

Lattice theory of solvation and dissociation in macromolecular fluids. I. Mean field approximation

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This paper analyzes solvation and association in macromolecular solvents using mean-field theory applied to several lattice-gas models. The thermodynamic functions of solvation and the equilibrium constant for association is calculated in terms of the temperature, pressure, and solvent molecular size. Applications to ion association in polymer electrolytes are discussed and the advantages and flaws of the model are critically analyzed. Exact results for a simple one dimensional model are also obtained and discussed.

I. INTRODUCTION

Ionic dissociation and ion mobility in electrolyte solutions is a long studied problem. This subject has come back into focus with the increasing interest in solid ionic conductors, and more recently in polymeric ionic conductors. The latter systems are essentially solutions of salt in polymeric hosts and their conductivity properties are determined as in other electrolyte solutions by the ion-host and ion-ion interactions. Considerable effort has been spent over the last decade in attempts to elucidate the effect of the polymer environment on these interactions and their consequences.

The present study was motivated by the recent series of papers of Torell and co-workers¹⁻³ in which ion association and mobility in polymer-salt complexes based on poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) were studied for several salts as functions of temperature, pressure, and molecular weight of the polymer. Ion association was monitored by Raman spectroscopy and the formation of ion pairs (tentatively assigned as contact rather than solvent separated pairs) was inferred from Raman shift in the vibrational spectrum of the associated anion relative to that of the "free" anion. The following observations of these studies are relevant to the present work.

(1) Ion pairing increases with increasing salt concentration in qualitatively similar fashion as in simple electrolytes.

(2) Ion pairing and association increases with temperature, above the host glass transition temperature, for perchlorate and triflate salts of Li^+ , Na^+ in PEO and PPO. The temperature dependence of ion association depends however on the system studied. It is practically temperature independent (in the range studied) for Cu^{2+} triflate complexes and it decreases with increasing temperature for complexes containing Nd^{3+} cations.

(3) Detailed thermodynamic analysis by Schantz⁴ of the ion association equilibrium in the NaCF_3SO_3 -PPO and LiClO_4 -PPO systems show a considerable negative free energy for the $M^+ + A^- \rightarrow MA$ reaction at room temperature ($\Delta G^0 = -26 \pm 5$ and -22 ± 5 kJ/mol, respectively),

small positive enthalpy ($\Delta H^0 = 4 \pm 8$ and 13 ± 8 kJ/mol, respectively) and large positive entropy ($T\Delta S^0 = 30 \pm 12$ and 36 ± 12 kJ/mol, respectively). The large entropy change which accompanies the association indicates that ion dissociation and linking with the host matrix has strong ordering effect on the system.

(4) Ion association strongly depends on the pressure: For the LiCF_3SO_3 -PPO complex (ratio of oxygen to cation content, O:M=32) the number of unpaired ions doubled when P increased from 1 atm to 3 kbar.

(5) The association constant $K_A = [MA]/[M^+][A^-]$ depends on the molecular weight of the host polymer. While earlier studies with NaCF_3SO_3 (O:M=16) in PPG (poly propylene glycol-PPO terminated with OH groups) show an increase of K_A with increasing molecular weight, M_{host} , in the range $M_{\text{host}} = 400-4000$ ($\sim 7-70$ repeat units) it was realized that this host size dependence could be associated with strong H-bond formation between the triflate anion and OH end groups of the polymer. Indeed, more recent studies with "endcapped chains"— CH_3 terminated PEO, show the opposite effect: K_A decreases with increasing size between 4 and 8 repeat units. Unfortunately, there is no overlap between the size ranges of these two groups of experiments. One can infer from the results published so far that with CH_3 -capped host polyethers, for which cation coordination to the electronegative oxygens is the main driving force for salt solvation and dissociation, that K_A decreases with increasing M_{host} . It has also been suggested, however, that the trend is reversed for longer chains ($r \geq 8$, where r is the number of repeat units) in which the cations may form transient crosslinks.

Schantz, Torell, and co-workers¹⁻⁴ have pointed out that the dependence of the conductivity of these salt-polymer complexes on the salt concentration and on the temperature, is mostly related to the effect of these factors on the local flexibility of the host. For example,¹ in PPO- NaCF_3SO_3 (O:M=30) the number of dissociated ions drop by $\sim 50\%$ when T increases from $T_g \sim 220$ to 300 K, whereas the conductivity increases in this range by 5 orders of magnitude. Still the issue of ion association in polymer electrolyte environments is of interest, both because of the

fundamental thermodynamic issues involved and because nonassociated ions affect, through the formation of transient crosslinks, the rigidity of the polymer solvent itself.

The observed temperature dependence of ion association in the Li^+ and Na^+ salt-polymer systems seems to be in accord with the observed salt precipitation from several sodium salt-PPO systems when the temperature is increased above ~ 340 K.⁵⁻⁷ The observation of the opposite trend in the Nd^{3+} system³ indicates that the temperature dependence is affected by details of the ion-ion and ion-host interactions. Also, recent experimental results of Boden *et al.*⁸ raises new questions concerning the dynamic implications of ionic association-dissociation equilibria in these systems.

The observed increase in the concentration of associated ion pairs in the monovalent salt-polymer systems with increasing T was contrary to initial intuitive expectations for "weak electrolytes"⁹ and also to earlier experimental work.¹⁰ However, similar trends are observed in many electrolyte solutions^{11,12(a),13,14} and has been explained in terms of the temperature dependence of the solvent dielectric constant. In the Bjerrum,¹⁵ Fuoss,¹⁶ and Denison and Ramsey¹⁷ theories of ion pairing, the fraction of ion pairs depends on the temperature through the inverse product, $(DT)^{-1}$, of the solvent dielectric constant, D , and the temperature. This fraction will increase with increasing temperature if

$$T \frac{\partial \ln D}{\partial T} < -1. \quad (1)$$

The same result is obtained from any theory which assumes that the free energy for the reaction $M^+ + A^- \rightarrow MA$ is negative and proportional to D^{-1} : If $\Delta G = -a/D$, ($a > 0$) then $\Delta H = \Delta G + T\Delta S = \Delta G - T(\partial\Delta G/\partial T) = -a/D[1 + T(\partial \ln D/\partial T)]$ implying that $\Delta H > 0$ if Eq. (1) holds. For the common model $D = D_0 e^{-T/\theta}$ this implies $T > \theta$, which holds for many liquids at room temperature.^{11,12(a)} For ethers and polyethers the temperature dependence of the dielectric constant is much weaker than in more polar solvents (c.g., $-dD/dT$ at 298 K is 0.36 K^{-1} for water, 0.2 K^{-1} for methanol, 0.194 K^{-1} for ethylene glycol but only 0.018 K^{-1} for di-2-propyl ether^{12(a)}). For amorphous high molecular weight PPO $-dD/dT \approx 0.016$ (Ref. 18) and the inequality (1) is less likely to hold. Indeed, from the T dependence of D for PPO¹⁸ we may infer that ion pairing should increase with temperature for $T \approx 310 \text{ K}$,¹⁹ whereas such increase is observed for $T > T_g \approx 220 \text{ K}$.

The observed decrease in ion association with increasing pressure in the Li-triflate-PPO complex is also in qualitative accord with observations in simple electrolytes.^{12(a)} The usual explanation^{12(a),20,21} involves the increase with pressure of the solvent dielectric constant and, possibly, the decrease with pressure of the effective ionic solvation radius. From the thermodynamic point of view this is related to the pressure dependence of the free energy of reaction

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \quad (2)$$

and to the expectation that the volume change ΔV associated with the $M^+ + A^- \rightarrow MA$ reaction in a dielectric solvent is positive because of the electrostriction effect which accompanies ion solvation. These considerations in turn point out to the solvent compressibility as a major source of the pressure effect, underlining the importance of the free volume of the solvent.

It is also of interest to consider the inter-relationship between the temperature and the pressure effect, e.g., by considering the temperature dependence of the association equilibrium constant at constant volume and at constant pressure. Note that while constant volume experiments are difficult, most numerical simulations in ionic solutions, including simulations of ion pairing processes^{22,23} are done at constant volume. Experimentally one can obtain constant volume data by extrapolating results obtained at different constant pressures. General thermodynamic relations lead to

$$\begin{aligned} \left(\frac{\partial H}{\partial \xi}\right)_{P,T} &= \left(\frac{\partial E}{\partial \xi}\right)_{V,T} + T \left(\frac{\partial P}{\partial T}\right)_{\xi,V} \left(\frac{\partial V}{\partial \xi}\right)_{P,T} \\ &= \left(\frac{\partial E}{\partial \xi}\right)_{V,T} + T \frac{\alpha}{\beta} \left(\frac{\partial V}{\partial \xi}\right)_{P,T}, \end{aligned} \quad (3)$$

where ξ is the reaction coordinate (e.g., for $M^+ + A^- \rightarrow MA$, ξ is the fraction of MA molecules which are associated) and where

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P, \quad \beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (4)$$

are the isobaric thermal expansion coefficient and the isothermal compressibility, respectively. On the other hand, the derivatives $(\partial H/\partial \xi)_{P,T}$ and $(\partial E/\partial \xi)_{V,T}$ determine the temperature dependence of ξ via the thermodynamical expression of the Le Chatellier principle

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{1}{TG''} \left(\frac{\partial H}{\partial \xi}\right)_{P,T}, \quad (5)$$

$$\left(\frac{\partial \xi}{\partial T}\right)_V = \frac{1}{TA''} \left(\frac{\partial E}{\partial \xi}\right)_{V,T}, \quad (6)$$

where $G'' = (\partial^2 G/\partial \xi^2)_{P,T,\text{eq}}$ and $A'' = (\partial^2 G/\partial \xi^2)_{V,T,\text{eq}}$ are the second derivatives of the Gibbs and Helmholtz free energies, respectively, at equilibrium of the reaction, and are both positive. Since $(\partial V/\partial \xi)_{P,T}$ is generally positive for the ionic association process, Eq. (3) implies that $(\partial E/\partial \xi)_{V,T} < (\partial H/\partial \xi)_{P,T}$. In particular it is possible that $(\partial E/\partial \xi)_{V,T} < 0$ whereas $(\partial H/\partial \xi)_{P,T} > 0$, implying qualitatively different behavior of $(\partial \xi/\partial T)_P$ and $(\partial \xi/\partial T)_V$. The factor $T\alpha/\beta$ in Eq. (3) is essentially the internal pressure ($P_{\text{int}} = T\alpha/\beta - P \approx T\alpha/\beta$, if P is not too high) of the solvent. For polyethylene glycols above T_g it is $\sim 0.4 \text{ kJ/cm}^3$,²⁴ and for a modest guess for $(\partial V/\partial \xi)_{P,T} \sim 15 \text{ cm}^3/\text{mol}$ we get $(\partial H/\partial \xi)_{P,T} - (\partial E/\partial \xi)_{V,T} \sim 6 \text{ kJ/mol}$, which is of the same order as the experimental enthalpy of association in the systems under consideration.⁴

While the thermodynamic factors governing ionic association-dissociation equilibria are known and have

been widely discussed, little is known about the dependence of these factors on solvent structure and on the details of solvent ion interactions. Our focus in the present work is on the macromolecular nature of the host. Specifically we pose the question: how does the molecular size and the molecular nature of the host affect the association–dissociation equilibrium? This issue is underlined by two observations:

(1) The (positive) entropy of ion pairing in the monovalent salt–PPG complexes [≥ 100 J/(K mol)] is larger than could be expected. This number is of the same order observed for NaClO₄ in 1-propanol²⁵ for which, at room temperature, $dD/dT = -0.14$ K⁻¹ whereas in the polyethers $|dD/dT|$ is an order of magnitude smaller. In acetone, where $dD/dT = -0.019$ K⁻¹ the association entropy of NaClO₄ is ~ 27 J/(K mol).²⁶

(2) The increase in association with increasing temperature in the 1:1 salt–polyether complexes and the salt precipitation observed at higher temperatures, is reminiscent of the common occurrence of lower critical solution temperature in polymer solutions. This phenomenon has been traced to the free volume dissimilarity between the mixture components,²⁷ and has been argued to be an entropically driven process.^{28,29} It has been speculated³ that the two phenomena, ion pairing and salt precipitation in salt–polymer complexes and phase separation in polymer–solvent mixtures are related phenomena.

In the present work we examine these issues within the lattice theory of liquids and of liquid mixtures. In particular we examine the equilibrium $A + B \rightleftharpoons AB$ where A and B are simple solutes, occupying one site on the lattice, in a solvent S whose molecules occupy r sites (r -mer). If A and B are taken identical, their association may be viewed as the first step in the process of phase separation. We are interested in the thermodynamic quantities which control the equilibrium and in their dependence on temperature and pressure for different sizes of the solvent. An important feature of the model is that it allows for finite solvent compressibility by including vacant sites. This feature is known to be necessary for the model to show, when applied to liquid mixtures, lower critical solution temperature,²⁸ and it can be therefore used to study the relation of this phenomenon to the behavior of the association–dissociation equilibrium.

The model is characterized by nearest neighbor interactions and, except for one dimension it relies on the mean field approximation. We recall that our focus includes possible entropic effects associated with the solvent molecular size and with the nature of the molecule ion binding. Two potential sources for such effects may be identified: (a) The effect of the molecular size on the entropy of mixing, a long studied problem in the lattice theories of fluid mixtures. (b) Cations dissolved in polyether hosts are known to form transient crosslinks and consequently reduce the configurational entropy of the host. The present mean-field treatment cannot account for the latter effect, and should be viewed as an approximate estimate of the importance of the former. The implications of crosslink formation in polymer

solvents for equilibria involving crosslinking agents remains an open problem to be treated in future work.

The use of short range interactions in the present study raises a question concerning the validity of the present calculation to the real polymer electrolytes. The systems considered are believed to be characterized by strong selective binding of the cations to the ether oxygens, with the maximum coordination number being probably four. At infinite dilution, ion–ion interactions (except between the ions constituting the pair) are negligible, and, in view of the large distance between oxygen atoms, cation interactions with oxygens which are not nearest neighbors to it are also expected to be relatively small. Finally, the entropic effects described above can clearly be discussed in terms of short range ion–host interactions, whereas long range effects may be incorporated in the dielectric response. As emphasized above, the latter cannot account by itself for the experimental observation. It appears therefore that short range interaction models of solvation equilibrium in these systems can supply relevant information.

Our focus is the equilibrium constant for ion pairing (or, more generally, the association reaction $A + B \rightleftharpoons AB$) and its dependence on temperature, pressure, and solvent molecular size. To this end we need to calculate the free energy of this reaction as a function of these parameters. The latter can be obtained from the solvation energies of the different components in the given medium. Mathematically this amounts to evaluating the free energy associated (within the present model) with inserting an impurity into the given lattice gas.

In what follows we first discuss solvation and dissociation–association equilibrium in two exactly solvable noninteracting lattice gas (NILG) models. Next we investigate the thermodynamics of association–dissociation equilibria in systems with nearest neighbor interactions within the framework of the mean field theory of fluid mixtures of Lacombe and Sanchez.²⁸ Implications of our results to the experimental work of Schantz, Torell, and co-workers are finally discussed. In addition we discuss the weakness of the present model when applied to systems with strong ion–solvent interaction. This weakness can be overcome by replacing the mean field approximation (MFA) by the quasichemical approximation (QCA) thereby taking into account short range correlations in the solvent structure about the ion. This version of the theory will be presented in a separate paper.

II. EXACTLY SOLUBLE MODELS

In this section we consider two simplified, exactly soluble models. The first is a simple NILG model where solvent–solvent interactions are only those forcing site exclusion, whereas solute–solvent interactions are limited to nearest neighbors. In the second model we take account of finite solvent molecule size, within a one dimensional NILG model. These models, even though simplistic, are useful in making clear some of the concepts developed afterwards.

A. The noninteracting lattice gas (NILG)

In this model each solvent molecule, s , occupies one site of the lattice ($r_s=1$) and multiple occupation of the same site is forbidden. The solute molecule, a , occupies r_a lattice sites and have l_a nearest-neighbor sites. The interaction between the solute and the solvent is taken as $-\epsilon_{as}$, ($\epsilon_{as}>0$, i.e., attractive interaction) for nearest-neighbors sites and zero otherwise. Note that this model, in the terms described above, is analogous to the adsorption of solvent molecules on l_a independent and indistinguishable sites.³⁰ In addition to solute and solvent particles, the lattice representation of the solvent contains vacancies (i.e., a component of the mixture which, except of the site blocking, does not interact with itself or with any of the other components). This is of course essential in describing phenomena where compressibility is expected to play a role.

The grand-canonical partition function (GPF) for the NILG monoatomic solvent containing one solute molecule, is given by

$$\Xi_\epsilon = \Xi_0 \left(\frac{1 + e^{\epsilon_{as}/kT} e^{\mu_s/kT}}{1 + e^{\mu_s/kT}} \right)^{l_a}, \quad (7)$$

where μ_s is the chemical potential of the pure solvent, M is the number of lattice sites, and Ξ_0 , the GPF for the pure solvent, is given by

$$\Xi_0 = (1 + e^{\mu_s/kT})^M. \quad (8)$$

The volume of the pure solvent is defined in terms of the number of the lattice sites as $V = Mv^*$, where v^* is the volume associated with a single site. Standard thermodynamical relations for the pressure P and the density of the pure solvent ρ_s yield

$$Pv^* = -kT \ln(1 - \rho_s), \quad (9)$$

$$\mu_s = kT \ln \frac{\rho_s}{1 - \rho_s}. \quad (10)$$

In general, the chemical potential of the solute, for the case of infinite dilution, is given by^{12(b)}

$$\begin{aligned} \mu_a &= kT \ln(\rho_a \Lambda_a^3 q_a^{-1}) - kT \ln \langle \exp[-W_s(R)/kT] \rangle_R \\ &= kT \ln(\rho_a \Lambda_a^3 q_a^{-1}) + \mu'_a, \end{aligned} \quad (11)$$

where k is the Boltzmann constant, ρ_a is the number density of the solute in the liquid, Λ_a is the momentum partition function or the thermal wavelength, q_a is the internal partition function of the solute, and $W_s(R)$ is the interaction energy of the solute, fixed at a certain position, with the solvent molecules when they are at a certain configuration R . The symbol $\langle \rangle_R$ represents the average over all the solvent configurations R . Expression (11) is obtained for a continuum model. For lattice models the general form is the same: μ_a is given by a sum of an intrinsic term which depends only on properties of the solute molecule and another term, μ'_a , which may be identified as the standard (infinite dilution) free energy of solvation ($\mu'_a = \Delta G_a$), provided that the changes in the internal partition function of the solute in passing from the gas phase to the solution are disregarded. For lattice gas models, where

$W_s(R)$ does not usually include the potential responsible for the restriction that two particles cannot occupy the same site, there is an additional term in the solvation energy which corresponds to the formation of a cavity in the solvent. Thus Eq. (11) is rewritten as

$$\mu_a = kT \ln(\rho_a \Lambda_a^3 q_a^{-1}) + \mu_a^{(c)} + \mu'_a, \quad (12)$$

where $\mu'_a = -kT \ln \langle \exp[-W_s(R)/kT] \rangle$ and where $W_s(R)$ represents the nearest neighbor and longer range solute-solvent interaction. $\mu_a^{(c)}$ is that part of the solvation free energy which is associated with cavity formation—inserting a noninteracting (except site exclusion) solute into the solvent.

Using the definition of μ'_a given by Eq. (11), it can be shown that it is given by (cf. Appendix A)

$$\mu'_a = \Delta G_a = -l_a kT \ln(1 - \rho_s + e^{\epsilon_{as}/kT} \rho_s). \quad (13)$$

The cavity formation term is easily shown to be

$$\mu_a^{(c)} = -r_a kT \ln(1 - \rho_s), \quad (14)$$

where r_a is the number of sites occupied by the solute. Here and in the following sections we will assume for simplicity that molecular sizes in the association reaction are additive so that $\mu_a^{(c)} + \mu_b^{(c)} = \mu_{ab}^{(c)}$. Under this assumption the cavity formation parts of the solvation free energy cancel out of the free energy of association and have no effect on the association equilibrium.

The changes in volume and enthalpy for this solvation process can be obtained from standard derivatives of ΔG_a together with the equation of state (9). A more instructive way is to use the average site occupation $\bar{\rho}_a$ for each of the l_a sites nearest to the solute³⁰

$$\bar{\rho}_a = \frac{e^{\mu_s/kT} e^{\epsilon_{as}/kT}}{1 + e^{\mu_s/kT} e^{\epsilon_{as}/kT}} = \frac{\rho_s e^{\epsilon_{as}/kT}}{1 - \rho_s + \rho_s e^{\epsilon_{as}/kT}}. \quad (15)$$

In terms of $\bar{\rho}_a$ the changes in volume, energy, enthalpy, and entropy are given by

$$\Delta E_a = -\epsilon_{as} l_a \bar{\rho}_a, \quad (16)$$

$$\Delta V_a = -\frac{l_a}{\rho_s} (\bar{\rho}_a - \rho_s) v^*, \quad (17)$$

$$\Delta H_a = \Delta E_a + P \Delta V_a, \quad (18)$$

$$\Delta S_a = \frac{1}{T} (\Delta H_a - \Delta G_a). \quad (19)$$

Note that $\bar{\rho}_a$ increases with increasing interaction ϵ_{as} . Also note that because of the noninteracting character of the NILG, it is necessary to use very high pressures (in the range of kbar) in order to obtain values of ρ_s in a range consistent with the liquid state ($\rho_s \approx 0.5-0.9$). Therefore, the value of P may be overestimated, assuming values of the order of the internal pressure P_{int} of common (interacting) solvents. Consequently, estimates of the $P \Delta V_a$ contribution in Eq. (18) may be exaggerated in this model.

Using the above results for the association reaction $A + B \rightarrow AB$ one gets for the changes in the thermodynamic functions of reaction

$$\Delta G_{\text{Assoc}} = \Delta G_{ab} - \Delta G_a - \Delta G_b - E_r = \mu'_{ab} - \mu'_a - \mu'_b - E_r, \quad (20)$$

$$\Delta E_{\text{Assoc}} = -E_r - (\epsilon_{ab} - l_{ab} \bar{p}_{ab} - \epsilon_{as} l_a \bar{p}_a - \epsilon_{bs} l_b \bar{p}_b), \quad (21)$$

$$\Delta V_{\text{Assoc}} = -\frac{v^*}{\rho_s} [l_{ab} \bar{p}_{ab} - l_a \bar{p}_a - l_b \bar{p}_b - (l_{ab} - l_a - l_b) \rho_s], \quad (22)$$

$$\Delta H_{\text{Assoc}} = \Delta E_{\text{Assoc}} + P \Delta V_{\text{Assoc}}, \quad (23)$$

$$\Delta S_{\text{Assoc}} = (1/T) (\Delta H_{\text{Assoc}} - \Delta G_{\text{Assoc}}), \quad (24)$$

where E_r is the energy of the opposite (dissociation) reaction ($E_r > 0$) and where μ'_i is given by Eq. (13), ($i = a, b, ab$). The equilibrium constant for the association-dissociation reaction is given by $K_{\text{Assoc}} = \exp(-\Delta G_{\text{Assoc}}/kT)$. Note that if one does not include the existence of empty sites in the fluid ($\rho_s = 1$) then $\Delta V_{\text{Assoc}} = 0$ while $\bar{p}_a = \bar{p}_b = \bar{p}_{ab} = 1$. ΔH_{Assoc} is then determined simply by the change in the interaction energies.

B. One-dimensional NILG with arbitrary solvent size

When the NILG solvent is polyatomic (occupying r_s adjacent sites) the calculation of the thermodynamic functions of solvation is considerably more involved and generally requires approximations. The results can no longer be represented as simple functions of the occupation probability of sites nearest neighbor to the solute. In fact, the number of configurations for a pure system of polyatomic molecules in a general lattice can be obtained exactly only in one dimension. The only exact result for $d > 1$ that is known to us is for a *completely filled* two dimensional lattice with molecules of size $r_s = 2$.³¹ For $d = 1$ an exact solution may be obtained; in fact in this case the problem may be shown to be isomorphic to the 1-D Ising model. In what follows we consider solvation in this one-dimensional model.

The system considered is a one-dimensional lattice gas in which the solute is the same as before whereas the solvent molecules are larger, each occupying r_s lattice sites. Note that this one-dimensional model lacks the important contributions of different molecular orientations that in higher dimensionalities will contribute to the partition function and to the thermodynamic functions. However, even this model shows dependence of the solvation thermodynamics on the solvent size.

It is convenient to use the canonical partition function (CPF) formulation of the problem. The CPF for the pure noninteracting solvent (Q_0) is determined by the number of configurations. The latter is given, for a lattice with M sites and N noninteracting molecules (blocking interactions only) of size r_s , by the number of ways to arrange $M - Nr_s$ identical holes and the N identical molecules on the lattice

$$Q_0(M, N) = \frac{(M - Nr_s + N)!}{(M - Nr_s)! N!}. \quad (25)$$

Using the standard thermodynamic relations for the CPF, namely, $A = -kT \ln Q$, $P = kT (\partial \ln Q / \partial V)_{N, T}$, and

$\mu_s = -kT (\partial \ln Q / \partial N)_{V, T}$, and using the Stirling's approximation for the factorials in Eq. (25), leads, in the thermodynamic limit, to

$$Pv^* = kT \ln \left[\frac{1 - \rho_s (1 - 1/r_s)}{1 - \rho_s} \right], \quad (26)$$

$$\mu_s = kT \left[\ln \left[\frac{\rho_s / r_s}{1 - \rho_s (1 - 1/r_s)} \right] - r_s \ln \left[\frac{1 - \rho_s}{1 - \rho_s (1 - 1/r_s)} \right] \right], \quad (27)$$

where $\rho_s = r_s N / M$. Equation (26) is the equation of state for the system. Note that the number of nearest neighbors l_a is 2 for this geometry. For $r_s = 1$ Eqs. (26) and (27) reduce to Eqs. (9) and (10), respectively.

The CPF for the system in which a solute molecule is introduced can be obtained in terms of Q_0 (see Appendix B). The final result for μ'_a is the difference between the free energies of the (solvent + solute) system with and without solute-solvent interaction (except exclusion). We get

$$\mu'_a = -2kT \ln \left[\frac{1 - \rho_s}{1 - \rho_s (1 - 1/r_s)} + \frac{\rho_s e^{\epsilon_{as}/kT} / r_s}{1 - \rho_s (1 - 1/r_s)} \right]. \quad (28)$$

Using standard relations for the thermodynamic derivatives of the free energy, together with the equation of state (26), then leads to

$$\Delta E_a = -2\epsilon_{as} \frac{\rho_s e^{\epsilon_{as}/kT} / r_s}{1 - \rho_s + \rho_s e^{\epsilon_{as}/kT} / r_s}, \quad (29)$$

$$\Delta V_a = 2v^* \frac{(1 - \rho_s)(1 - e^{\epsilon_{as}/kT})}{1 - \rho_s + \rho_s e^{\epsilon_{as}/kT} / r_s}, \quad (30)$$

$$\Delta H_a = \Delta E_a + P \Delta V_a, \quad (31)$$

$$\Delta S_a = \frac{1}{T} (\Delta H_a - \Delta G_a). \quad (32)$$

Here the contributions associated with the cavity formation were disregarded as discussed above. These exact results for the excess thermodynamical functions show, for a given solvent density ρ_s , explicit dependence on the solvent size r_s . It is interesting to note however that if we express the chemical potential of the solvent in terms of $\pi = \exp(-Pv^*/kT)$ instead of ρ_s , using Eq. (26), the resulting expression for μ'_a does not depend explicitly on the solvent size

$$\mu'_a = -2kT \ln [\pi + (1 - \pi) e^{\epsilon_{as}/kT}]. \quad (33)$$

Thus at constant pressure, μ'_a as well as quantities (e.g., ΔH_a , ΔV_a) derived from it by constant pressure derivatives, do not depend on the solvent size. This property of the excess thermodynamical quantities is special to the one dimensional model considered and is associated with the constraints imposed by the one dimensional geometry.

C. Mean field approximation

An exact calculation of solvation energies for solvents of arbitrary molecular size can be obtained only in one dimension, as described above. In the general $d > 1$ case

approximations are needed. Here we present the solution within the Flory–Huggins mean field approximation (MFA). The solvent is described as a mixture of molecules of size r_s and holes (of size 1) distributed on a lattice.^{32,33} The solvent–solute interaction is taken, as before, to be a nearest-neighbor interaction $-\epsilon_{as}$ ($\epsilon_{as} > 0$). The MFA is introduced by assuming that the solvent site occupation probability is ρ_s for sites not nearest neighbor to the solute, and is $\rho_s e^{\epsilon_{as}/kT} / (1 - \rho_s + \rho_s e^{\epsilon_{as}/kT})$ for sites nearest neighbor to the solute, where ρ_s is the pure solvent density.

This approximation is believed to be a good description for the pure (melt) polymer, since in this state the polymer behaves as ideal chains and the correlation length for the chains are of the size of a monomer.³⁴ Note however that changes in the internal entropy of the solvent associated with possible long range effects of its binding to the solute are disregarded.

Our pure solvent consists of N noninteracting (except site exclusion) r_s -mers distributed on a lattice of M sites (so the “free volume” is $N_0 \equiv M - r_s N$). For this system the Flory’s MFA³² assumes that the probability to insert subsequent monomer segments [of the $(n+1)$ th r -mer] into the lattice after n r -mers have been already inserted is taken to be proportional to the mean site availability. This leads to the canonical partition function (here—the number of configurations)

$$Q_0(M, N) = \left(\frac{\delta}{\sigma}\right)^N \frac{r_s^{r_s N}}{(M)^{N(r_s-1)} N!} \left[\frac{\left(\frac{M}{r_s}\right)!}{\left(\frac{M-r_s N}{r_s}\right)!} \right]^{r_s}, \quad (34)$$

where δ is the number of configurations of a chain with one of its ends at a given position. For a completely flexible chain without excluded volume effects, $\delta = z(z-1)^{r_s-2}$. σ is the symmetry number of the chain: For a chain with indistinguishable ends, $\sigma=2$; otherwise $\sigma=1$.

Using the Stirling’s approximation, the partition function (34) can be written in terms of the average occupation of a site, $\rho_s = r_s N / M$, in the form

$$Q_0(M, N) = \left(\frac{1}{1-\rho_s}\right)^{N_0} \left(\frac{\omega}{\rho_s}\right)^N, \quad (35)$$

where ω is given by

$$\omega = \frac{\delta r_s}{\sigma e^{r_s-1}}. \quad (36)$$

This is an internal entropy factor, and represents the number of configurations of the r -mer in the closed packed state.³³ From the partition function (35) we obtain the equation of state and the chemical potential of the solvent in the forms

$$Pv^* = kT \left[-\rho_s \left(1 - \frac{1}{r_s}\right) - \ln(1 - \rho_s) \right], \quad (37)$$

$$\mu_s = \ln \frac{\delta r_s}{\sigma} + r_s \ln(1 - \rho_s) - \ln(\rho_s). \quad (38)$$

Next consider the same solvent in the presence of a single impurity (“ion”) which interacts with nearest-neighbor solvent sites with interaction energy ϵ_{as} . We make the following ansatz for the solvent partition function $Q_\epsilon(M, N)$ in the presence of this impurity

$$Q_\epsilon(M, N) = [\rho_s e^{\epsilon_{as}/kT} + (1 - \rho_s)]^{l_a} Q_0(M, N). \quad (39)$$

The first factor on the right-hand side of Eq. (39) accounts for the solute–solvent interaction in the l_a sites nearest to the impurity, while the Q_0 factor represents the pure solvent. Equation (39) and the thermodynamic functions derived from it yield for $r_s=1$ the exact results of Sec. II A. Furthermore, the form (39) is consistent with the result obtained by applying the quasichemical approximation to the same model.³⁵ Using the same reasoning as in Sec. II B, the chemical potential of the solute (excess free energy at infinite dilution relative to the non-interacting solute case) is obtained in the form

$$\Delta G_a = \mu'_a = -l_a kT \ln(1 - \rho_s + \rho_s e^{\epsilon_{as}/kT}). \quad (40)$$

Standard derivatives of Eq. (40), together with equation of state (37) lead to the change in volume associated with the solvation

$$\Delta V_a = \frac{v^* r_s l_a (1 - \rho_s) (1 - e^{\epsilon_{as}/kT})}{(1 - \rho_s + \rho_s e^{\epsilon_{as}/kT}) [1 + \rho_s (r_s - 1)]} \quad (41)$$

and to the other excess thermodynamical quantities

$$\Delta E_a = -l_a \epsilon_{as} \frac{\rho_s e^{\epsilon_{as}/kT}}{1 - \rho_s + \rho_s e^{\epsilon_{as}/kT}}, \quad (42)$$

$$\Delta H_a = \Delta E_a + P \Delta V_a, \quad (43)$$

$$\Delta S_a = \frac{1}{T} (\Delta H_a - \Delta G_a). \quad (44)$$

Again, the cavity formation terms were disregarded, assuming that they cancel in ΔG_{Assoc} and related quantities. The equilibrium constant for the association reaction $A + B \rightleftharpoons AB$, is given, as in Sec. II A, in the form $K_{\text{Assoc}} = \exp(-\Delta G_{\text{Assoc}}/kT)$, where $\Delta G_{\text{Assoc}} = \Delta G_{ab} - \Delta G_a - \Delta G_b - E_r = \mu'_{ab} - \mu'_a - \mu'_b - E_r$.

Results based on this theory are displayed in Fig. 1. This figure shows the pure solvent density ρ_s (a), the solvation enthalpy ΔH_a (b), and the solvation entropy ΔS_a (c) as functions of the solvent molecular size r_s , for $Pv^*/kT = 1.609$ and for two values of the solute–solvent interaction: $\epsilon_{as}/kT = 2.0$ and $\epsilon_{as}/kT = 0.1$. In the present, mean-field, theory the results are independent of the lattice geometry, and when scaled by the number of nearest-neighbor sites l_a , are also independent of the dimensionality. For this pressure $\rho_s = 0.8$ for $r_s = 1$. In Figs. 1(b) and 1(c) only quantities derived from μ'_a are compared, in the spirit of the comment made after Eq. (44). In one dimension the MFA result is expected to be the least satisfactory, however, in this case the exact results, Eqs. (29)–(32) are available. As discussed above, the exact one-dimensional ΔH_a and ΔS_a do not depend on r_s at constant pressure, while the MFA results show such dependence.

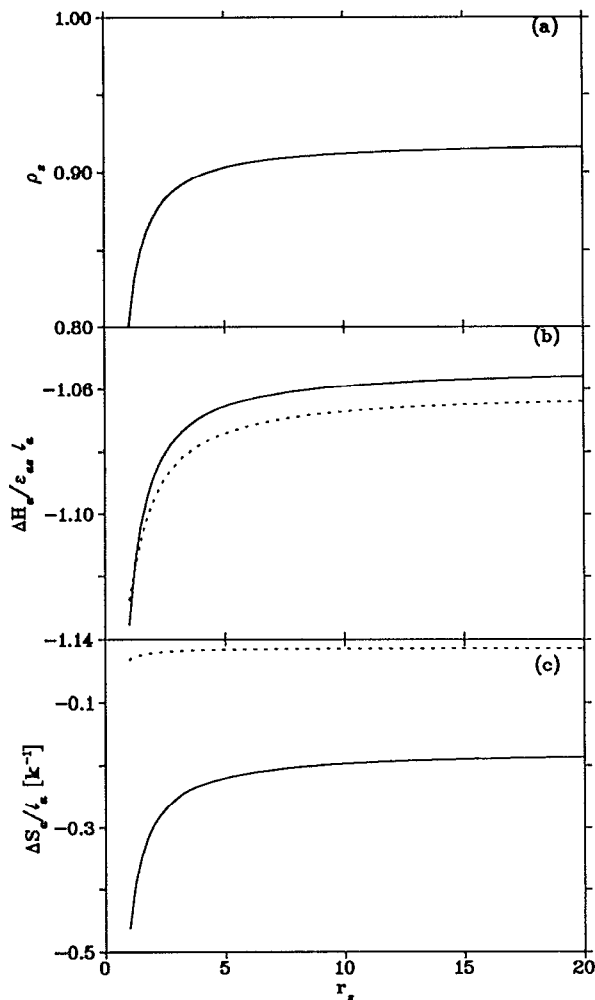


FIG. 1. The dependence of the pure solvent density (a), solvation enthalpy (b), and solvation entropy (c), on the solvent size expressed by r_s . The results are obtained from the mean-field theory for $\epsilon_{00}/kT=0.1$ (dotted line) and $\epsilon_{00}/kT=2$ (solid line), both at $Pv^*/kT=1.609$ (for this choice $\rho_s=0.8$ for $r_s=1$).

The models discussed so far are of the NILG type, with the solvent being the lattice equivalent of a hard-sphere fluid. In what follows we consider a model, due to Sanchez and Lacombe which takes into account interactions between solvent molecules in a mean-field scheme. We shall use the model in our first attempt to analyze the experimental result.

III. MEAN FIELD APPROXIMATION FOR INTERACTING LATTICE GAS

The models considered in Sec. II disregard solvent-solvent interactions. Another mean-field approach, due to Sanchez and Lacombe (SL)^{28,33} takes such interaction into account. The price paid in this approach is the neglect of correlations in the solvent structure near the solute which may be important for strong solvent-solute interactions. In this section we explore the consequences of this theory for the association reaction in general and for ion pairing in particular.

As before we consider the free energy associated with the insertion (at infinite dilution) of an impurity (solute) molecule to the pure solvent. From this solvation energy other thermodynamic quantities are derived. We again apply the result of this calculation to evaluate the thermodynamic quantities associated with a simple association reaction $A+B \rightarrow AB$. With appropriate choices for the interaction parameters for the different species, estimates for the equilibrium properties of ion-pairing reactions can be obtained. The dependence of this equilibrium on the nature of the solvent, on the solute-solvent interaction and on the temperature and the pressure is finally obtained within this model.

A brief review of the SL theory follows. The system studied consists of a mixture of N_i molecules of type i , ($i=1, \dots, k$), where i denotes the particular component of a k -component mixture. Each molecule occupies r_i sites on a lattice of coordination number z . The total number of sites is $M=N_0 + \sum_{i=1}^k r_i N_i$ where N_0 is the number of empty lattice sites. The average molecular size is defined as $r = \sum_{i=1}^k r_i N_i / N$, where $N = \sum_{i=1}^k N_i$ is the number of molecules. We also define $\phi_i = r_i N_i / rN$, so that $1/r = \sum_{i=1}^k \phi_i / r_i$. ϕ_i is the probability that a site is occupied by molecule of type i in a closed packed ($N_0=0$) mixture.

The volume of the system is defined, as before, by $V = Mv^*$, where v^* is the average volume of a lattice site in the mixture. In general, v^* is a function of the volumes v_i^* that will be used in a lattice description of the pure component i , but in this simplified approach we take $v_i^* = v^*$, independent of i . Using a closed-packed volume, defined as $V^* = v^* rN$, the reduced volume \tilde{v} and the reduced density ρ can be defined as $\tilde{v} = V/V^* = 1/\rho$. Then, using the definitions for ϕ_i and \tilde{v} , the probability of occupation of a given site by a molecule of kind i is given by $\rho_i = \phi_i \rho = r_i N_i / M$. It is also useful to define the closed packed mass density of component i , $\rho_i^* = m_i / (r_i v^*)$, where m_i is the corresponding molecular weight.

The energy of the system, considering only nearest neighbor interactions is given by

$$E = - \sum_{i=1}^k \sum_{j>i} N_{ij} \epsilon_{ij}, \quad (45)$$

where N_{ij} is the number of nearest-neighbor pairs of molecules of types i and j and where ϵ_{ij} is the (attractive) interaction energy between particles of kinds i and j . The latter is assumed to be temperature independent. The interaction between an empty site and its neighbors is taken zero. For N_{ij} Sanchez and Lacombe³³ use a mean-field approximation

$$N_{ij} = \frac{1}{2} z M \rho_i \rho_j \quad (46)$$

which leads to

$$E = -\frac{z}{2} M \sum_{i=1}^k \sum_{j=1}^k \rho_i \rho_j \epsilon_{ij}$$

$$= -M \sum_{i=1}^k \sum_{j=1}^k \rho_i \rho_j \epsilon_{ij}^* = -M \rho \epsilon^*, \quad (47)$$

where $\epsilon_{ij}^* \equiv (z/2)\epsilon_{ij}$ is the scaled attractive energy ϵ_{ij} ($=\epsilon_{ji}$) and ϵ^* is defined as

$$\epsilon^* = \sum_{i=1}^k \phi_i \epsilon_{ii}^* - \sum_{i=1}^k \sum_{j>i}^k \phi_i \phi_j \Delta \epsilon_{ij}^*, \quad (48)$$

where $\Delta \epsilon_{ij}^* = (\epsilon_{ii}^* + \epsilon_{jj}^* - 2\epsilon_{ij}^*)$.

The Gibb's free energy of the system can be obtained as the logarithm of the isothermal-isobaric partition function or, using standard procedures, as the logarithm of the maximum term in the corresponding sum over energy and volume. This is equivalent to considering the free energy as the logarithm of the generic term in the sum over V

$$G(V) = E(V) + PV - kT \ln \Omega(V) \quad (49)$$

[where $E(V)$ and $\Omega(V)$ correspond to the maximum term in the sum over E for a given V] then find its minimum with respect to the volume. In Eq. (49) the volume V is given by $V = Mv^* = \tilde{v}v^*rN$ and the number of configurations is estimated using the Flory approximation³²

$$\Omega = \left(\frac{1}{\rho_0}\right)^{N_0} \left(\frac{\omega_1}{\rho_1}\right)^{N_1} \left(\frac{\omega_2}{\rho_2}\right)^{N_2} \cdots \left(\frac{\omega_k}{\rho_k}\right)^{N_k}, \quad (50)$$

where ω_i are the internal entropy factors, defined by Eq. (36). This leads to

$$G(V) = rN \left\{ -\epsilon^* \rho + P\tilde{v}v^* + kT \left[(\tilde{v}-1) \ln(1-\rho) + \frac{1}{r} \ln \rho + \sum_{i=1}^k \frac{\phi_i}{r_i} \ln \left(\frac{\phi_i}{\omega_i} \right) \right] \right\}. \quad (51)$$

In the reduced representation of Eq. (51) the minimization with respect to V amounts to the condition $[\partial(G/rN)/\partial\tilde{v}]_{T,P} = 0$. The result is an equation of state of the mixture, which relates the value of \tilde{v} (or N_0) to the pressure P , T , and r ,

$$\epsilon^* \rho^2 + Pv^* + kT \left[\ln(1-\rho) + \left(1 - \frac{1}{r}\right) \rho \right] = 0. \quad (52)$$

Note that the values of r and ϵ^* in the above equations correspond to the average values for the mixture. The same equation of state is obtained for the pure components. A pure solvent is characterized by three independent parameters ϵ_{ii}^* , v^* , and r , that can be fitted to experimental data.^{29,33} The additional parameters ϵ_{ij}^* are, in general, estimated from empirical rules, e.g., the Berthelot (geometric mean) formula $\epsilon_{ij}^* = \sqrt{\epsilon_{ii}^* \epsilon_{jj}^*}$.

The isothermal compressibility (β) and the isobaric expansivity (α) are derived from the equation of state (52) as

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P = \frac{1}{T} \left[\frac{\epsilon^* \rho^2 + Pv^*}{kT \rho \left(\frac{\rho}{1-\rho} + \frac{1}{r} \right) - 2\epsilon^* \rho^2} \right], \quad (53)$$

$$\beta = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T = \frac{v^*}{kT \rho \left(\frac{\rho}{1-\rho} + \frac{1}{r} \right) - 2\epsilon^* \rho^2}. \quad (54)$$

Note that the average size r of the molecules in the mixture appears explicitly in the above equations. In addition α and β depend on r also via the r dependence of ρ . Equation (52) implies that the density increases with the size (r) of the chain, for constant interaction energies and site volume. Indeed,

$$\left(\frac{\partial \rho}{\partial r} \right)_{P,T} = \frac{\rho \beta}{r^2 v^*}. \quad (55)$$

This is in agreement with the analysis of Patterson²⁷ according to which the free volume decreases when the chain size becomes longer. Finally, the internal pressure of the mixture, P_{int} , which is a measure of the strength of the intermolecular interactions,²⁹ is given by

$$P_{\text{int}} = \left(\frac{\partial E}{\partial V} \right)_T = T \frac{\alpha}{\beta} - P = \frac{\epsilon^* \rho^2}{v^*}. \quad (56)$$

Consider now the thermodynamics of a binary mixture of a solute a and solvent s . The pure components are characterized by the parameters r_s , ϵ_{ss}^* , r_a , and ϵ_{aa}^* , however the thermodynamic properties in the limit of infinite dilution will not depend on ϵ_{aa}^* . r_s and ϵ_{ss}^* determine, via the equation of state (52) for the pure solvent, the density ρ_s . In addition, the mixture is characterized by the solvent solute interaction ϵ_{as}^* . The chemical potential of the solute in the mixture, μ_a , is obtained from Eq. (51)

$$\mu_a = \left(\frac{\partial G}{\partial N_a} \right)_{N_s, P, T}$$

$$= kT \ln \left(\frac{\phi_a \rho_s}{\omega_a} \right) + kT \phi_s + r_a \left\{ P\tilde{v}v^* - \rho \epsilon_{aa}^* + \rho \Delta \epsilon_{as}^* \phi_s^2 + kT \left[-\frac{\phi_s}{r_s} + (\tilde{v}-1) \ln(1-\rho) \right] \right\}. \quad (57)$$

In the infinite dilution limit ($\phi_a \rightarrow 0$, $\phi_s \rightarrow 1$, $\rho \rightarrow \rho_s$, and $\phi_a \rho_s \approx \rho_a$) this becomes

$$\mu_a = kT [1 + \ln(\rho_a \omega_a^{-1})] + r_a \left\{ P\tilde{v}v^* + \rho_s (\epsilon_{ss}^* - 2\epsilon_{as}^*) + kT \left[-\frac{1}{r_s} + (\tilde{v}_s - 1) \ln(1 - \rho_s) \right] \right\}$$

$$= kT [(1 - r_a) + \ln(\rho_a \omega_a^{-1})] + r_a [-2\epsilon_{as}^* \rho_s - kT \ln(1 - \rho_s)]. \quad (58)$$

The first term on the right-hand side of Eq. (58) depends on properties of the solute only and plays the same role as the first term of Eq. (11). The remaining term,

$$\Delta G_a = \mu_a^{(c)} + \mu'_a, \quad (59a)$$

$$\mu_a^{(c)} = -r_a kT \ln(1 - \rho_s), \quad (59b)$$

$$\mu'_a = -2r_a \epsilon_{as}^* \rho_s, \quad (59c)$$

may be identified as the free energy of solvation, ΔG_a , in infinite dilution. This energy is composed of two contributions. The first, $\mu_a^{(c)}$, which survives when $\epsilon_{as}^* \rightarrow 0$, is the cavity formation term. The other, μ'_a , is associated with the solute-solvent interaction. Note that the solvent-solvent interaction ϵ_{ss}^* do not appear explicitly in Eq. (59), in agreement with the general treatment of Yu and Karplus,³⁶ so that ΔG_a depends on this interaction only via ρ_s . Changes in the other thermodynamic quantities associated with the solvation can be calculated from μ'_a . The results are

$$\Delta H_a = r_a \left[-2\epsilon_{as}^* \rho_s + T\alpha_s \left(-2\epsilon_{as}^* \rho_s + kT \frac{\rho_s}{1 - \rho_s} \right) \right], \quad (60)$$

$$\begin{aligned} \Delta V_a &= r_a \beta_s \left[-2\epsilon_{as}^* \rho_s + kT \frac{\rho_s}{1 - \rho_s} \right] \\ &= r_a \left[\beta_s \left[2\rho_s (\epsilon_{ss}^* - \epsilon_{as}^*) - kT \frac{1}{r_s} \right] + \frac{v^*}{\rho_s} \right], \end{aligned} \quad (61)$$

$$\Delta E_a = \Delta H_a - P\Delta V_a, \quad (62)$$

$$\Delta S_a = \frac{1}{T} (\Delta H_a - \Delta G_a). \quad (63)$$

The same results can be obtained from the infinite dilution limit of the expressions derived by Sanchez and Lacombe.²⁹ Note that Eqs. (60)–(63) contain contributions associated with the cavity formation, that were disregarded in the results of Sec. II. Also note that because ϵ_{ss}^* does not appear explicitly in Eq. (59c), this result for μ'_a has the same form as the weak coupling, $\epsilon_{as}^* \ll kT$, limit of Eq. (40) (to see this the substitutions $\epsilon_{as}^* = \frac{1}{2}\epsilon_{as}$ and $r_{az} = l_a$ should be made). It should be kept in mind however that ρ_s is different, for given P and T , in these different models.

Using the above results for the association reaction $A + B \rightarrow AB$ we get for the thermodynamic functions of the association reaction

$$\begin{aligned} \Delta G_{\text{Assoc}} &= -E_r - \rho_s (\epsilon_{ab-s} l_{ab} - \epsilon_{as} l_a - \epsilon_{bs} l_b) \\ &\quad - kT (r_{ab} - r_a - r_b) \ln(1 - \rho_s), \end{aligned} \quad (64)$$

$$\begin{aligned} \Delta H_{\text{Assoc}} &= -E_r - \rho_s (1 + T\alpha_s) (\epsilon_{ab-s} l_{ab} - \epsilon_{as} l_a - \epsilon_{bs} l_b) \\ &\quad + kT^2 (r_{ab} - r_a - r_b) \frac{\alpha_s \rho_s}{1 - \rho_s}, \end{aligned} \quad (65)$$

$$\begin{aligned} \Delta V_{\text{Assoc}} &= -\rho_s \beta_s (\epsilon_{ab-s} l_{ab} - \epsilon_{as} l_a - \epsilon_{bs} l_b) \\ &\quad + kT \beta_s (r_{ab} - r_a - r_b) \frac{\rho_s}{1 - \rho_s}, \end{aligned} \quad (66)$$

$$\Delta E_{\text{Assoc}} = \Delta H_{\text{Assoc}} - P\Delta V_{\text{Assoc}}, \quad (67)$$

TABLE I. Parameters ϵ_{ss}^* and v^* for long chain PEO and PPO obtained from a non-linear fitting of the thermodynamic data given, respectively, by Refs. 24 and 38 to the equation of state (52).

	ϵ^* (kcal/mol)	v^* (cm ³ /mol)
PPO	1.127	11.41
PEO	1.339	11.07

$$\begin{aligned} \Delta S_{\text{Assoc}} &= -\rho_s \alpha_s (\epsilon_{ab-s} l_{ab} - \epsilon_{as} l_a - \epsilon_{bs} l_b) \\ &\quad + k (r_{ab} - r_a - r_b) \left[\ln(1 - \rho_s) + T \frac{\alpha_s \rho_s}{1 - \rho_s} \right], \end{aligned} \quad (68)$$

where E_r is the energy of the dissociation reaction ($E_r > 0$) and where $l_i = r_i z$ ($i = a, b, ab$). The terms proportional to $r_{ab} - r_a - r_b$ are associated with the cavity formation, and vanish if the solute sizes are additive, i.e., $r_{ab} = r_a + r_b$. The equilibrium constant for the association reaction is given as before by

$$K_{\text{Assoc}} = \exp(-\Delta G_{\text{Assoc}}/kT). \quad (69)$$

IV. IMPLICATIONS FOR POLYETHER ELECTROLYTES

In the case of a pure long chain polymer (i.e., very large r_s), the equation of state (52) depends only on the parameters ϵ_{ss}^* and v^* . These parameters are obtained in general from a nonlinear fit of the thermodynamic properties of the polymer to those inferred from the equation of state. Since the available data is usually the temperature dependence of the mass density (not the number density) at atmospheric pressure ($P \approx 0$), this procedure yields ϵ_{ss}^* and ρ^* . In order to obtain the value of v^* it is necessary to use one additional relation, e.g., Eq. (56), for the internal pressure.^{29,37} Applying this procedure, using the thermodynamic data for long chains ($r_s \rightarrow \infty$) PEO and PPO, given, respectively, in Refs. 24 and 38, leads to the values given in Table I.³⁹ Note that the interaction energy obtained for PEO is larger than that for PPO, implying a smaller free volume in PEO than in PPO. This is probably related to the partial crystalline structure of PEO and may not reflect the correct properties of amorphous PEO. Using the temperature dependence of the mass density for long chain PPG given by Stevens and co-workers⁴⁰ one finds a value for ϵ_{ss}^* that is only 5% larger than the one for PPO in Table I. Therefore, we use the values in Table I for all the experiments involving PPO and PPG.

In what follows we assume that the solute molecular sizes are additive, namely, $r_{ab} = r_a + r_b$ so that terms in the free energy of solvation associated with the cavity formation will cancel in the free energy of the association reaction. We also assume that the interactions ϵ_{ab-s} , ϵ_{as} , ϵ_{bs} , E_r and the numbers of nearest neighbors l_a , l_b , and l_{ab} are temperature independent constants. Under this assumption the dissociation-association equilibrium is determined by the pure solvent properties expressed by ρ_s , $T\alpha_s$, and β_s and by the two energy constants E_r —the ion-ion binding energy and $E_s \equiv (\epsilon_{ab-s} l_{ab} - \epsilon_{as} l_a - \epsilon_{bs} l_b)$. It is interesting to

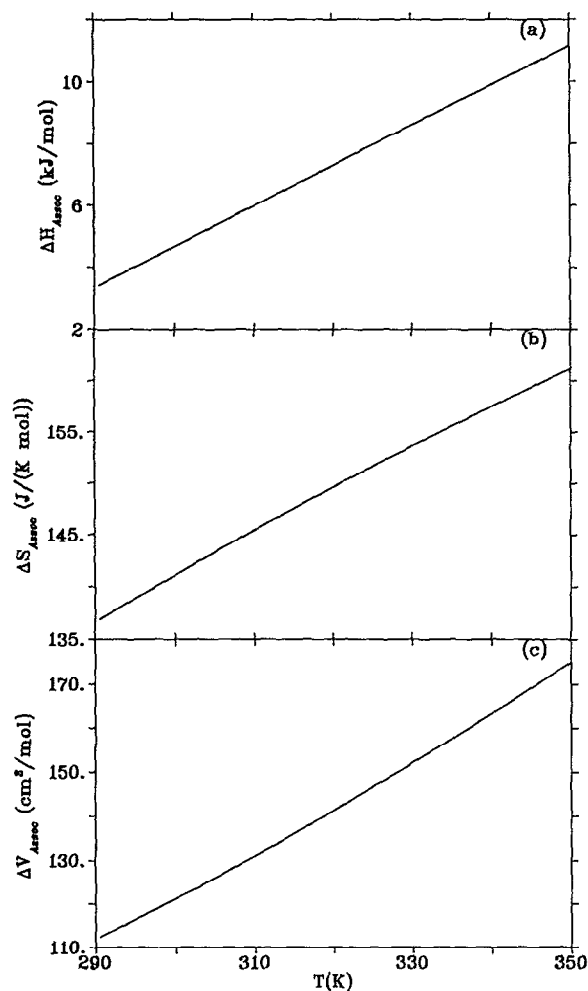


FIG. 2. Temperature dependence of the thermodynamic functions (enthalpy, entropy, and volume) of the association reaction, for constant pressure ($P=1$ atm) and solvent molecular size ($r_s=10\,000$).

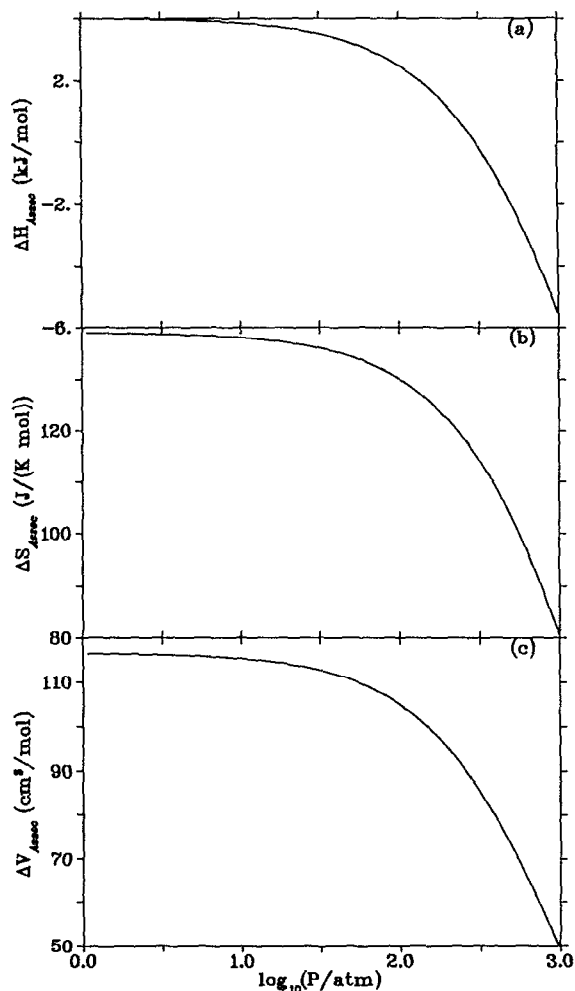


FIG. 3. Pressure dependence of the thermodynamic functions of the association reaction, for constant temperature ($T=295$ K) and solvent molecular size ($r_s=10\,000$).

note that, within the present model, the equilibrium constant Eqs. (64) and (69) depend on the pure solvent properties and on the external pressure and temperature only through the solvent density ρ_s .

Not enough is known about the molecular parameters to make the theory fully predictive, and in any case the model may be too restrictive to fully account for the experimental observations, as discussed below. In what follows we compare the behavior of the model with experimental observations in order to see whether consistency can be obtained with a reasonable choice of parameters.

In order to use the data for ΔH_{Assoc} and ΔS_{Assoc} provided by Schantz⁴ we note that these values were calculated by identifying $\Delta \bar{G}_{\text{Assoc}} = -kT \ln \bar{K}_{\text{Assoc}}$ with \bar{K}_{Assoc} calculated in units of ℓ/mol . Our K_{Assoc} is dimensionless since the concentrations were expressed in number of molecules per site. Therefore, $\bar{K}_{\text{Assoc}} = v^* K_{\text{Assoc}}$ and v^* , the volume per site should be expressed in ℓ/mol . Therefore a factor of $-kT \ln v^*$ should be added to our ΔG_{Assoc} and ΔS_{Assoc} in order to correspond to Schantz's data. (This factor is sometimes referred to as the "molar translational

entropy change in the association reaction."^{12(a)}) In what follows we denote $\Delta \bar{G}_{\text{Assoc}} = \Delta G_{\text{Assoc}} - kT \ln v^* = \Delta H_{\text{Assoc}} - T \Delta S_{\text{Assoc}}$.

Using the results of Schantz:⁴ $\Delta H_{\text{Assoc}} = 4$ kJ/mol and $\Delta S_{\text{Assoc}} = 101.7$ J/(K mol) for NaCF_3SO_3 -PPO at 295 K together with $\rho_s = 0.9223$ and $\alpha_s = 7.205 \times 10^{-4}$ K⁻¹ (obtained from Eqs. (52) and (53), respectively, using the parameters of Table I and $r=10\,000$) and $v^* = 11.41 \times 10^{-3}$ ℓ/mol (cf. Table I), we get from Eqs. (65) and (68) $E_r = 229.7$ kJ/mol and $E_s = -209.0$ kJ/mol for this system. A similar analysis for LiClO_4 -PPO where, at 295 K, $\Delta H_{\text{Assoc}} = 13$ kJ/mol and $\Delta S_{\text{Assoc}} = 122.0$ J/(K mol) (Ref. 4) yields $E_r = 249.3$ kJ/mol and $E_s = -234.5$ kJ/mol.

The value obtained for E_r is about half of the electrostatic interaction between the two bare ions separated by 3 Å. This low value reflects the fact that only short range interactions are included in our description: E_s includes only such short range contributions to the solvation energy of the ions and of the associated pair, therefore E_r represents the energy needed to separate the ions in vacuum

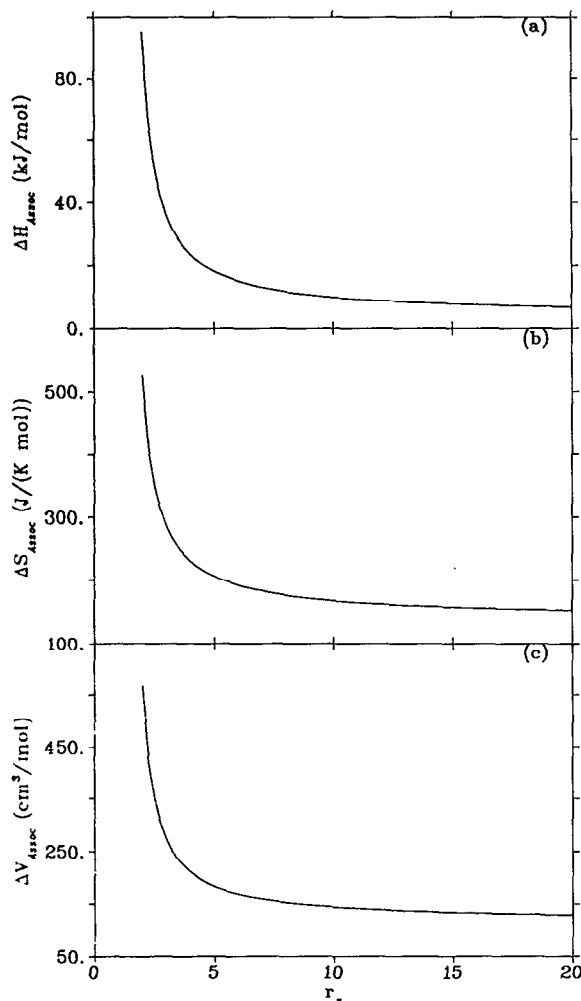


FIG. 4. The dependence of the thermodynamic functions of the association reaction on the solvent size expressed by r_s . The temperature and the pressure are $T=295$ K and $P=1$ atm.

reduced by the long range part of the contribution from the solvent polarization.

If, following Papke *et al.*⁴¹ we take $\epsilon_{as}=59$ kJ/mol and $l_a=4$, where a is Na^+ in NaCF_3SO_3 -PPO, the above estimate of E_s leads to $\epsilon_{ab-s}l_{ab}-\epsilon_{bs}l_b \approx 32.0$ kJ/mol, where b

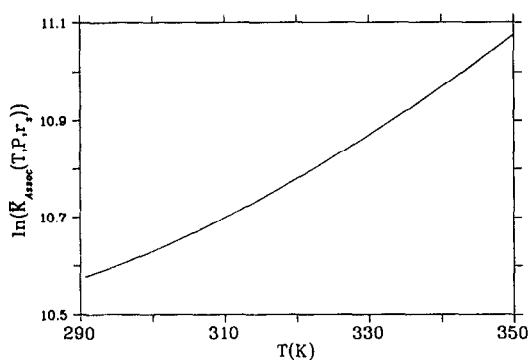


FIG. 5. Temperature dependence of the association equilibrium constant at constant pressure for $P=1$ atm and $r_s=10000$.

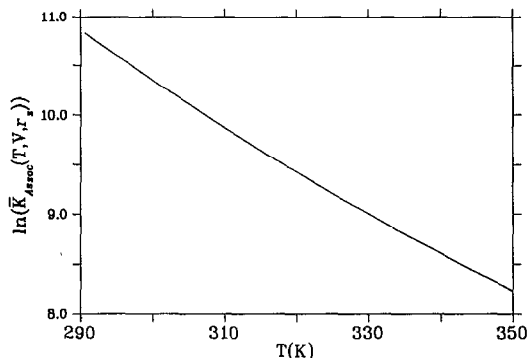


FIG. 6. Temperature dependence of the association equilibrium constant at constant volume (i.e., constant solvent density). The value of ρ_s used is $\rho_s=0.92$, which is the density calculated from Eq. (52) at $P=1$ atm and $T=295$ K. Solvent size is $r_s=10000$.

represents the triflate anion. This is a reasonable result considering the fact that both the anion and the ion pair interact considerably more weakly with the PPO solvent.

Consider now the implications of these results on the temperature, pressure, and solvent molecular size dependence of the thermodynamic functions of the association reaction. Figures 2, 3, and 4 show the change in enthalpy, entropy, and volume per association-mole as functions of T , P , and r_s , respectively, using $E_s=-209.0$ kJ/mol and $E_r=229.7$ kJ/mol. Figures 5 and 6 show the temperature dependence of the association constant at constant pressure and at constant volume respectively for a solvent of large molecular weight ($r_s=10000$). Note that these figures (as well as Figs. 7 and 8) show $\bar{K}_{\text{Assoc}}=v^*K_{\text{Assoc}}$. The pressure dependence of \bar{K}_{Assoc} is displayed for the same r_s in Fig. 7. Finally, Fig. 8 shows the r_s dependence of \bar{K}_{Assoc} at standard temperature and pressure. It should be emphasized that r_s , the number of "chain units," does not necessarily represent the number of real ether monomers in the chain. It is however proportional to this number.

From the results displayed in Figs. 2–8 the following conclusions can be drawn:

(a) The enthalpy and entropy of the association reaction vary in a reasonable range with temperature and pressure. It is interesting to note that ΔH_{Assoc} changes sign with

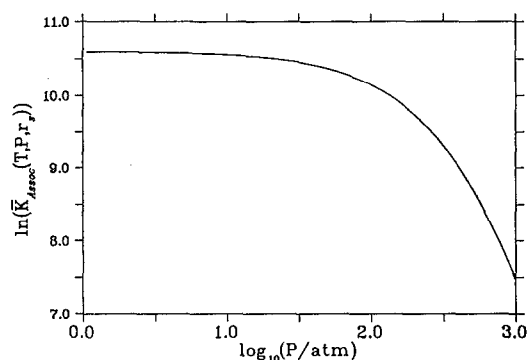


FIG. 7. Pressure dependence of the association equilibrium constant at $T=295$ K, for $r_s=10000$.

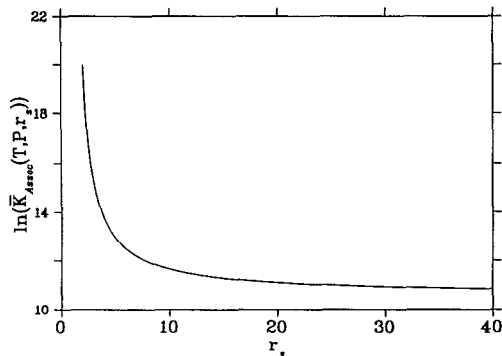


FIG. 8. Solvent size dependence of the association equilibrium constant at $P=1$ atm and $T=295$ K.

increasing pressure which indicates that the observation of increasing ionic association at higher temperatures may be pressure dependent. The temperature and pressure dependence of \bar{K}_{Assoc} is consistent with the experimental observation.

(b) The dependence of the thermodynamic functions of association on the solvent molecular size and in particular the decrease of \bar{K}_{Assoc} with r_s shown in Fig. 8 is consistent with the observation of Torell and co-workers³ on short (4–8) chain methyl capped PPO, but not with the observation of the opposite effect in longer chain PPG.² Unfortunately, there is no overlap between the size range of these two groups of experiments and the results of Fig. 8 suggest that the trend observed in PPG is due to chain-end effect as discussed in Ref. 3. This statement cannot be made conclusively, however, in view of the shortcomings of the present model as discussed below.

(c) The results for the volume change which accompanies the association reaction greatly overestimate what is reasonably expected. Typical volume changes per reaction mol are expected to be of order of $10 \text{ cm}^3/\text{mol}$, an order of magnitude lower than the results displayed in Figs. 2–4. The reason for this failure of the SL model is the use of the simple mean field assumption (46) as the estimate of the number of nearest-neighbor pairs, as discussed below.

(d) As pointed out in Sec. I, the increase in association with increasing temperature in the 1:1 salt–polyether complexes is reminiscent of the phenomenon of lower critical solution temperature observed in many polymer solutions. Indeed, in a simple mixture composed of a “solvent” s and a “solute” a , the association reaction $a+a \rightleftharpoons aa$ may be viewed as a first step in a phase separation process. However, a closer look at the theoretical results indicates that no direct connection exists between the two phenomena. To see this note that our arguments are derived from the thermodynamics of the system at infinite dilution where phase stability [see Eq. (58b) of Ref. 28] is automatically satisfied. It is nevertheless interesting to examine the implications of Eqs. (64)–(68) for this simple association reaction. Taking $b=a$, $r_{aa}=2r_a$, $\epsilon_{aa-s}=\epsilon_{as}$, and $l_{aa}-2l_a=-2$ we find from Eqs. (65) and (68)

$$\Delta H_{\text{Assoc}} = -E_r + 2\rho_s(1 + T\alpha_s)\epsilon_{as}, \quad (70)$$

$$\Delta S_{\text{Assoc}} = 2\rho_s\alpha_s\epsilon_{as}, \quad (71)$$

so that

$$\Delta H_{\text{Assoc}} = (-E_r + 2\rho_s\epsilon_{as}) + T\Delta S_{\text{Assoc}}. \quad (72)$$

The terms in brackets in Eq. (72) is of energetic origin and measures the net reaction free energy (bare reaction energy + difference in solvation energy between an aa dimer and two a monomers). The other, entropic, term is positive (provided that the vacancy concentration is not zero so that $\alpha_s > 0$) and its presence enhances the possibility that ΔH_{Assoc} will be positive, namely, that association will be enhanced at higher temperatures.

(e) The structure of the result for ΔH_{Assoc} , Eq. (65) is consistent with the observation that the trend in the temperature dependence of the ionic association is reversed for species of higher ionic charges (e.g., Nd^{+3} –triflate complexes³): within the present model it simply implies that the ratio E_r/E_s is usually larger for systems with more highly charged species.

While, except for the prediction for the volume change upon association, the SL model seems to behave reasonably in the present context, the structure of Eqs. (64)–(68) reveals a major weakness: Consider, for example, the first term in the expression for ΔS_{Assoc} , Eq. (68). This term is linear in E_s so that when, e.g., $\epsilon_{bs}=\epsilon_{ab-s}=0$ this term diverges when $\epsilon_{as} \rightarrow \infty$. This is unphysical: in reality once the solvent occupation is saturated in the sites nearest to species a , further increase in the interaction energy cannot affect ΔS_{Assoc} in this nearest-neighbor interaction model. The same reservation holds for the similar term in ΔV_{Assoc} . Since E_s was fitted to the experimental value of ΔS_{Assoc} , the entropy behaves reasonably but the volume change is overestimated.

The origin of this unphysical behavior lies in the approximation (46) which takes N_{ij} to be independent of ϵ_{ij} . This is a poor approximation unless $\epsilon_{ij} < kT$. Note that this simplification is avoided in the mean-field treatment of Sec. II C, where our ansatz (39) takes the solvent density in sites nearest to the solute to explicitly depend on the Boltzmann factor $e^{\epsilon_{as}/kT}$. This may be achieved more rigorously and without sacrificing solvent–solvent interactions by using the Guggenheim quasichemical approximation (QCA).³⁵

V. CONCLUSION

In the present paper we have presented a model for association–dissociation reactions in polymer solvents in the framework of lattice gas models, and have discussed ion solvation in polymer–salt complexes in this context. After introducing the theoretical concepts using several noninteracting lattice gas models, we have focused on the Sanchez–Lacombe theory in our first attempt to analyze experimental data. Our model focus on the effect of short range interactions on the temperature, pressure, and solvent size dependence of the thermodynamic functions of solvation and of association equilibrium. Although the formalism has sufficient physical contents to enable such analysis, and even though most general behaviors predicted by

the model are reasonable, the analysis shows a critical flaw in the model associated with its inability to correctly account for strong solvent-solute interactions. In a following paper this flaw is remedied by applying the QCA to the same model.

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APPENDIX A: DETAILS OF THE CALCULATION OF μ'_a

Using the definition of μ'_a given by Eq. (11), one has

$$\mu'_a = -kT \ln \langle \exp[-W_s(R)/kT] \rangle_R, \quad (\text{A1})$$

where the average is over all the configurations R of the solvent. In the present model W_s is a sum over the sites nearest to the solute of the nearest neighbor interactions, and the average is over the occupation probability of these sites: each site can be occupied or not with probability proportional respectively to 1 and $e^{\mu_s/kT}$. Therefore, the average in Eq. (A1) leads to

$$\begin{aligned} \langle \exp[-W_s(R)/kT] \rangle_R &= \left(\frac{1 + e^{\epsilon_{as}/kT} e^{\mu_s/kT}}{1 + e^{\mu_s/kT}} \right)^{l_a} \\ &= (1 - \rho_s + \rho_s e^{\epsilon_{as}/kT})^{l_a}, \end{aligned} \quad (\text{A2})$$

where in the last equality Eq. (10) was used. This leads to Eq. (13). Note that the average $\langle \exp[-W_s(R)/kT] \rangle_R$ is equal to the ratio Ξ_e/Ξ_0 of Eq. (7), with the substitution of $e^{\mu_s/kT}$ in terms of ρ_s .

APPENDIX B: THE CHEMICAL POTENTIAL OF AN IMPURITY IN A 1D NILG

We consider a one-dimensional lattice with $M+1$ sites containing N solvent molecules of size r_s (each occupying r_s consecutive sites) and one impurity molecule of size 1. The impurity interacts with nearest-neighbor solvent sites with energy $-\epsilon_{as}$. We use cyclic boundary conditions (ring geometry) and take $M \rightarrow \infty$ at the end of the calculation. This system has three energy levels: $E=0$ (when sites adjacent to the impurity are vacant), $E=-\epsilon_{as}$ (when one of the two sites adjacent to the impurity is occupied by the edge site of the solvent molecule) and $E=-2\epsilon_{as}$ (when both sites neighboring the impurity are so occupied). The rest of the system behaves as a free solvent. Correspondingly the partition function for this system can be written as

$$\begin{aligned} Q_\epsilon(M, N) &= Q_0(M-2, N) + 2Q_0(M-1-r_s, N-1)e^{\epsilon_{as}/kT} \\ &\quad + Q_0(M-2r_s, N-2)e^{2\epsilon_{as}/kT}. \end{aligned} \quad (\text{B1})$$

Using Eq. (25) this can be rewritten in the form

$$\begin{aligned} Q_\epsilon(M, N) &= Q_0(M-2, N) \left[1 + \frac{2Ne^{\epsilon_{as}/kT}}{M-1-Nr_s} \right. \\ &\quad \left. + \frac{N(N-1)e^{2\epsilon_{as}/kT}}{(M-Nr_s)(M-1-Nr_s)} \right]. \end{aligned} \quad (\text{B2})$$

Using the Stirling's approximation and neglecting $O(1/M)$ terms we have

$$\ln Q_0(M-2, N) = \ln Q_0(M, N) - 2 \ln \left(\frac{M-Nr_s+N}{M-Nr_s} \right) \quad (\text{B3a})$$

and to the same order

$$\begin{aligned} \ln \left(1 + \frac{2Ne^{\epsilon_{as}/kT}}{M-1-Nr_s} + \frac{N(N-1)e^{2\epsilon_{as}/kT}}{(M-Nr_s)(M-1-Nr_s)} \right) \\ = 2 \ln \left(1 + \frac{Ne^{\epsilon_{as}/kT}}{M-Nr_s} \right). \end{aligned} \quad (\text{B3b})$$

These equations lead to

$$Q_\epsilon(M, N) = Q_0(M, N) \cdot \left[\frac{1-\rho_s}{1-\rho_s \left(1-\frac{1}{r_s}\right)} + \frac{\rho_s e^{\epsilon_{as}/kT}/r_s}{1-\rho_s \left(1-\frac{1}{r_s}\right)} \right]^2. \quad (\text{B4})$$

The excess free energy, or the solute chemical potential at infinite dilution is obtained from

$$\mu'_a = A_\epsilon - A_0 = -kT (\ln Q_\epsilon - \ln Q_0), \quad (\text{B5})$$

where A is the Helmholtz free energy. Equations (B4) and (B5) lead to Eq. (28). Note that the result does not depend on the system size M , as expected from a local perturbation.

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