}') \cdot \nabla' (1/|\mathbf{r} - \mathbf{r}'|) \mathbf{dr}'$. Employing Gauss's theorem twice converts the latter of these two integrals to $\int \int [\nabla \cdot \mathbf{P}(\mathbf{r}) \nabla \cdot \mathbf{P}(\mathbf{r}')] \mathbf{dr} \mathbf{dr}' / |\mathbf{r} - \mathbf{r}'|$. The final result is then seen to be equivalent to that in eq A1 of ref 15, taking into account the remark included with ref 15 regarding any surface terms. The class of $\mathbf{D}^*$'s considered in deriving eq 2.11 is restricted, on the other hand, to those given by eq 2.14. Equation 2.14a, for example, assumes a longitudinal $\mathbf{P}_u^*(\mathbf{r})$.

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References and Notes

- (1) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 979 (Part I).
- (2) Examples include the following: Pekar, S. I. *Untersuchungen über die Elektronentheorie der Kristalle*; Akademie Verlag: Berlin, 1954. Dogonadze, R. R. In *Reactions of Molecules at Electrodes*; Hush, N. S., Ed.; McGraw Hill: New York, 1971. Ulstrup, J. *Charge Transfer Processes in Condensed Media*; Springer-Verlag: Berlin, 1979. Dogonadze, R. R.; Kuznetsov, A. M. *Progr. Surf. Sci.* **1979**, *6*, 1. See also: Schmidt, P. P. *Electrochemistry. A Specialist Periodical Report*; Chemical Society: London, 1975; Vol. 5, p 21.
- (3) Marcus, R. A. *J. Chem. Phys.* **1963**, *38*, 1858 (Part II). A statistical mechanical linear response treatment is given in part III: Marcus, R. A. *Ibid.* **1963**, *39*, 1734. Applications of the potential-charge expression are given in part II itself and in the following: Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 1261; *J. Phys. Chem.* **1990**, *94*, 1050.
- (4) Liu, Y.-P.; Newton, M. D. *J. Phys. Chem.*, in press. See, particularly, Appendix A. These authors also discuss the relation of the ideas in part I on nonequilibrium polarization systems to others in the literature.
- (5) Longitudinal and transverse field components (curl-free and divergence-free components, respectively) and the decomposition of a vector field into

them are discussed in the following: Craig, D. P.; Thirunamachandran, T. *Molecular Quantum Electrodynamics*; Academic Press: New York, 1984; pp 9 and 53 ff. Since the $\mathbf{E}^*(\mathbf{r})$ in eq 2.12 is derivable from a potential, it has only a curl-free component in $\mathbf{r}$ space, $\mathbf{E}_1^*(\mathbf{r})$ and so only a longitudinal component in Fourier transform $\mathbf{k}$ space. Since $\nabla \cdot (\mathbf{D}_n^f - \mathbf{D}^*)$ equals $4\pi(\rho^f - \rho^*)$, it vanishes, and therefore the $\mathbf{D}_n^f - \mathbf{D}^*$ in eq 2.12 has at most a divergence-free component in $\mathbf{r}$ space, $\mathbf{D}_{n,\perp}^f - \mathbf{D}_\perp^*$, and so only a transverse component in $\mathbf{k}$ space. It has no constant term since we consider $\mathbf{D}$'s (and $\mathbf{E}$'s) which vanish at any large distance from the reactants. Thus, the scalar product in eq 2.12 vanishes.

(6) The proof parallels that in ref 5. For example, $\mathbf{E}_{op}^{*-r}$ has only a longitudinal component, since it is derivable from a potential, while $\delta\mathbf{D}_{op}^{*-r} - \delta\mathbf{D}_0^{*-r}$ has only a transverse component, since its divergence, which equals $4\pi(\rho^* - \rho^f - \rho^* + \rho^{r*})$, vanishes. The scalar product of the two therefore vanishes, so showing that the $\delta\mathbf{D}_{op}^{*-r}$ can be replaced by $\delta\mathbf{D}_0^{*-r}$. The same argument applies to the s -subscripted term in eq 3.1.

(7) E.g.: Marcus, R. A. *Discuss. Faraday Soc.* 1960, 29, 21.

(8) The proof parallels that in ref 6. The $(\mathbf{D}^* - \mathbf{D}_n^f)/\epsilon_{op}$ is written as $\mathbf{E}^* - \mathbf{E}_n^f$, and the $(\mathbf{D}^f - \mathbf{D}^*)/\epsilon_s$ is written as $\mathbf{E}^f - \mathbf{E}^*$.

(9) Felderhof, B. U. *J. Chem. Phys.* 1977, 67, 493, eq 3.1, where we omit the magnetic field terms and treat a tensor α^{-1} there as a scalar.

(10) Gauss's theorem is used after writing $\mathbf{D}_0$ as $-\nabla\psi_0$, and the resulting surface integral over the large volume V vanishes as $V \rightarrow \infty$. For the last term in eq 4.8 the theorem and this result are applied twice.

(11) Mason, M.; Weaver, W. *The Electromagnetic Field*; University of Chicago Press: Chicago, 1929.

(12) Chandra, A.; Bagchi, B. *J. Chem. Phys.* 1991, 94, 2258.

(13) Calef, D. F.; Wolynes, P. G. *J. Phys. Chem.* 1983, 87, 3387.

(14) The terminology of curl-free ($\mathbf{r}$ space) or longitudinal ($\mathbf{k}$ space) for $\mathbf{P}_u^*$ given by eq 4.2 is strictly applicable in the interior of each domain of $\mathbf{r}$ space only when α_u is piecewise constant. $\mathbf{E}^*$ on the other hand is always curl-free. Thus, the restriction on $\mathbf{P}_u^*$ is not so much that it is curl-free but rather that it is given by the first half of eq 4.2.

(15) Lee, S.; Hynes, J. T. *J. Chem. Phys.* 1988, 88, 6853. Equation A1 of this reference also contains surfaces terms, which could be added to eq 4.9. Alternatively, since a piecewise constant dielectric behavior (e.g., α_u) is assumed in the present eq 4.1, any surface can be replaced by a very thin volume which encloses the surface, and eq 4.1 then can be used as before.