

Swelling mechanism unique to charged gels: Primary formulation of the free energy

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This paper discusses the principal origin of the swelling behaviors inherent in charged gels. We start from a general formula for the free energy of the system consisting of a charged gel and the surrounding reservoir. First, it is clarified that the main term in the ionic contribution to the system free energy when the backbone network of gel is smeared with uniform density over the gel region is the translational entropy term of small ions freely mobile *over the entire system*, and therefore has no contribution to the swelling. Moreover, it is derived, from the system free energy within the Gaussian approximation, that the effective electrostatic interactions energy between charged groups on the network is obtained from summing the Yukawa-type potential which is screened by small ions inside a gel as has been speculated before, but that the corresponding interactions energy in smearing charged groups is to be subtracted from the total. These theoretical investigations reduce the starting formula for the system free energy to a more tractable form, which reveals that the ionic swelling behaviors are mainly ascribed to conformational changes of the backbone networks induced by alterations of the effective electrostatic interaction between charged groups. [S1063-651X(98)01911-4]

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I. INTRODUCTION

Charged gels are jellylike materials consisting of backbone charged networks (or crosslinked polymer chains with charged groups) and absorbed polar solvents, i.e., sucked mixtures of nonionic solvent molecules (water, for example) and small ions (counterions dissociated from the charged groups and added salts ions). The gels have some remarkable macroscopic properties [1]. First of all, the swelling degree of aqueous gels with charged groups of the same sign is much larger than that of uncharged ones in the absence of added salts. The superabsorbent characteristic has been widely applied to industrial products. Other fascinating phenomena are abrupt volume changes (volume phase transition) induced by changing either the quality of nonionic solvent or ionic conditions such as added salt concentration and pH, by applying the electric field, and so on [1]. The structural transition on a mesoscopic scale has been also discovered [1,2]: neutron scattering measurement suggests a possibility that charged gels may undergo the microphase separation by changing temperature.

In spite of the attractive features, an ambiguity remains concerning the theoretical treatment for charged gels, in that so far there have coexisted three different interpretations for the swelling mechanism unique to charged gels: the ionic swelling behaviors have been explained by the translational entropy difference of small ions between the inside and outside of gel (the entropic origin) [1,3–6], the averaged difference of the Coulomb potential between the both sides (the potential difference origin) [3,7], or the effective electrostatic interactions between charged groups (the electrostatic origin) [6–11].

In classical theories, it seems to have been considered that the difference between these explanations is due to the distinct simplifications of the system generally including local-

ized polymers with charged groups [3,7,12]. Recent theories also lack deliberate discussions about the uncertainty; there are two types of theories for explaining the dependence of the swelling degree and the elasticity on the ionic conditions experimentally reported [13]: some [1,5,6] are mainly based on the entropic interpretation (the first explanation) and additionally take into account the effect of the effective electrostatic interactions between charged groups, whereas others [8–11] suppose that the third electrostatic origin is essential in the ionic behaviors. In addition, all of theoretical treatments on more advanced subjects, e.g., the volume phase transition [1,14,15] and the microphase separation [16,17], belong to the former type.

Thus the present paper aims at settling the swelling mechanism unique to charged gels. To this end, it is indispensable to start from a general formula for the free energy of the system, including not only a charged gel but also the surrounding reservoir, which is presented in Sec. II. In Sec. III, we clarify the main term in the ionic contribution to the system free energy when the backbone network is smeared with uniform density over the gel region; the principal term definitely determines if the entropic or the potential difference interpretation is convincing, or both of them are misleading. In Sec. IV, the starting formula for the system free energy introduced in Sec. II is reduced to a more tractable form by evaluating the effective electrostatic interactions energy between charged groups within the Gaussian approximation. In Sec. V, the reduced form of the system free energy leads to the conclusion on the swelling mechanism. Section VI is for concluding remarks.

II. STARTING FORMULA OF THE SYSTEM FREE ENERGY

In experimental studies [1,2,13], a charged gel usually exists surrounded by a polar solvent. Then, for the purpose of explaining the swelling behaviors inherent in charged gels, one has to consider the gel system with the volume V_{sys}

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consisting of a charged gel with the volume V_{gel} and the surrounding reservoir, which is illustrated in Fig. 1.

The free energy F of the gel system (the system free energy) averaged over all possible crosslink realizations may be expressed as [8–10,18]

$$F = -k_B T \sum_{\mathbf{S}} P(\mathbf{S}) \ln Z(\mathbf{S}), \quad (2.1)$$

with use of the thermal energy $k_B T$, the distribution function $P(\mathbf{S})$ for a particular crosslink configuration \mathbf{S} , and the constrained partition function $Z(\mathbf{S})$ being of the functional integral form [19]

$$Z(\mathbf{S}) = \int D\mathbf{R}(s) \prod_i \int D\rho_i(\mathbf{r}) C(\{\mathbf{R}(s)\}; \mathbf{S}) \delta \left[\int d\mathbf{r} \rho_i(\mathbf{r}) - N_i \right] \exp \left[-\beta F_{\text{ion}} \left(\{\mathbf{R}(s_g)\}; \sum_i \{\rho_i(\mathbf{r})\} \right) \right]. \quad (2.2)$$

The meanings of symbols in Eq. (2.2) are as follows. $\{\mathbf{R}(s)\}$ and $\{\mathbf{R}(s_g)\}$ are coordinates sets of monomers and charged groups, respectively, which are specified by the arc length variables s and s_g (a subset of s). $\{\rho_i(\mathbf{r})\}$ is a set of densities for small ions of the i th kind located at the position vectors $\{\mathbf{r}\}$ covering the entire system. The integral measures are formally given as $D\mathbf{R}(s) \equiv \prod_{0 \leq s \leq L} d\mathbf{R}(s)$ with the total contour length of the network L and $D\rho_i(\mathbf{r}) \equiv \prod_{\{\mathbf{r}\}} d\rho_i(\mathbf{r})$. $C(\{\mathbf{R}(s)\}; \mathbf{S})$ stands for the constraint regarding the network and is written as

$$C(\{\mathbf{R}(s)\}; \mathbf{S}) = \prod_{0 \leq s \leq L} \delta[(\partial \mathbf{R}(s)/\partial s)^2 - 1] \prod_{c=1}^{N_c} \delta[\mathbf{R}(s_c) - \mathbf{R}(s'_c)], \quad (2.3)$$

where the first δ function on the right hand side (rhs) of Eq. (2.3) arises from the geometric constraint for a differentiable curve and the second with the number of crosslinks N_c is due to a set of crosslinks being at $\mathbf{S} = \{s_c, s'_c\}$. The δ function in Eq. (2.2) relating the density ρ_i to the total number N_i of the i th small ions describes the number invariance of the canonical system. Lastly the ionic free energy $F_{\text{ion}}(\{\mathbf{R}(s_g)\}; \sum_i \{\rho_i\})$, as a function of both given coordinates set of charged groups $\{\mathbf{R}(s_g)\}$ and specified densities sets of small ions $\sum_i \{\rho_i(\mathbf{r})\}$, is given in the form [19]

$$\beta F_{\text{ion}} \left(\{\mathbf{R}(s_g)\}; \sum_i \{\rho_i\} \right) = \frac{l_B}{2} \int d\mathbf{r} \int d\mathbf{r}' \left\{ z_g \rho_g(\mathbf{r}) + \sum_i z_i \rho_i(\mathbf{r}) \right\} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left\{ z_g \rho_g(\mathbf{r}') + \sum_i z_i \rho_i(\mathbf{r}') \right\} + \int d\mathbf{r} \sum_i \rho_i(\mathbf{r}) \ln \rho_i(\mathbf{r}). \quad (2.4)$$

Here the concentration of charged groups $\rho_g(\mathbf{r})$ is related to the position vectors $\{\mathbf{R}(s_g)\}$ as

$$\rho_g(\mathbf{r}) = \sum_{g=1}^{N_g} \delta[\mathbf{r} - \mathbf{R}(s_g)] \quad (2.5)$$

with use of the number of charged groups N_g , $l_B = e^2/4\pi\epsilon k_B T$ is the Bjerrum length with the elementary charge e and the dielectric constant ϵ , and z_g and z_i are the valences of charged groups (the sign of which is considered the same for simplicity in the following) and small ions, respectively. Note that the condition, $z_g N_g + \sum_i z_i N_i = 0$, is imposed on the numbers, so that the global electrical neutrality of the system is satisfied.

III. MAIN TERM IN THE IONIC FREE ENERGY FOR THE SMEARED NETWORK

First, let us consider the ionic contribution to the system free energy when the backbone network is smeared with uniform density over the gel region. Denoting such free energy by $F_{\text{ion}}(\bar{\rho}_g)$, with the smeared value of the charged groups density given as $\bar{\rho}_g = N_g/V_{\text{gel}}$, we have

$$\exp[-\beta F_{\text{ion}}(\bar{\rho}_g)] = \prod_i \int D\rho_i \delta \left[\int d\mathbf{r} \rho_i - N_i \right] \times \exp \left[-\beta F_{\text{ion}} \left(\bar{\rho}_g; \sum_i \{\rho_i\} \right) \right], \quad (3.1)$$

where $F_{\text{ion}}(\bar{\rho}_g; \sum_i \{\rho_i\})$ is obtained by replacing $\rho_g(\mathbf{r})$ in Eq. (2.4) with $\bar{\rho}_g$.

In terms of the density functional integral form (3.1), the corresponding mean-field free energy F_{MF} is identified with the contribution from the saddle-point path [20]

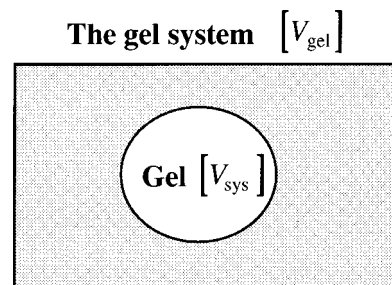


FIG. 1. Schematic of the gel system with the volume V_{sys} consisting of a charged gel with the volume V_{gel} and the surrounding reservoir of a polar solvent.

$$\begin{aligned} \beta F_{\text{MF}} = & \frac{l_B}{2} \int d\mathbf{r} \int d\mathbf{r}' \left\{ z_g \bar{\rho}_g + \sum_i z_i \langle \rho_i(\mathbf{r}) \rangle \right\} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\ & \times \left\{ z_g \bar{\rho}_g + \sum_i z_i \langle \rho_i(\mathbf{r}') \rangle \right\} \\ & + \int d\mathbf{r} \sum_i \langle \rho_i(\mathbf{r}) \rangle \ln \langle \rho_i(\mathbf{r}) \rangle, \end{aligned} \quad (3.2)$$

where the mean-field density $\langle \rho_i(\mathbf{r}) \rangle$, satisfying the relation

$$\left. \frac{\delta F_{\text{ion}}(\bar{\rho}_g, \sum_i \{\rho_i\})}{\delta \rho_i} \right|_{\rho_i = \langle \rho_i \rangle} = 0 \quad (3.3)$$

under the condition that $\int d\mathbf{r} \rho_i = N_i$, is obtained as

$$\langle \rho_i(\mathbf{r}) \rangle = \frac{N_i}{\int d\mathbf{r} \exp\{-\beta z_i e \psi(\mathbf{r})\}} \exp\{-\beta z_i e \psi(\mathbf{r})\}, \quad (3.4)$$

with the Coulomb potential $\psi(\mathbf{r})$ defined by

$$\psi(\mathbf{r}) = \frac{e}{4\pi\epsilon} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left\{ z_g \bar{\rho}_g + \sum_i z_i \langle \rho_i(\mathbf{r}') \rangle \right\}. \quad (3.5)$$

Incidentally, the excess free energy due to the deviation of small ions density from the mean-field value is evaluated within the Gaussian approximation in Appendix A, which gives the conventional Debye-Hückel correction term [7,21]. In the following, however, the additional part is ignored for simplicity and we set $F_{\text{ion}}(\bar{\rho}_g) = F_{\text{MF}}$.

Substituting Eq. (3.4) into the entropy term, i.e., the last term on the rhs of Eq. (3.2), we have

$$\begin{aligned} \int d\mathbf{r} \sum_i \langle \rho_i \rangle \ln \langle \rho_i \rangle = & \sum_i N_i \ln \frac{N_i}{V_{\text{sys}}} \\ & - \sum_i N_i \ln \frac{\int d\mathbf{r} \exp(-\beta z_i e \psi)}{V_{\text{sys}}} \\ & - \int d\mathbf{r} \beta \sum_i z_i e \langle \rho_i \rangle \psi. \end{aligned} \quad (3.6)$$

With the help of the parameter λ for charging process ($0 \leq \lambda \leq 1$), the last two terms on the rhs of Eq. (3.6) are rewritten as

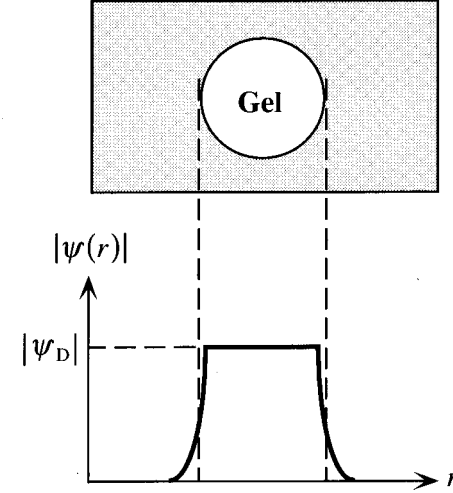


FIG. 2. Schematic of the Coulomb potential $\psi(\mathbf{r})$ when charged groups are smeared uniformly over the gel region. The potential satisfies the Poisson-Boltzmann equation, i.e., the combination of Eqs. (3.4) and (3.11) with setting $\lambda = 1$.

$$\begin{aligned} & - \sum_i N_i \ln \frac{\int d\mathbf{r} \exp(-\beta z_i e \psi)}{V_{\text{sys}}} \\ & = - \int_0^1 d\lambda \frac{\partial}{\partial \lambda} \left[\sum_i N_i \ln \left\{ \int d\mathbf{r} \exp(-\beta z_i \lambda e \psi_\lambda) \right\} \right] \\ & = \beta \int_0^1 d\lambda \int d\mathbf{r} \sum_i z_i e \langle \rho_i \rangle_\lambda \frac{\partial(\lambda \psi_\lambda)}{\partial \lambda} \end{aligned} \quad (3.7)$$

and

$$\begin{aligned} & - \beta \int d\mathbf{r} \sum_i z_i e \langle \rho_i \rangle \psi \\ & = - \beta \int_0^1 d\lambda \int d\mathbf{r} \frac{\partial}{\partial \lambda} \left\{ \sum_i z_i \lambda e \langle \rho_i \rangle_\lambda \psi_\lambda \right\}, \end{aligned} \quad (3.8)$$

with $\langle \rho_i(\mathbf{r}) \rangle_\lambda$ and $\psi_\lambda(\mathbf{r})$ obtained from replacing e in Eqs. (3.4) and (3.5) by λe . In the same way, the mean-field electrostatic energy, i.e., the first term on the rhs of Eq. (3.2), reads

$$\frac{l_B}{2} \int d\mathbf{r} \int d\mathbf{r}' \left\{ z_g \bar{\rho}_g + \sum_i z_i \langle \rho_i(\mathbf{r}) \rangle \right\} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left\{ z_g \bar{\rho}_g + \sum_i z_i \langle \rho_i(\mathbf{r}') \rangle \right\} = \frac{\beta}{2} \int_0^1 d\lambda \int d\mathbf{r} \frac{\partial}{\partial \lambda} \left[\lambda \left\{ z_g e \bar{\rho}_g + \sum_i z_i e \langle \rho_i \rangle_\lambda \right\} \psi_\lambda \right]. \quad (3.9)$$

Equations (3.6)–(3.9) transform expression (3.2) for the mean-field free energy F_{MF} to [22]

$$\beta F_{\text{MF}} = - \frac{\beta \epsilon}{2} \int_0^1 d\lambda \int d\mathbf{r} \left[\Delta \Phi_\lambda \frac{\partial(\lambda^2 \Phi_\lambda)}{\partial \lambda} - \frac{\partial(\Delta \Phi_\lambda)}{\partial \lambda} (\lambda^2 \Phi_\lambda) \right] + \sum_i N_i \ln \frac{N_i}{V_{\text{sys}}} = \int_0^1 d\lambda \frac{2}{\lambda} \left[\frac{\beta \epsilon}{2} \int d\mathbf{r} E_\lambda^2 \right] + \sum_i N_i \ln \frac{N_i}{V_{\text{sys}}}. \quad (3.10)$$

Here we have used the Poisson equation

$$\Delta\psi_\lambda(\mathbf{r})\equiv\lambda\Delta\Phi_\lambda(\mathbf{r})=-\frac{\lambda}{\varepsilon}\left\{z_g e\bar{\rho}_g+\sum_i z_i e\langle\rho_i(\mathbf{r}')\rangle_\lambda\right\}, \quad (3.11)$$

and the relations, $\Delta\Phi_\lambda\{\partial(\Phi_\lambda)/\partial\lambda\}-\{\partial(\Delta\Phi_\lambda)/\partial\lambda\}\Phi_\lambda=0$ and $\nabla\cdot(\Phi_\lambda\nabla\Phi_\lambda)=\Delta\Phi_\lambda(\Phi_\lambda)+(\nabla\Phi_\lambda)^2$. Also $\mathbf{E}_\lambda=-\nabla\psi_\lambda$ is the electric field with an arbitrary charging parameter λ .

As found from solving the Poisson-Boltzmann equation [e.g., the combination of Eqs. (3.4) and (3.11) for $\lambda=1$], the electric field \mathbf{E}_λ in Eq. (3.10) is localized in the vicinity of the gel surface, except in the trivial case of $\lambda=0$, to satisfy the local electrical neutrality elsewhere (see Fig. 2), and hence the first term on the rightmost side of Eq. (3.10) is negligible in comparison with the other terms for larger gels which are the concerns of the present paper [23]. In other words, setting $F_{\text{ion}}(\bar{\rho}_g)=F_{\text{MF}}$ as stated above, the main term in the ionic free energy for the smeared network is the translational entropy term of small ions which are freely mobile *over the entire system*:

$$\beta F_{\text{ion}}(\bar{\rho}_g)\approx\sum_i N_i \ln \frac{N_i}{V_{\text{sys}}}. \quad (3.12)$$

IV. REDUCED FORM OF THE SYSTEM FREE ENERGY

Introducing the ionic free energy for the actual network $F_{\text{ion}}\{\mathbf{R}(s_g)\}$,

$$\exp[-\beta F_{\text{ion}}\{\mathbf{R}(s_g)\}]=\prod_i \int D\rho_i \delta\left[\int d\mathbf{r} \rho_i - N_i\right] \exp\left[-\beta\left\{F_{\text{ion}}\left(\{\mathbf{R}(s_g)\};\sum_i \{\rho_i\}\right)\right\}\right], \quad (4.1)$$

similarly to Eq. (3.1), the starting formula (2.2) for the constrained partition function $Z(\mathbf{S})$ is rewritten as

$$Z(\mathbf{S})=\exp[-\beta F_{\text{ion}}(\bar{\rho}_g)] \int D\mathbf{R}(s) C(\{\mathbf{R}(s)\};\mathbf{S}) \exp[-\beta(F_{\text{ion}}\{\mathbf{R}(s_g)\}-F_{\text{ion}}(\bar{\rho}_g))]. \quad (4.2)$$

In Appendix B, the difference between the actual ionic free energy $F_{\text{ion}}\{\mathbf{R}(s_g)\}$ and the smeared one $F_{\text{ion}}(\bar{\rho}_g)$ is evaluated within the Gaussian approximation as

$$\beta(F_{\text{ion}}\{\mathbf{R}(s_g)\}-F_{\text{ion}}(\bar{\rho}_g))=-\frac{2\pi l_B z_g^2}{\kappa_{\text{in}}^2} \bar{\rho}_g^2 V_{\text{gel}} + \frac{l_B z_g^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_g(\mathbf{r}) \frac{\exp(-\kappa_{\text{in}}|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \rho_g(\mathbf{r}'), \quad (4.3)$$

where κ_{in}^{-1} is the screening length determined by the concentration of small ions inside gel [see also definition (A13) in Appendix A].

Thus, the combination of Eqs. (2.5), (3.12), (4.2), and (4.3) reduces the system free energy F given by Eqs. (2.1) and (2.2) to

$$\beta F = \sum_i N_i \ln \frac{N_i}{V_{\text{sys}}} - \frac{2\pi l_B}{\kappa_{\text{in}}^2} (z_g \bar{\rho}_g)^2 V_{\text{gel}} - \sum_{\mathbf{S}} P(\mathbf{S}) \ln Z_{\text{net}}(\mathbf{S}) \quad (4.4)$$

and

$$Z_{\text{net}}(\mathbf{S}) = \int D\mathbf{R}(s) C(\{\mathbf{R}(s)\};\mathbf{S}) \exp\left\{-\frac{l_B z_g^2}{2} \sum_{g,h=1}^{N_g} \frac{\exp(-\kappa_{\text{in}}|\mathbf{R}(s_g)-\mathbf{R}(s_h)|)}{|\mathbf{R}(s_g)-\mathbf{R}(s_h)|}\right\}. \quad (4.5)$$

$Z_{\text{net}}(\mathbf{S})$ is dependent only on the position vectors of monomers $\{\mathbf{R}(s)\}$, and may be called the constrained partition function of the backbone network. It is seen from the exponent on the rhs of Eq. (4.5) that the potential of the effective electrostatic interactions between charged groups is of the Yukawa type, which is screened by small ions not outside but inside a gel, as has been often speculated before excepting Ref. [7].

To be noted here, the additional osmotic pressure $\Delta\Pi$ produced by the second term on the rhs of Eq. (4.4) is obtained in the form (see Appendix C)

$$\beta\Delta\Pi = -\frac{\bar{\rho}_g}{2} \left(\frac{2C_s}{\bar{\rho}_g}\right)^2 \left\{1 + \left(\frac{2C_s}{\bar{\rho}_g}\right)^2\right\}^{-3/2}, \quad (4.6)$$

with C_s being the concentration of added salt. Equation (4.6) indicates that $\Delta\Pi$ vanishes with little added salts (i.e., $2C_s/\bar{\rho}_g \ll 1$) even though $\Delta\Pi$ converges to the conventional Donnan form with the opposite sign, i.e., $\beta\Delta\Pi \approx -\bar{\rho}_g^2/4C_s$, in the case of fully added salt satisfying $2C_s/\bar{\rho}_g \gg 1$ [6,7]. That is, the second term on the rhs of Eq. (4.4)

plays no significant role in the ionic swelling behaviors which are remarkable in weakly screening regime such as $2C_s/\bar{\rho}_g \ll 1$.

Thus it is found that the ionic contribution to the system free energy given by Eqs. (4.4) and (4.5) mainly arises from the screened electrostatic interactions energy between charged groups in the constrained partition function of the charged network $Z_{\text{net}}(\mathbf{S})$.

V. SWELLING MECHANISM UNIQUE TO CHARGED GELS

The free energy of the system including a neutral gel has been often evaluated in the simplest approximation under the Flory-Rehner (FR) hypothesis [24] that the part from the interactions of the free energy may be determined independently of the network configuration. Applying the assumption to the present charged gel system, Eq. (4.5) reads

$$Z_{\text{net}}(\mathbf{S}) = \exp\left(-\frac{l_B z_g^2}{2} \bar{\rho}_g^2 \int d\mathbf{r} \int d\mathbf{r}' \frac{e^{-\kappa_{\text{in}}|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\right) \times \int D\mathbf{R}(s) C(\{\mathbf{R}(s)\}; \mathbf{S}). \quad (5.1)$$

Since the exponent in Eq. (5.1) is equal to the second term on the rhs of Eq. (4.4), expressions (4.4) and (4.5) for the system free energy F are further simplified as

$$\beta F = \sum_i N_i \ln \frac{N_i}{V_{\text{sys}}} - \sum_{\mathbf{S}} P(\mathbf{S}) \ln \left\{ \int D\mathbf{R}(s) C(\{\mathbf{R}(s)\}; \mathbf{S}) \right\}, \quad (5.2)$$

denoting by X the term which arises from the electrostatic interactions of excluded volume type. The first term on the rhs of Eq. (5.5) stands for the bending energy of the network and reveals the inapplicability of the FR hypothesis; the effective electrostatic interactions energy is strongly dependent on the network configuration. As speculated upon in Ref. [11], the sensitive stiffness of the charged network to ionic conditions would play an essential role in the swelling and elastic properties of highly charged gels.

Finally, we arrive at the conclusion that the ionic swelling behaviors of charged gels are mainly ascribed to conformational changes of the backbone networks induced by alterations of the screened electrostatic interaction between charged groups.

VI. CONCLUDING REMARKS

In the present paper, the primary formulation for the free energy of the gel system has been performed to obtain the correct explanation for swelling mechanism unique to

which has no ionic term, and hence reveals that the FR hypothesis is misleading explicitly in the case of the charged gel system.

Indeed, for weakly charged gels, the invalidity of the FR hypothesis has been confirmed from evaluating the third term on the rhs of Eq. (4.4), with use of both the replica trick and the well-known replacements [8–10]:

$$\prod_{0 \leq s \leq L} \delta[(\partial \mathbf{R} / \partial s)^2 - 1] \rightarrow \int_0^L ds \frac{3}{2l} \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \quad (5.3)$$

and

$$\frac{l_B z_g^2}{2} \sum_{g,h=1}^{N_g} \frac{e^{-\kappa_{\text{in}}|\mathbf{R}(s_g) - \mathbf{R}(s_h)|}}{|\mathbf{R}(s_g) - \mathbf{R}(s_h)|} \rightarrow \frac{l_B}{2} \left(\frac{z_g \alpha}{l} \right)^2 \int_0^L ds \int_0^L ds' \frac{e^{-\kappa_{\text{in}}|\mathbf{R}(s) - \mathbf{R}(s')|}}{|\mathbf{R}(s) - \mathbf{R}(s')|}, \quad (5.4)$$

where l is the monomer length (or the cutoff length), and α is the number ratio of charged groups to monomers.

For highly charged gels, on the other hand, the analogy with the corresponding polyelectrolyte solutions suggests that the charged network with little added salts behaves like a rigid rod at least in a local scale. Hence, according to Odijk and Skolnick and Fixman theories [25], we have

$$\frac{l_B}{2} \left(\frac{z_g \alpha}{l} \right)^2 \left(\int_0^L ds \int_0^L ds' \frac{e^{-\kappa_{\text{in}}|\mathbf{R}(s) - \mathbf{R}(s')|}}{|\mathbf{R}(s) - \mathbf{R}(s')|} - \int_0^L ds \int_0^L ds' \frac{e^{-\kappa_{\text{in}}|s-s'|}}{|s-s'|} \right) = \frac{l_B}{8\kappa_{\text{in}}^2} \left(\frac{z_g \alpha}{l} \right)^2 \int_0^L ds \left(\frac{\partial^2 \mathbf{R}}{\partial s^2} \right)^2 + X \quad (5.5)$$

charged gels. First, it was clarified in Sec. III that the main term in the ionic free energy for the smeared network is the translational entropy term of small ions freely mobile *over the entire system*, and therefore has no contribution to the swelling of charged gels. This means the incorrectness of the first two interpretations described in Sec. I, that the ionic swelling is due to the entropic or the potential difference origin. Moreover, it was confirmed in Secs. IV and V that the effective electrostatic interactions between charged groups screened by small ions inside a gel (i.e., the electrostatic origin) determine the swelling inherent in charged gels. In other words, the superabsorptions of aqueous gels with charged groups of the same sign are due to the screened electrostatic repulsive forces between charged groups stretching out the backbone networks.

This paper suggests the next step: experimental results such as the dependence of the swelling degree and the elasticity on the ionic conditions [1,13], the volume phase transition [1], and the microphase separation [1,2] are to be re-

examined on the basis of the obtained picture [or by starting with expressions (4.4) and (4.5) for the system free energy].

In closing, we would like to stress that the present formulation of the charged gel system is general, and is applicable to other systems where some charges are localized in subregion while others are freely mobile over the entire system: such as asymmetric electrolytes (mixtures of small ions and either linear polyions or charged colloids), polyelectrolyte brushes where the chains are attached to planar solid surfaces, Donnan membrane systems consisting of both ‘‘inside’’ to which some charges are confined and ‘‘outside,’’ and so on. For a single polyelectrolyte chain and grafted polyelectrolyte layers, path-integral representations similar to Eq. (4.5) using replacements (5.3) and (5.4) have often been (but somewhat *a priori*) used in studying the chain conformations [26]. Similar discussions to that in this paper would clarify the validity of the previous treatments. For Donnan membrane systems, on the other hand, although extensive theoretical investigations of the McMillan-Mayer type [21], where the ‘‘inside’’ is regarded as a grand canoni-

cal system, have elucidated that nonideal terms of the Donnan osmotic pressure are produced by the effective interactions between confined charges and not by the translational entropy of charges permeable through the membrane, the canonical formulation within our framework would present an alternative derivation.

APPENDIX A: EVALUATION OF THE IONIC FREE ENERGY FOR THE SMEARED NETWORK WITHIN THE GAUSSIAN APPROXIMATION

Let $\varphi_i(r)$ be the density difference between the actual value ρ_i and the mean-field one $\langle \rho_i \rangle$:

$$\varphi_i = \rho_i - \langle \rho_i \rangle, \quad (\text{A1})$$

and $F_{\Delta}(\bar{\rho}_g; \sum_i \{\varphi_i\})$ be the difference between $F_{\text{ion}}(\bar{\rho}_g; \sum_i \{\rho_i\})$ obtained from replacing $\rho_g(\mathbf{r})$ in Eq. (2.4) with $\bar{\rho}_g$ and F_{MF} given by Eq. (3.2). Then, $F_{\Delta}(\bar{\rho}_g; \sum_i \{\varphi_i\})$ is given as

$$\begin{aligned} \beta F_{\Delta}(\bar{\rho}_g; \sum_i \{\varphi_i\}) &= \frac{l_B}{2} \int d\mathbf{r} \int d\mathbf{r}' \left\{ \sum_i z_i \varphi_i(\mathbf{r}) \right\} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left\{ \sum_i z_i \varphi_i(\mathbf{r}') \right\} \\ &+ \int d\mathbf{r} \left[\sum_i \{ \langle \rho_i(\mathbf{r}) \rangle + \varphi_i(\mathbf{r}) \} \ln \left\{ 1 + \frac{\varphi_i(\mathbf{r})}{\langle \rho_i(\mathbf{r}) \rangle} \right\} + \sum_i \varphi_i(\mathbf{r}) \{ \beta z_i e \psi(\mathbf{r}) + \ln \langle \rho_i(\mathbf{r}) \rangle \} \right]. \end{aligned} \quad (\text{A2})$$

The last two terms on the rhs of Eq. (A2) cancel out due to both Eq. (3.4) and the number conservation condition, i.e.,

$$\int d\mathbf{r} \varphi_i(\mathbf{r}) = 0. \quad (\text{A3})$$

Moreover, by expanding the logarithmic term in Eq. (A2) up to quadratic terms within the Gaussian approximation and using condition (A3), Eq. (A2) is reduced to

$$\begin{aligned} \beta F_{\Delta} &= \frac{l_B}{2} \int d\mathbf{r} \int d\mathbf{r}' \left\{ \sum_i z_i \varphi_i(\mathbf{r}) \right\} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \left\{ \sum_i z_i \varphi_i(\mathbf{r}') \right\} \\ &+ \int d\mathbf{r} \sum_i \frac{\{\varphi_i(\mathbf{r})\}^2}{2\langle \rho_i(\mathbf{r}) \rangle}. \end{aligned} \quad (\text{A4})$$

Since the additional electrostatic interactions energy between inside and outside of gel in Eq. (A4) is principally ascribed to the supplementary electric field localized to the surface region of gel and thus may be ignored, Eq. (A4) is further simplified as

$$F_{\Delta} = \sum_{m=\text{in},\text{out}} F_{\Delta m}$$

and

$$\begin{aligned} \beta F_{\Delta m} &= \frac{l_B}{2} \int d\mathbf{r} \int d\mathbf{r}' \left\{ \sum_i z_i \varphi_{im}(\mathbf{r}) \right\} \frac{e^{-|\mathbf{r} - \mathbf{r}'|/d}}{|\mathbf{r} - \mathbf{r}'|} \\ &\times \left\{ \sum_i z_i \varphi_{im}(\mathbf{r}') \right\} + \int d\mathbf{r} \sum_i \frac{\{\varphi_{im}(\mathbf{r})\}^2}{2\langle \rho_i \rangle_m}. \end{aligned} \quad (\text{A5})$$

Here in and out denote the inside and outside of gel, respectively, and the first term on the rhs of Eq. (A5) is multiplied by the standard convergence factor, $e^{-|\mathbf{r} - \mathbf{r}'|/d}$ ($d^3 \sim V_{\text{sys}}$) [21], due to which the infrared divergence is regularized without use of the electrical neutrality condition as will be seen from Eq. (A10). Also $\varphi_{im}(\mathbf{r})$ ($m = \text{in}$ and out) are defined as $\varphi_{im} = \rho_{im} - \langle \rho_i \rangle_m$, and $\langle \rho_i \rangle_m$ are spacially invariant values given as

$$\langle \rho_i \rangle_{\text{out}} = \frac{N_i}{\int d\mathbf{r} \exp\{-\beta z_i e \psi(\mathbf{r})\}} \quad (\text{A6})$$

and

$$\langle \rho_i \rangle_{\text{in}} = \langle \rho_i \rangle_{\text{out}} \exp\{-\beta z_i e \psi_D\} \quad (\text{A7})$$

in terms of the potential difference ψ_D between the inside and outside of gel (see Fig. 2). Thus, considering $D\rho_{im} = D\varphi_{im} \equiv \prod_{\{r\}} d\varphi_{im}(\mathbf{r})$ and separating the mean-field free energy F_{MF} , Eq. (3.1) reads

$$\exp(-\beta F_{\text{ion}}(\bar{\rho}_g)) = \exp(-\beta F_{\text{MF}}) \prod_i \prod_{m=\text{in,out}} \int D\varphi_{im} \delta \left[\int d\mathbf{r} \varphi_i \right] \exp \left(-\beta F_{\Delta m} \left(\bar{\rho}_g; \sum_i \{\varphi_i\} \right) \right). \quad (\text{A8})$$

To proceed further, it is convenient to use the Fourier transform of $\varphi_{im}(\mathbf{r})$:

$$\varphi_{im}(\mathbf{p}) = \frac{1}{V_m} \int d\mathbf{r} \exp(i\mathbf{p} \cdot \mathbf{r}) \varphi_{im}(\mathbf{r}) \quad (\text{A9})$$

or $\varphi_{im}(\mathbf{r}) = \sum_{\mathbf{p}} \exp(-i\mathbf{p} \cdot \mathbf{r}) \varphi_{im}(\mathbf{p})$, where $V_{\text{in}} = V_{\text{gel}}$ and $V_{\text{out}} = V_{\text{sys}} - V_{\text{gel}}$. With use of $\varphi_{im}(\mathbf{p})$, Eq. (A5) is rewritten in the form

$$\beta F_{\Delta m} = 2\pi l_B V_m \sum_{\mathbf{p}} \left[\frac{\left\{ \sum_i z_i \varphi_{im}(\mathbf{p}) \right\}^2}{\mathbf{p}^2 (1/d)^2} + \sum_i \frac{\{z_i \varphi_{im}(\mathbf{p})\}^2}{4\pi l_B z_i^2 \langle \rho_i \rangle_m} \right]. \quad (\text{A10})$$

It is to be noted here that constraint (A3), i.e., $\int d\mathbf{r} \varphi_i(\mathbf{r}) \approx \sum_{m=\text{in,out}} \varphi_{im}(\mathbf{p})|_{\mathbf{p}^2=0} = 0$ in Eq. (A8), does not necessarily lead to $\varphi_{im}(\mathbf{p})|_{\mathbf{p}^2=0} = 0$: the terms of $\mathbf{p}^2 = 0$ in Eq. (A10) are relevant.

In the transformation from variables $\varphi_{im}(\mathbf{r})$ to $\varphi_{im}(\mathbf{p})$, we have $D\varphi_{im} = (J_i/z_i) \prod_{\mathbf{p}} d\{z_i \varphi_{im}(\mathbf{p})\}$ with the Jacobian J_i . Then, the density functional integral in Eq. (A8) is equivalent to the Gaussian integral over $z_i \varphi_{im}(\mathbf{p})$, which yields [27]

$$\exp(-\beta F_{\text{ion}}(\bar{\rho}_g)) = \exp(-\beta F_{\text{MF}}) \times \exp \left\{ -\beta \sum_{m=\text{in,out}} F_{\text{DH}m}(\bar{\rho}_g) \right\} \quad (\text{A11})$$

and

$$\beta F_{\text{DH}m} = \frac{1}{2} \frac{V_m}{(2\pi)^3} \int d\mathbf{p} \ln \left(\frac{\mathbf{p}^2 + (1/d)^2 + \kappa_m^2}{\mathbf{p}^2 + (1/d)^2} \right). \quad (\text{A12})$$

Here the screening length κ_m^{-1} ($m=\text{in}$ and out) is defined as

$$\kappa_m^2 = 4\pi l_B \sum_i z_i^2 \langle \rho_i \rangle_m, \quad (\text{A13})$$

and we have introduced the usual continuum limit

$$\sum_{\mathbf{p}} \cong \frac{V_m}{(2\pi)^3} \int d\mathbf{p}, \quad (\text{A14})$$

and have ignored the terms which do not affect the swelling and elastic properties of charged gels.

Performing the integral in Eq. (A12), we obtain

$$F_{\text{ion}}(\bar{\rho}_g) = F_{\text{MF}} + F_{\text{DH}} \quad (\text{A15})$$

and

$$\beta F_{\text{DH}} \cong - \sum_{m=\text{in,out}} \frac{\kappa_m^3}{12\pi} V_m, \quad (\text{A16})$$

where the ultraviolet divergent terms have been omitted and $\kappa_m^{-1} \ll d$ ($m=\text{in}$ and out) has been considered. Note that F_{DH} corresponds to the Debye-Hückel correction term of simple electrolyte solutions [7,21].

APPENDIX B: DERIVATION OF EQ. (4.3)

To derive expression (4.3), we have only to evaluate the ionic free energy for the actual network, i.e., $F_{\text{ion}}\{\mathbf{R}(s_g)\}$, since the smeared one has been obtained in Sec. III and Appendix A. The evaluation of $F_{\text{ion}}\{\mathbf{R}(s_g)\}$ below is performed in parallel to that of Appendix A.

Let $\varphi_i(\mathbf{r})$ be the concentration difference of the i th small ions, and $F_{\Delta}(\{\mathbf{R}(s_g)\}; \sum_i \{\varphi_i\})$ be the difference between $F_{\text{ion}}(\{\mathbf{R}(s_g)\}; \sum_i \{\rho_i\})$ defined by Eq. (2.4) and F_{MF} given as Eq. (3.2). By tracing the discussion from Eqs. (A2) to (A7), we obtain

$$\beta F_{\Delta}(\{\mathbf{R}(s_g)\}; \sum_i \{\rho_i\}) = \sum_{m=\text{in,out}} \beta F_{\Delta m}, \quad (\text{B1})$$

$$\beta F_{\Delta \text{in}} = \frac{l_B}{2} \int d\mathbf{r} \int d\mathbf{r}' \left\{ z_g(\rho_g(\mathbf{r}) - \bar{\rho}_g) + \sum_i z_i \varphi_{im}(\mathbf{r}) \right\} \frac{e^{-|\mathbf{r}-\mathbf{r}'|/d}}{|\mathbf{r}-\mathbf{r}'|} \left\{ z_g(\rho_g(\mathbf{r}') - \bar{\rho}_g) + \sum_i z_i \varphi_{im}(\mathbf{r}') \right\} \Bigg|_{m=\text{in}} + \int d\mathbf{r} \sum_i \frac{\{\varphi_{im}(\mathbf{r})\}^2}{2\langle \rho_i \rangle_m} \Bigg|_{m=\text{in}}, \quad (\text{B2})$$

and

$$\beta F_{\Delta\text{out}} = \frac{l_B}{2} \int d\mathbf{r} \int d\mathbf{r}' \left\{ \sum_i z_i \varphi_{im}(\mathbf{r}) \right\} \frac{e^{-|\mathbf{r}-\mathbf{r}'|/d}}{|\mathbf{r}-\mathbf{r}'|} \left\{ \sum_i z_i \varphi_{im}(\mathbf{r}') \right\} \Bigg|_{m=\text{out}} + \int d\mathbf{r} \sum_i \frac{\{\varphi_{im}(\mathbf{r})\}^2}{2\langle\rho_i\rangle_m} \Bigg|_{m=\text{out}}. \quad (\text{B3})$$

Then, Eq. (4.1) reads analogously to Eq. (A8):

$$\exp(-\beta F\{\mathbf{R}(s_g)\}) = \exp(-\beta F_{\text{MF}}) \prod_i \prod_{m=\text{in,out}} \int D\varphi_{im} \delta \left[\int d\mathbf{r} \varphi_i \exp \left(-\beta F_{\Delta m} \left(\{\mathbf{R}(s_g)\}; \sum_i \{\varphi_i\} \right) \right) \right]. \quad (\text{B4})$$

With use of the Fourier transforms of $\varphi_{im}(\mathbf{r})$ and $\rho_g(\mathbf{r})$ [which are defined as Eq. (A9)] and $\rho_g(\mathbf{p}) = (1/V_{\text{gel}}) \int d\mathbf{r} \exp(i\mathbf{p}\cdot\mathbf{r}) \rho_g(\mathbf{r})$, Eqs. (B2) and (B3) are transformed to

$$\begin{aligned} \beta F_{\Delta\text{in}} = & 2\pi l_B V_m \left[\frac{\left\{ \sum_i z_i \varphi_{im}(\mathbf{p}) \Big|_{\mathbf{p}^2=0} \right\}^2}{(1/d)^2} + \sum_i \frac{\{z_i \varphi_{im}(\mathbf{p}) \Big|_{\mathbf{p}^2=0}\}^2}{4\pi l_B z_i^2 \langle\rho_i\rangle_m} \right] \Bigg|_{m=\text{in}} \\ & + 2\pi l_B V_m \sum_{\mathbf{p}^2 \neq 0} \left(\frac{\left\{ z_g \rho_g(\mathbf{p}) + \sum_i z_i \varphi_{im}(\mathbf{p}) \right\}^2}{\mathbf{p}^2 + (1/d)^2} + \sum_i \frac{\{z_i \varphi_{im}(\mathbf{p})\}^2}{4\pi l_B z_i^2 \langle\rho_i\rangle_m} \right) \Bigg|_{m=\text{in}} \end{aligned} \quad (\text{B5})$$

and

$$\beta F_{\Delta\text{out}} = 2\pi l_B V_m \sum_{\mathbf{p}} \left[\frac{\left\{ \sum_i z_i \varphi_{im}(\mathbf{p}) \right\}^2}{\mathbf{p}^2 + (1/d)^2} + \sum_i \frac{\{z_i \varphi_{im}(\mathbf{p})\}^2}{4\pi l_B z_i^2 \langle\rho_i\rangle_m} \right] \Bigg|_{m=\text{out}} \quad (\text{B6})$$

respectively, where $\varphi_{im}(\mathbf{p}) \Big|_{\mathbf{p}^2=0} \neq 0$ ($m=\text{in}$ and out) is noted similarly to Appendix A. Thus, the Gaussian integral over $z_i \varphi_{im}(\mathbf{p})$ in Eq. (B4) yields

$$\exp(-\beta F\{\mathbf{R}(s_g)\}) = \exp(-\beta F_{\text{MF}}) \exp \left\{ -\beta \sum_{m=\text{in,out}} F_{\text{DH}m}(\{\mathbf{R}(s_g)\}) \right\}, \quad (\text{B7})$$

$$\begin{aligned} \beta(F_{\text{DH}})_{m=\text{in}}(\{\mathbf{R}(s_g)\}) &= \frac{1}{2} \ln \left(\frac{(1/d)^2 + \kappa_{\text{in}}^2}{(1/d)^2} \right) + \sum_{\mathbf{p}^2 \neq 0} \left[\frac{1}{2} \ln \left(\frac{\mathbf{p}^2 + (1/d)^2 + \kappa_{\text{in}}^2}{\mathbf{p}^2 + (1/d)^2} \right) + \frac{2\pi l_B V_{\text{gel}} \{z_g \rho_g(\mathbf{p})\}^2}{\mathbf{p}^2 + (1/d)^2 + \kappa_{\text{in}}^2} \right] \\ &= -\frac{2\pi l_B V_{\text{gel}} \{z_g \rho_g(\mathbf{p}) \Big|_{\mathbf{p}^2=0}\}^2}{(1/d)^2 + \kappa_{\text{in}}^2} + \sum_{\mathbf{p}} \left[\frac{1}{2} \ln \left(\frac{\mathbf{p}^2 + (1/d)^2 + \kappa_{\text{in}}^2}{\mathbf{p}^2 + (1/d)^2} \right) + \frac{2\pi l_B V_{\text{gel}} \{z_g \rho_g(\mathbf{p})\}^2}{\mathbf{p}^2 + (1/d)^2 + \kappa_{\text{in}}^2} \right], \end{aligned} \quad (\text{B8})$$

and

$$\beta(F_{\text{DH}})_{m=\text{out}}(\{\mathbf{R}(s_g)\}) = \sum_{\mathbf{p}} \frac{1}{2} \ln \left(\frac{\mathbf{p}^2 + (1/d)^2 + \kappa_{\text{out}}^2}{\mathbf{p}^2 + (1/d)^2} \right) \quad (\text{B9})$$

with the screening length κ_m^{-1} defined in Eq. (A13).

Comparing Eqs. (B7), (B8), and (B9) with Eqs. (A11) and (A12), Eq. (4.3) is derived:

$$\begin{aligned} \beta(F_{\text{ion}}\{\mathbf{R}(s_g)\} - F_{\text{ion}}(\bar{\rho}_g)) &= -\frac{2\pi l_B V_{\text{gel}} \{z_g \rho_g(\mathbf{p}) \Big|_{\mathbf{p}^2=0}\}^2}{(1/d)^2 + \kappa_{\text{in}}^2} + 2\pi l_B V_{\text{gel}} \sum_{\mathbf{p}} \frac{\{z_g \rho_g(\mathbf{p})\}^2}{\mathbf{p}^2 + (1/d)^2 + \kappa_{\text{in}}^2} \\ &= -\frac{2\pi l_B z_g^2}{\kappa_{\text{in}}^2} \bar{\rho}_g^2 V_{\text{gel}} + \frac{l_B z_g^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_g(\mathbf{r}) \frac{\exp(-\kappa_{\text{in}} |\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \rho_g(\mathbf{r}'). \end{aligned} \quad (\text{B10})$$

In the second line of Eq. (B10), we have used $\rho_g(\mathbf{p}) \Big|_{\mathbf{p}^2=0} = \bar{\rho}_g$ and $\kappa_{\text{in}}^{-1} \ll d$.

APPENDIX C: DERIVATION OF EQ. (4.6)

The screening length κ_{in}^{-1} inside a gel defined in Eq. (A13) is evaluated by taking $|z_g| = |z_i| = 1$ and $\langle \sum_i \rho_i \rangle_{\text{out}} = 2C_s$, with the concentration of added salt C_s as follows: since the total concentration $\langle \sum_i \rho_i \rangle_{\text{in}}$ of small ions inside a gel is given as

$$\left\langle \sum_i \rho_i \right\rangle_{\text{in}} = 2C_s \cosh(\beta e \psi_D), \quad (\text{C1})$$

and the local electrical neutrality condition inside a gel is written as

$$z_g \bar{\rho}_g = 2C_s \sinh(\beta e \psi_D), \quad (\text{C2})$$

we obtain

$$\kappa_{\text{in}}^2 = 4\pi l_B (\bar{\rho}_g^2 + 4C_s^2)^{1/2} \quad (\text{C3})$$

with use of the relation $\cosh^2 x - \sinh^2 x = 1$. Substituting Eq. (C3) into the second term on the rhs of Eq. (4.4), the additional osmotic pressure $\Delta\Pi$ is obtained:

$$\beta\Delta\Pi = \bar{\rho}_g^2 \frac{\partial}{\partial \bar{\rho}_g} \left\{ \frac{1}{\bar{\rho}_g V_{\text{gel}}} \left(-\frac{\bar{\rho}_g^2 V_{\text{gel}}}{2\{\bar{\rho}_g^2 + 4C_s^2\}^{1/2}} \right) \right\} = -\frac{\bar{\rho}_g}{2} \left(\frac{2C_s}{\bar{\rho}_g} \right)^2 \left\{ 1 + \left(\frac{2C_s}{\bar{\rho}_g} \right)^2 \right\}^{-3/2}. \quad (\text{C4})$$

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previous theoretical investigations of the charged gel system, though Eq. (3.10) is explicitly more tractable than Eq. (3.2).

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