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Sol−Gel Transition in Nonlinear Hydrogen Bonding Solutions

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ABSTRACT: Hydrogen bonding (HB) in a mixed nonlinear system consisting of $A_{a_1}D_{d_1}$ and $\bar{A}_{a_2}\bar{D}_{d_2}$ types of molecules is studied with the different activities of the groups being taken into account. Under the framework of the mean field theory, the partition function concerned the HB process of the system is given by two different statistical viewpoints. By which the equilibrium free energy of the system in the pregel regime, the law of mass action of HB process and the equilibrium size distribution of the HB clusters are carried out. The sol−gel phase transition is shown to take place in such a HB system with the gelation condition being given, and then the sol and gel free energies in the postgel regime are also obtained. Furthermore, the scaling laws satisfied by the *k*th moments and the gel fraction near the critical point are obtained for describing this kind of phase transition.

I. Introduction

Hydrogen bonding (HB) is a kind of specific interaction between a proton donor and a proton acceptor, and usually involves many complicated mechanisms. To date, some problems concerning the HB process have become an important subject and attracted intensive interests. Hydrogen bonds can lead to some significant effects on the physical and chemical properties of the related systems.[1] These effects are, in essence, due to the hydrogen bonded association of molecules possessing proton donor and acceptor groups. Therefore, the molecular connectivity induced by hydrogen bonds plays an important role in the HB systems.

Because of hydrogen bonds' importance in chemistry, biology, physics and molecular engineering, it is interesting to study and reveal its actions. Theoretically, the statistical mechanics method becomes one of the powerful tools since there exist a great number of hydrogen bonds in HB liquids or solutions. So far there are two major methods on the statistical theory of HB liquids, one is the association approach,[2−5] and another is the lattice-fluid hydrogen bonding (LFHB) theory.[6,7] The former considered the HB system as an equilibrium mixture of monomers, dimers, trimers, etc., on which the system is studied. The LFHB approach, however, investigated the HB systems by enumerating the configurations of contacts between the proton donors and acceptors. These two approaches, as stated by Panayiotou and Sanchez,[7] are essentially equivalent in some applications.[8−11]

The HB connectivity can give rise to a macroscopic HB network in the nonlinear HB systems provided the number of hydrogen bonds approaches a critical value. This phenomenon is called the HB induced gelation. The gelation, as is well-known, can occur in various systems, which is closely related to the sol and gel phases of the associated nonlinear system. For instance, in nonlinear polycondensations, gelation is induced by the covalent bonds and has been demonstrated to be a kind of phase transition named the sol−gel transition (SGT).[12]

Recently, we have considered the SGT in the nonlinear HB liquid system consisting of identical A_aD_d type molecules (each of them possesses *a* proton acceptors *A* and *d* proton donors *D*).[13] In this paper we study a modeling system of HB solution consisting of N_1 molecules of $A_{a_1}D_{d_1}$ and N_2 molecules of $\bar{A}_{a_2}\bar{D}_{d_2}$ types, and the corresponding symbols have the similar interpretations as that in A_aD_d type. Note that, now the proton acceptor $\bar{A}$ and proton donor $\bar{D}$ may be identical with *A* and *D* or not, then such a system is obviously more complicated than the HB liquid system. The reason is twofold. On the one hand, the proton donors and acceptors of distinct molecules usually possess different activities in HB process, and thus the activity difference should be taken into account. On the other hand, the various HB clusters can be formed in the self-association and cross-association manners. (The self-association denotes the association of the same type of molecules, while the cross-association denotes the association of different types of molecules.) This leads to a large number of the conformations for a HB clusters with a given size.

The major purpose of this article is to consider the SGT and related problems in HB solution system, where the activity difference in HB process has been taken into account. In this paper the enumerations of Veytsman−Panayiotou[6,7] and Flory−Stockmayer[14,15] are used, which would be shown to be consistent with each other. The present discussions are performed on the basis of two approximations, (1) without regard for the HB cooperativity and (2) by neglecting the intramolecular hydrogen bonds in the sol phase. Here the intramolecular hydrogen bond is referred to a hydrogen bond between a proton donor and a proton acceptor that belong to a same cluster (the monomers are excluded), while the intermolecular hydrogen bond is referred to a hydrogen bond that can link two clusters together. This means that the HB clusters in the sol phase are treelike. It should be noted that these two factors can lead to the corresponding modifications in some physical quantities.[16−19]

The paper is organized as follows. In section II, the equilibrium HB free energy is given by two different statistical viewpoints, and as an application we derive the equilibrium size distribution of the HB clusters. In section III, the critical condition on the SGT is given, the sol and gel free energies in postgel regime are also obtained. In section IV, for describing

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the SGT, the scaling laws satisfied by the *k*th moments of the HB clusters and the gel fraction in the vicinity of the critical point are carried out. In section V, some relevant problems on the SGT in HB systems are discussed, and then we summarize the results of the paper.

II. The Equilibrium Free Energy and Its Applications

The HB processes in the present system include the self- and cross-associations, and there are four types of hydrogen bonds in this system, which are $A-D$, $A-\bar{D}$, $\bar{A}-D$ and $\bar{A}-\bar{D}$ types represented by T_{11}, T_{12}, T_{21}, and T_{22}, respectively. For convenience, hereafter the first and second subscripts in some physical quantities will always correspond to the proton acceptor and donor groups, respectively. In addition, two Greek letters of μ and ν always range from 1 to 2. In doing so, if the number of hydrogen bonds of $T_{\mu\nu}$ type is denoted by $\Lambda_{\mu\nu}$, then $\Lambda_{\mu\nu}$ denotes the number of hydrogen bonds formed by the proton acceptor of μ type with the proton donor of ν type. Bear this in mind, the canonical partition function of the system with a series of $\{\Lambda_{\mu\nu}\}$ hydrogen bonds can be expressed as

$$Q(\{\Lambda_{\mu\nu}\}) = \prod_{\mu}\left[\frac{(q_{a_\mu})^{a_\mu N_\mu - \Lambda_{a_\mu}}}{(a_\mu N_\mu - \Lambda_{a_\mu})!}\right] \times \prod_{\nu}\left[\frac{(q_{d_\nu})^{d_\nu N_\nu - \Lambda_{d_\nu}}}{(d_\nu N_\nu - \Lambda_{d_\nu})!}\right]\prod_{\mu,\nu}\frac{(q_{\mu\nu})^{\Lambda_{\mu\nu}}}{\Lambda_{\mu\nu}!} \quad (1)$$

where q_{a_μ}, q_{d_ν} and $q_{\mu\nu}$ are the corresponding partition functions of a proton acceptor of μ type, a proton donor of ν type and a hydrogen bond of $T_{\mu\nu}$ type. In this equation, $\Lambda_{a_\mu} = \Lambda_{\mu 1} + \Lambda_{\mu 2}$, $\Lambda_{d_\nu} = \Lambda_{1\nu} + \Lambda_{2\nu}$, are the numbers of the corresponding hydrogen-bonded groups, and obviously satisfy the relationship of $\Lambda_{a_1} + \Lambda_{a_2} = \Lambda_{d_1} + \Lambda_{d_2}$. This is just the physical requirement of the HB process.

Taking the initiate state with partition function $Q(\{0\})$ as the reference state, we can define a HB partition function, $Q_{hb}(\{\Lambda_{\mu\nu}\}) = Q(\{\Lambda_{\mu\nu}\})/Q(\{0\})$, which can be expressed as

$$Q_{hb}(\{\Lambda_{\mu\nu}\}) = \Omega_{ad}(\{\Lambda_{\mu\nu}\})\prod_{\mu,\nu}\left(\frac{q_{\mu\nu}}{q_{a_\mu}q_{d_\nu}}\right)^{\Lambda_{\mu\nu}} \quad (2)$$

in which the factor

$$\Omega_{ad}(\{\Lambda_{\mu\nu}\}) = \prod_{\mu}\left[\frac{(a_\mu N_\mu)!}{(a_\mu N_\mu - \Lambda_{a_\mu})!}\,\frac{(d_\mu N_\mu)!}{(d_\mu N_\mu - \Lambda_{d_\mu})!}\right]\prod_{\mu,\nu}\frac{1}{\Lambda_{\mu\nu}!} \quad (3)$$

is the different ways of forming a set of $\{\Lambda_{\mu\nu}\}$ hydrogen bonds through Λ_{a_1} groups of type A, Λ_{a_2} groups of type $\bar{A}$ with Λ_{d_1} groups of type D and Λ_{d_2} groups of type $\bar{D}$. This factor enumerates the configurations of proton donor−acceptor contacts as stated in the Veytsman−Panayiotou method.[6,7]

The free energy of the system $F_1(\{\Lambda_{\mu\nu}\}) = -k_B T \ln Q_{hb}(\{\Lambda_{\mu\nu}\})$ with the Boltzmann constant k_B and absolute temperature T then becomes

$$F_1(\{\Lambda_{\mu\nu}\}) = -k_B T\left[\sum_{\mu,\nu}\Lambda_{\mu\nu}\ln\left(\frac{q_{\mu\nu}}{q_{a_\mu}q_{d_\nu}}\right) + \ln \Omega_{ad}(\{\Lambda_{\mu\nu}\})\right] \quad (4)$$

Note that, as molecules connect through hydrogen bonds, a large number of HB clusters appear in the system. Then we can also construct a partition function for these clusters formed by $\{\Lambda_{\mu\nu}\}$ hydrogen bonds as follows

$$Q_{cl}(\{\Lambda_{\mu\nu}\}) = \Omega_{cl}(\{\Lambda_{\mu\nu}\})\prod_{\mu,\nu}\left[\frac{\upsilon_{\mu\nu}}{V}\exp\left(-\frac{\epsilon_{\mu\nu}}{k_B T}\right)\right]^{\Lambda_{\mu\nu}} \quad (5)$$

where the factor $\Omega_{cl}(\{\Lambda_{\mu\nu}\})$ takes the form

$$\Omega_{cl}(\{\Lambda_{\mu\nu}\}) = (N_1)!(N_2)!\prod_{m,n}\left(\frac{\omega_{mn}}{m!n!}\right)^{P_{m,n}}\frac{1}{(P_{m,n})!} \quad (6)$$

This factor denotes the number of ways that N_1 and N_2 monomers form all the possible $P_{m,n}$ clusters of $(m \wedge n)$ type by $\{\Lambda_{\mu\nu}\}$ hydrogen bonds. In eq 6, ω_{mn} is the number of different ways of forming a $P_{m,n}$ cluster from m molecules of $A_{a_1}D_{d_1}$ type and n molecules of $\bar{A}_{a_2}\bar{D}_{d_2}$ type. This kind of enumeration is due to Flory and Stockmayer in polycondensations.[14,15]

In eq 5, the factor $\upsilon_{\mu\nu}/V \exp(-\epsilon_{\mu\nu}/k_B T)$ is a ratio of the probability of forming a hydrogen bond of $T_{\mu\nu}$ type in the mixed system of volume V. Its physical interpretation is the statistical weight of creating a hydrogen bond of $T_{\mu\nu}$ type relative to the non-hydrogen-bonded groups of a proton acceptor of μ-type and a proton donor of ν-type. This means that to create such a hydrogen bond, the corresponding free proton donor and acceptor groups must first close each other into a bonding volume $\upsilon_{\mu\nu}$, and then the change of energy $\epsilon_{\mu\nu}$ must also satisfy the requirement of creating such a hydrogen bond. According to the physical interpretation of the partition functions, we have $q_{\mu\nu}/(q_{a_\mu}q_{d_\nu}) = \upsilon_{\mu\nu}/V \exp(-\epsilon_{\mu\nu}/k_B T)$.

It can be seen from the partition function in eq 5 that the reference state has been chosen as the state where no hydrogen bonds formed, and the corresponding free energy is

$$F_2(\{\Lambda_{\mu\nu}\}) = -k_B T\left\{\sum_{\mu,\nu}\Lambda_{\mu\nu}\ln\left[\frac{\upsilon_{\mu\nu}}{V}\exp\left(-\frac{\epsilon_{\mu\nu}}{k_B T}\right)\right] + \ln \Omega_{cl}(\{\Lambda_{\mu\nu}\})\right\} \quad (7)$$

Now we have obtained two partition functions and the corresponding free energies for the same system with the same reference state.

In terms of the Stirling approximation, minimizing the free energy $F_1(\{\Lambda_{\mu\nu}\})$ given by eq 4 with respect to $\Lambda_{\mu\nu}$, the equilibrium free energy $\mathscr{F}_{\text{eq}}(\{\lambda_{\mu\nu}\})$, and also the minimum of the free energy of the system can be carried out as

$$\mathscr{F}_{\text{eq}}(\{\lambda_{\mu\nu}\}) = k_B T\sum_{\mu}N_\mu \ln\left[\left(1 - \frac{\lambda_{a_\mu}}{a_\mu N_\mu}\right)^{a_\mu}\left(1 - \frac{\lambda_{d_\mu}}{d_\mu N_\mu}\right)^{d_\mu}\right] + k_B T\sum_{\mu,\nu}\lambda_{\mu\nu} \quad (8)$$

where $\lambda_{\mu\nu}$, λ_{a_μ}, and λ_{d_ν} are the values of $\Lambda_{\mu\nu}$, Λ_{a_μ}, and Λ_{d_ν} at the equilibrium state, respectively. The corresponding equilibrium condition is $\lambda_{\mu\nu}/((a_\mu N_\mu - \lambda_{a_\mu})(d_\nu N_\nu - \lambda_{d_\nu})) = \upsilon_{\mu\nu}/V \exp(-\epsilon_{\mu\nu}/k_B T)$. Combining the analysis mentioned above, we have

$$\frac{\lambda_{\mu\nu}}{(a_\mu N_\mu - \lambda_{a_\mu})(d_\nu N_\nu - \lambda_{d_\nu})} = \frac{\upsilon_{\mu\nu}}{V}\exp\left(-\frac{\epsilon_{\mu\nu}}{k_B T}\right) \quad (9)$$

These relationships are just the laws of mass action expressed by the numbers of hydrogen bonds, proton donors and acceptors.

The results given by eqs 8−9 agree with that given by Veytsman[6] and Panayiotou and Sanchez,[7] who considered the contacts between the proton donors and acceptors no matter whether the hydrogen bonds are intermolecular or intramolecular. This indicates that the equilibrium free energy can be applied for any value of $\{\lambda_{\mu\nu}\}$, in particular, holds true for both pregel and postgel regimes.

For the HB system under consideration, all the clusters must be subject to the restrictions by writing $N_1 + N_2 = \Sigma_{m,n}\,(m + n)P_{m,n}$ and $\Lambda = \Lambda_{\mathrm{inter}} + \Lambda_{\mathrm{intra}}$, where Λ_{inter} and Λ_{intra} are the numbers of intermolecular and intramolecular hydrogen bonds, respectively. The approximation of regardless of the intramolecular hydrogen bonds in the sol phase signifies that there are $(m + n - 1)$ hydrogen bonds in a cluster of $P_{m,n}$. This yields

$$N_1 + N_2 = \sum_{m,n} (m+n)P_{m,n}, \quad \sum_{\mu,\nu} \Lambda_{\mu\nu} = \sum_{m,n} (m+n-1)P_{m,n} \tag{10}$$

As the system approaches the equilibrium state with $\{\lambda_{\mu\nu}\}$ hydrogen bonds, the free energies derived by the two ways must be equal to each other. This provides a new method to derive the equilibrium number distributions function (ENDF) of HB clusters as shown below. With eq 9 and making a comparison between eqs 4 and 7, we have $\Omega_{ad}(\{\Lambda_{\mu\nu}\}) = \Omega_{cl}(\{\Lambda_{\mu\nu}\})$. Using the Stirling approximation and differentiating both sides of this equation with respect to $P_{m,n}$ under the above restrictions, the ENDF of HB clusters of $(m \wedge n)$ type, $\mathscr{P}_{m,n}(N_1, N_2, \{\lambda_{\mu\nu}\})$, can be directly given by

$$\mathscr{P}_{m,n} = \frac{\omega_{mn}}{m!n!}(\mathscr{P}_{1,0})^m(\mathscr{P}_{0,1})^n \times \sum_i \left[\prod_{\mu,\nu}\left(\frac{\lambda_{\mu\nu}}{(a_\mu N_\mu - \lambda_{a_\mu})(d_\nu N_\nu - \lambda_{d_\nu})}\right)^{\lambda_{\mu\nu}^{mn}(i)}\right] \tag{11}$$

where the quantities

$$\mathscr{P}_{1,0}(N_1, \{\lambda_{\mu\nu}\}) = N_1\left(1 - \frac{\lambda_{a_1}}{a_1N_1}\right)^{a_1}\left(1 - \frac{\lambda_{d_1}}{d_1N_1}\right)^{d_1}$$

$$\mathscr{P}_{0,1}(N_2, \{\lambda_{\mu\nu}\}) = N_2\left(1 - \frac{\lambda_{a_2}}{a_2N_2}\right)^{a_2}\left(1 - \frac{\lambda_{d_2}}{d_2N_2}\right)^{d_2} \tag{12}$$

are the ENDF of two types of monomers (nonbonded molecules). The summation of index i runs over the total ways of decomposing $(m + n - 1)$ hydrogen bonds of treelike clusters of $(m \wedge n)$ type into all possible self- and cross-associations. In eq 11, the quantity of $\lambda_{\mu\nu}^{mn}(i)$ is the number of hydrogen bonds of $T_{\mu\nu}$ type in HB cluster of the ith component of $\mathscr{P}_{m,n}$. It is evident that the quantities $\{\lambda_{\mu\nu}^{mn}(i)\}$ must be subject to the equations of $\Sigma_{m,n}\lambda_{\mu\nu}^{mn}(i)\mathscr{P}_{m,n} = \lambda_{\mu\nu}$ and $\Sigma_{\mu,\nu}\,\lambda_{\mu\nu}^{mn}(i) = m + n - 1$.

The ENDF in eq 11 can also be derived in terms of the theory of chemical equilibration. The chemical potential of a cluster of $(m \wedge n)$ type is defined by $\mu_{m,n} = \partial F_1(\{\Lambda_{\mu\nu}\})/\partial P_{m,n}$, which must satisfy the condition $\mu_{m,n} \equiv m\mu_{1,0} + n\mu_{0,1}$ at equilibrium state. On the basis of this equilibrium condition together with the restrictions in eq 10, the results given by eqs 8 and 9 can be obtained. Meanwhile, we find that the equilibrium chemical potential $\mu_{m,n}^{\mathrm{eq}}$ becomes

$$\mu_{m,n}^{\mathrm{eq}} = k_{\mathrm{B}}T\left[m \ln\frac{\mathscr{P}_{1,0}}{N_1} + n \ln\frac{\mathscr{P}_{0,1}}{N_2}\right] \tag{13}$$

Starting with this equation and the expression of $F_2(\{\Lambda_{\mu\nu}\})$, eq 11 can be derived again. Furthermore, substituting the ENDF of eq 11 into eq 7, one can obtain eq 8 again. Hence the results given by the two statistical viewpoints are consistent with each other.

III. The Properties of the System in the Postgel Regime

The ENDF varies with the variation of the number of hydrogen bonds, and gives rise to some effects on the average properties of the system. The SGT induced by hydrogen bonds' connectivity is just such an interesting topic. Now we consider the relevant properties of the system in postgel regime. At first, we determine the critical point of the SGT.

For this purpose, we introduce the sol faction S of the system, which can be expressed as $S = 1/(N_1 + N_2)\,(N_1S_1 + N_2S_2)$, where S_1 and S_2 are the sol fractions of the molecules of $A_{a_1}D_{d_1}$ and $\bar{A}_{a_2}\bar{D}_{d_2}$ types, respectively. The physical interpretation of the sol fraction can be considered as the probability of finding a molecule being in the sol or equivalently, connecting with a finite cluster. It is evident that if a molecule is in sol, then all its groups must be in sol, too. Assume that Z_{a_1}, Z_{d_1}, Z_{a_2} and Z_{d_2} are respectively the probabilities of finding the groups of A, D, $\bar{A}$, and $\bar{D}$ being in the sol, thus we have

$$S_1 = (Z_{a_1})^{a_1}(Z_{d_1})^{d_1}, \; S_2 = (Z_{a_2})^{a_2}(Z_{d_2})^{d_2} \tag{14}$$

There are two situations that each of these groups can be in the sol: one is that the group does not form the hydrogen bond at all, and another is that it forms a hydrogen bond but associates with a finite cluster. On the basis of these considerations, we have

$$Z_{a_\mu} = \left(1 - \frac{\lambda_{a_\mu}}{a_\mu N_\mu}\right) + \frac{\lambda_{a_\mu}}{a_\mu N_\mu}\left[\sum_\nu \frac{\lambda_{d_\nu}}{\lambda}(Z_{a_\nu})^{a_\nu}(Z_{d_\nu})^{d_\nu - 1}\right]$$

$$Z_{d_\nu} = \left(1 - \frac{\lambda_{d_\nu}}{d_\nu N_\nu}\right) + \frac{\lambda_{d_\nu}}{d_\nu N_\nu}\left[\sum_\mu \frac{\lambda_{a_\mu}}{\lambda}(Z_{a_\mu})^{a_\mu - 1}(Z_{d_\mu})^{d_\mu}\right] \tag{15}$$

where $\lambda = \lambda_{a_1} + \lambda_{a_2} = \lambda_{d_1} + \lambda_{d_2}$, is the total number of the hydrogen bonds in equilibrium state. Here, for brevity we only explain Z_{a_1}, while the others have the similar explanations. Clearly, $\lambda_{a_1}/(a_1N_1)$ denotes the ratio of the number of hydrogen-bonded groups of A to the total number of the groups A. Then $(1 - \lambda_{a_1}/(a_1N_1))$ stands for the probability that a group of A is non-hydrogen-bonded, and $\lambda_{a_1}/(a_1N_1)[\Sigma_\nu\, \lambda_{d_\nu}/\lambda(Z_{a_\nu})^{a_\nu}(Z_{d_\nu})^{d_\nu - 1}]$ denotes the probability of finding it connecting with sol molecules in either self-association $(\nu = 1)$ or cross-association $(\nu = 2)$ manners.

Note that, the activity differences of the HB groups have been embodied by λ_{a_μ}/λ and λ_{d_ν}/λ, since the activity differences must be reflected through the corresponding numbers of the hydrogen bonds of different types. For the case of equal activity, the quantities of λ_{a_μ}/λ and λ_{d_ν}/λ reduce to $a_\mu N_\mu/\Sigma_\mu(a_\mu N_\mu)$ and $d_\nu N_\nu/\Sigma_\nu(d_\nu N_\nu)$, respectively.

When the system approaches the critical point, the sol fraction S approaches 1. Assume that $\lambda_{a_\mu}^c$ and $\lambda_{d_\nu}^c$ are the critical values of λ_{a_μ} and λ_{d_ν}. This signifies that as $\lambda_{a_\mu} \rightarrow \lambda_{a_\mu}^c$ and $\lambda_{d_\nu} \rightarrow \lambda_{d_\nu}^c$, $S_\mu \rightarrow 1$ and also $Z_{a_\mu} \rightarrow 1$ and $Z_{d_\mu} \rightarrow 1$. From this fact, the gelation condition satisfied by $\lambda_{a_\mu}^c$ and $\lambda_{d_\nu}^c$ can be obtained by the following steps. First, re-forming all the equations listed in eq 15, e.g., recasting the first equation as $\lambda_{a_1}/(a_1N_1) = \lambda(1 - Z_{a_1})/\{\lambda - \Sigma_\mu[\lambda_{d_\mu}(Z_{a_\mu})^{a_\mu}(Z_{d_\mu})^{d_\mu - 1}]\}$. Second, calculating the limitation of $\lambda_{a_1}/(a_1N_1)$ under the condition of $Z_{a_\mu} \rightarrow 1$ and $Z_{d_\nu} \rightarrow 1$. On the calculating, one can find that $\lambda^c_{a_1}/(a_1N_1)$ becomes an indeterminate (0/0). Applying L'Hospital's rule together with all the equations, the desired gelation condition can be given by

$$D(\{\lambda^c_{\mu\nu}\}) = 0 \tag{16}$$

with $D(\{\lambda_{\mu\nu}\}) = [\lambda - \Sigma_\mu(\lambda_{a_\mu}\lambda_{d_\mu})/N_\mu]^2 - [(a_\mu - 1)/a_\mu\lambda_{a_\mu}{}^2/N_\mu][(d_\nu - 1)/d_\nu\ \lambda_{d_\nu}{}^2/N_\nu]$. This result can reduce the form of the single component HB system as reported in our previous letter.[13] In addition, by changing the corresponding symbols, one can easily check this gelation condition recovers the result proposed by Flory and Stockmayer for polycondensation of $A_a{-}B_b$ type.[14,15]

When the SGT takes place, one can further consider the free energy corresponding to the sol and gel phases. To this end, it is convenient to introduce the sol variables by marking a superscript of "prime" in a variable in order to distinguish from the system variable. In doing so, we know that N'_1, N'_2 and $\lambda'_{\mu\nu}$ denote the molecular numbers of $A_{a_1}D_{d_1}$ type, $A_{a_2}D_{d_2}$ type and the number of hydrogen bonds of $T_{\mu\nu}$ type in the sol phase, respectively. It is evident that the number of monomers of each type in the sol phase must be equal to that in the total system. Thus, in postgel regime, making use of the sol variables, we have

$$\mathscr{P}_{1,0}(N_1, \{\lambda_{\mu\nu}\}) = \mathscr{P}_{1,0}(N'_1, \{\lambda'_{\mu\nu}\}),\quad \mathscr{P}_{0,1}(N_2, \{\lambda_{\mu\nu}\}) = \mathscr{P}_{0,1}(N'_2, \{\lambda'_{\mu\nu}\}) \tag{17}$$

Moreover, under the same external conditions, the formation of each type of hydrogen bonds must obey the same law of mass action no matter whether it is in the sol phase or in the total system. This yields

$$\frac{\lambda_{\mu\nu}}{(a_\mu N_\mu - \lambda_{a_\mu})(d_\nu N_\nu - \lambda_{d_\nu})} = \frac{\lambda'_{\mu\nu}}{(a_\mu N_\mu{}' - \lambda'_{a_\mu})(d_\nu N_\nu{}' - \lambda'_{d_\nu})} \tag{18}$$

From eqs 11, 17, and 18, we can find that

$$\mathscr{P}_{m,n}(N_1, N_2, \{\lambda_{\mu\nu}\}) = \mathscr{P}_{m,n}(N'_1, N'_2, \{\lambda'_{\mu\nu}\}) \tag{19}$$

where $\mathscr{P}_{m,n}(N_1, N_2, \{\lambda_{\mu\nu}\})$ and $\mathscr{P}_{m,n}(N'_1, N'_2, \{\lambda'_{\mu\nu}\})$ denote the numbers of clusters of $(m \wedge n)$ type expressed by the system variables and sol variables in the postgel regime, respectively.

Equation 19 enables us to find an invariant property of an average physical quantity as that in polycondensations proposed by Xiao and co-workers.[20] For an average physical quantity $\mathscr{H}(N_1, N_2, \{\lambda_{\mu\nu}\})$ defined by $\mathscr{H}(N_1, N_2, \{\lambda_{\mu\nu}\}) = \Sigma_{m,n}\, \mathscr{H}_{m,n}\mathscr{P}_{m,n}(N_1, N_2, \{\lambda_{\mu\nu}\})$ with $\mathscr{H}_{m,n}$ being only related to the index m and n, this invariant property states that if $\mathscr{H}(N_1, N_2, \{\lambda_{\mu\nu}\})$ in pregel is known, then the corresponding quantity $\mathscr{H}$ in postgel can be directly obtained via the replacement of the system variables N_1, N_2 and $\{\lambda_{\mu\nu}\}$ by the corresponding sol variables N'_1, N'_2 and $\{\lambda'_{\mu\nu}\}$ in the postgel regime. As an application of the invariant property, from eq 8, we can obtain the equilibrium free energy of the sol phase in the postgel regime, $\mathscr{F}^{\text{sol}}_{\text{eq}}(N_1, N_2, \{\lambda_{\mu\nu}\})$, as follows

$$\mathscr{F}^{\text{sol}}_{\text{eq}}(N_1, N_2, \{\lambda_{\mu\nu}\}) = k_{\text{B}}T\left[N'_1 \ln\frac{\mathscr{P}_{1,0}}{N'_1} + N'_2 \ln\frac{\mathscr{P}_{0,1}}{N'_2} + \sum_{\mu,\nu}\lambda'_{\mu\nu}\right] \tag{20}$$

The gel free energy $\mathscr{F}^{\text{gel}}_{\text{eq}} = \mathscr{F}_{\text{eq}}(N_1, N_2, \{\lambda_{\mu\nu}\}) - \mathscr{F}^{\text{sol}}_{\text{eq}}(N'_1, \text{N}'_2, \{\lambda'_{\mu\nu}\})$ therefore becomes

$$\mathscr{F}^{\text{gel}}_{\text{eq}} = k_{\text{B}}T\left[\sum_{\mu,\nu}(\lambda_{\mu\nu} - \lambda'_{\mu\nu}) + \left(N_1 \ln\frac{\mathscr{P}_{1,0}}{N_1} - N'_1 \ln\frac{\mathscr{P}_{1,0}}{N'_1}\right) + \left(N_2 \ln\frac{\mathscr{P}_{0,1}}{N_2} - N'_2 \ln\frac{\mathscr{P}_{0,1}}{N'_2}\right)\right] \tag{21}$$

Below the critical point of SGT, one can find $\mathscr{F}^{\text{sol}}_{\text{eq}} = k_{\text{B}}T[N_1 \ln \mathscr{P}_{1,0}/N_1 + N_2 \ln \mathscr{P}_{0,1}/N_2 + \Sigma_{\mu,\nu}\, \lambda_{\mu\nu}]$ and $\mathscr{F}^{\text{gel}}_{\text{eq}} = 0$ since $N_\mu = N'_\mu$ and $\lambda_{\mu\nu} = \lambda'_{\mu\nu}$ in the pregel regime. The free energies of the two phases are obviously not equal to each other at the critical point. This is clear because in the pregel regime, no the gel phase exists at all.

IV. The Scaling Laws for the Sol−Gel Transition

The SGT in nonlinear HB system is induced by the hydrogen bonds between molecules, then how to describe this kind of phase transition? In this section, an attempt is made to give the scaling law associated with the SGT. In some following equations concerned the scaling problem only some key factors are kept as is usually the case.[21]

Taking the kth moment M_k for the various clusters as an example, it reflects the change induced by the connectivity of the system and has the definition of

$$M_k = \sum_{m,n}(m + n)^k \mathscr{P}_{m,n}(N_1, N_2, \{\lambda_{\mu\nu}\}) \tag{22}$$

Differentiating both sides of eq 22 with respect to $\{\lambda_{\mu\nu}\}$, a recursion formula associated with M_{k+1} and M_k can be given by

$$M_{k+1} = \frac{1}{D(\{\lambda_{\mu\nu}\})}\left[R_0(\{\lambda_{\mu\nu}\}) + \sum_{\mu\nu} R_{\mu\nu}\frac{\partial}{\partial\lambda_{\mu\nu}}\right]M_k \tag{23}$$

in which the quantities of $R_0(\{\lambda_{\mu\nu}\})$ and $\{R_{\mu\nu}\}$ are the functions of N_1, N_2, and $\{\lambda_{\mu\nu}\}$, whose detailed forms are omitted for brevity since they do not affect the discussions on the scaling problems. Through this recursion formula, M_{k+1} can be easily calculated by M_k.

In the pregel regime, M_1 denotes the total numbers of monomers, i.e., $M_1 = (N_1 + N_2)$. Then we can obtain $M_2 = ((N_1 + N_2)R_0(\{\lambda_{\mu\nu}\}))/D(\{\lambda_{\mu\nu}\})$ via the recursion formula. Obviously, M_2 diverges as the system approaches the critical point, at which $\{\lambda_{\mu\nu}\} \rightarrow \{\lambda^c_{\mu\nu}\}$ and $D(\{\lambda_{\mu\nu}\}) \rightarrow 0$ (see eq 16). In fact, with the above recursion formula, it can be found that the kth moment ($k \geq 2$) displays the behavior as $M_k \sim 1/[D(\{\lambda_{\mu\nu}\})]^{2k-3}$ as $D(\{\lambda_{\mu\nu}\}) \rightarrow 0$. This means that near the critical point, a drastic change of the connectivity occurs. Furthermore, using the invariant property of the average physical quantity mentioned in section III, we can find that in the postgel regime, M'_k, the kth moment of the sol clusters displays the behavior as $M'_k \sim 1/[D(\{\lambda'_{\mu\nu}\})]^{2k-3}$ as $D(\{\lambda'_{\mu\nu}\}) \rightarrow 0$. The behaviors of these average physical quantities therefore reflect the essentiality induced by hydrogen bonds. In the vicinity of the critical point, the kth moment M_k can therefore be unitedly expressed as the following form

$$M_k \sim \frac{1}{|D(\{\lambda_{\mu\nu}\})|^{\gamma_k}}, (k \geq 2, |\lambda_{\mu\nu} - \lambda^c_{\mu\nu}| \rightarrow 0) \tag{24}$$

where $\gamma_k = 2k - 3$, is the critical exponent of the *k*th moment near the critical point.

When the system is near the critical point, some physical quantities are only related to the asymptotic size distribution $\mathscr{P}_{m,n}$ for large *m* and *n*.[12] Using the definition of the *k*th moment, the asymptotic second moment $\tilde{M}_2$ can be expressed as $\tilde{M}_2 = \int\int (m + n)^2 \mathscr{P}_{m,n}\ \mathrm{d}m\ \mathrm{d}n$, where the summations over *m* and *n* have been replaced by the integrals. Let $(m + n) = \eta$, this equation can be re-formed as $\tilde{M}_2 = \int \eta^2 \mathscr{P}_\eta\ \mathrm{d}\eta$ with $\mathscr{P}_\eta = \int_0^\eta \mathscr{P}_{m,n-m}\ \mathrm{d}m$. In doing so, by the method proposed by Tang and co-workers,[22] the asymptotic distribution can be expressed as

$$\tilde{\mathscr{P}}_\eta = B\eta^{-\tau} \exp\left(-\frac{\eta}{\eta_c}\right) \tag{25}$$

in which *B* is a constant and $\tau = 5/2$ is the scaling exponent of the asymptotic distribution. The quantity $\eta_c \sim \xi^{-1/\sigma}$, is the critical correlation length with the scaling exponent $\sigma = 1/2$ and $\xi \sim |D(\{\lambda^c_{\mu\nu}\})|$.

Through the asymptotic distribution and the definition of the *k*th moment, an integral calculation yields

$$\tilde{M}_k \sim \xi^{-(k+1-\tau)/\sigma}, (k \geq 2, |\lambda_{\mu\nu} - \lambda^c_{\mu\nu}| \rightarrow 0) \tag{26}$$

Obviously, in the vicinity of the critical point, the asymptotic *k*th moment should display the same behavior as that given by eq 24. In comparison with eqs 24 and 26, the scaling law satisfied by the *k*th moment near the critical point can be given by

$$\sigma\gamma_k = k + 1 - \tau, (k \geq 2) \tag{27}$$

Meanwhile, in terms of $\mathscr{P}_\eta$, we know that $\tilde{M}_1 = B \int_1^\infty \eta^{1-\tau} \exp(-\eta/\eta_c)\ \mathrm{d}\eta$. It can be re-formed as $\tilde{M}_1 = B \int_1^{\eta_c} \eta^{1-\tau}\ \mathrm{d}\eta$, where the function $\exp(-\eta/\eta_c)$ has been played the role of cutoff function. The calculated $\tilde{M}_1$ should converge to M_1 and M_1' near the critical point, respectively. This can be considered as the corresponding boundary condition, and then we have $\tilde{M}_1 = (N_1 + N_2)(1 - \eta_c^{2-\tau})$. Note that the quantity $\tilde{M}_1/(N_1 + N_2)$ just describes the behavior of sol fraction near the critical point, thus the gel fraction $G(G = 1 - S)$ becomes $G = \eta_c^{2-\tau} \sim \xi^{(\tau-2)/\sigma}$. Alternatively, expanding the sol fraction about the critical point and neglecting the higher-order infinitesimal terms, one can find $G \sim \xi^\beta$ with exponent $\beta = 1$. Collecting these relations, we have

$$\sigma\beta = \tau - 2 \tag{28}$$

This is the scaling law satisfied by the gel fraction in the vicinity of the critical point. The two scaling laws given by eqs 27 and 28 show that the SGT is indeed a kind of phase transition.

V. Discussion and Conclusion

Having obtained these results, several problems in regard to the SGT in HB systems naturally arise: (1) Is the SGT induced by hydrogen bonds a thermodynamical phase transition? (2) Is the SGT related to the liquid−solid and liquid−liquid transitions in HB systems?

For the thermoreversible associated system, whether or not the SGT is a thermodynamic phase transition has attracted the attention of several groups.[5,23−31] Up to date, the essence of the SGT in the thermoreversible associated system keeps still open. The only consensus seems to be that under the approximations of the mean field theory, the SGT is a pure geometrical phase transition.[3,5,23,24,29,32] This is also confirmed in the present HB solution system by two ways: (1) Any order of the derivation of equilibrium energy $\mathscr{F}_{\mathrm{eq}}(\{\lambda_{\mu\nu}\})$ with respect to $\{\lambda_{\mu\nu}\}$ at the critical point dose not diverge. (2) At the critical point, the free energies of the sol and gel phases are not equal to one another, which does not satisfy the requirement of a thermodynamics phase transition. Note that there must exist the loop structures in an associated network, the cyclization effect therefore becomes a considerable factor. In doing so, the related conclusion might be changed.[29−31]

As to the HB systems, the orientation of the hydrogen bonds plays an important role, which can lead to the ordered structure in HB networks and some other fascinating properties. This is different from the random network formed in the usual associated systems. Interestingly, the studies on the relationships between the SGT and liquid−solid and liquid−liquid transitions in HB systems are noteworthy. Perhaps the following clues are helpful for understanding this issue in the nonlinear HB systems.

(a) Gel phase as a transition phase. For the nonlinear HB systems, both the sol and gel phases are the two compositions of the liquid phase. It is inside the liquid-phase that the SGT occurs. The gel phase can turn into the solid phase only by further losing the energy. Then in the nonlinear HB systems, the gel phase is a transition phase which bridges the liquid and solid phases.

(b) Nucleation. A thermodynamic phase transition requires a relative stable "nucleus" to enable the new phase to grow. In the HB systems, the HB network can serve as a "nucleus" for the imminent liquid−solid transition. This is because a large number of the intramolecular hydrogen bonds can greatly enhance the lifetime of HB networks and make it stable. Thus, the SGT provides the matter condition for the liquid−solid transition.

(c) Phase separation. In HB solution systems, the binodal curves of liquid mixtures with self- and cross-associated hydrogen bonds exhibited complex phase behavior.[33−36] These rich phases and complicated phase behaviors are closely related to the strengths of the self- and cross-associated hydrogen bonds and the dispersive interaction. Temperature and the hydrogen-bonding degree play a key role in the phase separation process. The latter described the average molecular connectivity and it can be considered as a new order parameter.

(d) Entropy induced liquid−liquid transition (LLT). The LLT is referred to the transition between two distinct liquid forms with different entropy and density. Recently, LLT has shown considerable interests in HB systems.[37−40] In our opinion, LLT in HB systems is closely related to the gel phase. First, the HB network with a large number of the intramolecular hydrogen bonds has much smaller entropy relative to the sol cluster of the same size since HB process reduces the entropy. Second, a loose or compact network structure can be formed because of the orientation of hydrogen bonds, then the density of the gel phase may be lower or higher than that of the sol phase. Therefore, in nonlinear HB systems, the LLT should be related to the SGT, at least, to some extent.

In conclusion, we have studied a mixed nonlinear HB system consisting of molecules of $A_{a_1}D_{d_1}$ and $\bar{A}_{a_2}\bar{D}_{d_2}$ types from two statistical viewpoints. It is shown that such a HB system may undergo a SGT. For description of this kind of phase transition, the sol and gel free energies in pregel and postgel regimes are obtained. The corresponding scaling laws of the *k*th moment and the gel fraction in the vicinity of critical point are given. It should be noted that, however, the above conclusions are valid only under the approximations used in this article, hence the present model is still crude. Moreover, the cooperativity and the intramolecular HB are noteworthy in the HB process.[18,19] Then how to consider the effects of these factors in the present method is an interesting topic, so are the studies on the statistical parameters of HB networks and the relevant applications.

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