

## Equation of State for Hydrogen-Bonded Systems

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Hydrogen-bonded systems have a surprisingly simple equation of state in the mean field approximation. If we know the equation of state  $P_{\text{ref}}(T, V, N_1, N_2, \dots)$  of the reference system (without hydrogen bonds), then the equation of state of the system with hydrogen bonds can be written as  $P(T, V, N_1, N_2, \dots) = P_{\text{ref}}(T, V - \sum V_{ij}^H M_{ij}, N_1, N_2, \dots) - kT \sum M_{ij}/V$ , where  $M_{ij}$  is the number of bonds of the corresponding kind and  $V_{ij}^H$  is the volume change upon a bond formation. It is interesting that this equation is valid for fluids, gases, solids—as long as the system is far from the critical point and the basic presumptions of the mean field theory are valid. This equation as well as other useful thermodynamic relations for hydrogen-bonded systems are proved, and their consequences are discussed.

Hydrogen-bonded systems are interesting from the fundamental point of view. Their importance for various industrial, biological, and other applications made this field attractive for many researchers. The modern mean field theory of hydrogen bonds<sup>1–3</sup> turned out to describe phase equilibria and degree of hydrogen bonding very well.<sup>2–12</sup> Therefore, the question of the equation of state predicted by this theory is quite interesting and relevant.

The equation of state for hydrogen-bonded fluids in the framework of mean field theory was discussed by several researchers in application to many different systems.<sup>2,3,13</sup> As a rule, the authors of these works derived it for some particular system (binary or ternary fluid with prescribed number of hydrogen-bonding groups) and compared it to the available experimental data. It turns out that these results follow from a very simple and quite general equation. This equation is obtained in this Letter.

First let us recall the basic ideas of mean field approach to hydrogen-bonded systems.<sup>1,3</sup> We write the partition function of the system as the product  $\Xi = \Xi_{\text{ref}} \Xi_{\text{HB}}$ , where  $\Xi_{\text{ref}}$  represents the reference system (i.e., the system without hydrogen bonds) and  $\Xi_{\text{HB}}$  is the contribution of hydrogen bonds. It should be noted that this factorization is the central idea of the mean field theory.

For any given values  $M_{ij}$ —the numbers of hydrogen bonds between the  $i$ th and the  $j$ th kinds of proton donors and acceptors—we calculate  $\tilde{\Xi}(M_{ij})$ , the partition function of the system with the prescribed values of  $M_{ij}$ . Then we maximize  $\tilde{\Xi}$ , or, equivalently, minimize the free energy  $\tilde{A} = -kT \ln \tilde{\Xi}$ , to obtain simultaneously equilibrium values of free energy and numbers of hydrogen bonds. If  $V$  is the volume of the system and  $N_i$ ,  $i = 1, 2, \dots$ , are the numbers of particles of the corresponding kinds, then equilibrium conditions can be written as

$$\left( \frac{\partial \tilde{A}(T, V, N_1, N_2, \dots, M_{12}, \dots)}{\partial M_{ij}} \right)_{T, V, N_1, N_2, \dots} = 0 \quad (1)$$

and the free energy of the system is

$$A(T, V, N_1, N_2, \dots) = \min_{M_{ij}} \tilde{A}(T, V, N_1, N_2, \dots, M_{12}, \dots) \quad (2)$$

Let us now calculate the pressure in such a system. To do this we must differentiate  $A$  with respect to  $V$  at constant  $T, N_1, N_2, \dots$ . It should be noted that  $A$  depends on  $V$  both explicitly and implicitly—through  $M_{ij}$ . If we change the volume, the numbers of hydrogen bonds change, and therefore we must include terms like  $\partial M_{ij}/\partial V$ . Since  $M_{ik}$  are determined by the set of nonlinear eqs 1, the task might seem formidable. However, it can be greatly simplified through the following reasoning. Let  $M_{ij}(T, V, N_1, N_2, \dots)$  be the solution of eq 1. If we substitute this solution into  $\tilde{A}$ , we will obtain  $A$  due to eq 2. Therefore we can write

$$\begin{aligned} \left( \frac{\partial A}{\partial V} \right)_{T, V, N_1, N_2, \dots} &= \left( \frac{\partial \tilde{A}(V, T, N_1, N_2, \dots, M_{12}(V, T, N_1, N_2, \dots), \dots)}{\partial V} \right)_{T, V, N_1, N_2, \dots} = \\ &= \left( \frac{\partial \tilde{A}}{\partial V} \right)_{T, V, N_1, N_2, \dots, M_{12}, \dots} + \sum_{ij} \left( \frac{\partial \tilde{A}}{\partial M_{ij}} \right)_{T, V, N_1, N_2, \dots} \left( \frac{\partial M_{ij}}{\partial V} \right)_{T, V, N_1, N_2, \dots} \end{aligned} \quad (3)$$

The first term in the last expression describes the explicit dependence of  $\tilde{A}$  on  $V$ , and the last ones, the implicit dependencies. However, owing to eq 1 these terms are actually zero, and therefore we can write just

$$P = - \left( \frac{\partial \tilde{A}}{\partial V} \right)_{T, V, N_1, N_2, \dots, M_{12}, \dots} \quad (4)$$

This equation shows that we might account only for *explicit* dependence of  $\tilde{A}$  on  $V$ . This greatly simplifies the calculation of pressure.

Now let us use formula 4. There could be two possibilities:

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1. The volume of the system does not change upon formation of a hydrogen bond (this was the case discussed in ref 1).

2. There is a volume change  $V_{ij}^H$  upon formation of a  $(i, j)$ -hydrogen bond.<sup>3</sup>

Let us consider the first possibility. In this case we can write

$$\tilde{A}(V, N_1, N_2, \dots, M_{12}, \dots) = A_{\text{ref}}(T, V, N_1, N_2, \dots) + \tilde{A}_{\text{HB}}(T, V, N_1, N_2, \dots, M_{12}, \dots) \quad (5)$$

where  $A_{\text{ref}} = -kT \ln \Xi_{\text{ref}}$  is the free energy of the reference system and does not depend on  $M_{ij}$ , and  $\tilde{A}_{\text{HB}} = -kT \ln \tilde{\Xi}_{\text{HB}}$ . The differentiation of  $A_{\text{ref}}$  gives just  $P_{\text{ref}}$ .

To differentiate the second term in eq 5, let us note that  $\tilde{A}_{\text{HB}}$  can be written as<sup>1</sup>

$$\tilde{A}_{\text{HB}} = \sum_{ij} \Delta A_{ij} M_{ij} - kT \ln \mathcal{N} \quad (6)$$

where  $\Delta A_{ij}$  is the free energy of formation of one hydrogen bond between neighboring functional groups and  $\mathcal{N}$  is the number of ways to distribute the prescribed number of hydrogen bonds between the molecules. In its turn the value of  $\mathcal{N}$  can be calculated as

$$\mathcal{N} = \mathcal{N}_0 \prod_{ij} p_{ij}^{M_{ij}} \quad (7)$$

where  $\mathcal{N}_0$  is the number of ways to distribute the given number of hydrogen bonds between the functional groups, not necessary neighboring, and  $p_{ij}$  is the probability for a given pair of functional groups to be neighbors. The actual meaning of the word “neighbors” is simple for lattice models and rather less obvious for off-lattice ones. However, the only thing we need is the fact the  $p_{ij}$  scales like  $1/V$ —the probability for a given molecule to be at a certain place is inversely proportional to the total volume available for the molecule. Since  $\mathcal{N}_0$  is a purely combinatorial factor and does not depend on  $V$ , the only volume dependence of  $\tilde{A}_{\text{HB}}$  comes from  $p_{ij}$  and has the form  $kT \sum_{ij} M_{ij} \ln V$ . Differentiating this, we have

$$P(T, V, N_1, N_2, \dots) = P_{\text{ref}}(T, V, N_1, N_2, \dots) - kT \sum_{ij} M_{ij}/V \quad (8)$$

Let us now discuss the second case—when there is a volume change associated with hydrogen bond formation. Suppose<sup>3</sup> that the formation of an  $(i, j)$ -bond leads to the volume change  $V_{ij}^H$ . It means that the relevant reference system is the system with the volume  $V - V_{ij}^H$ . If we consider  $M_{ij}$   $(i, j)$ -bonds, we obtain instead of eq 5:

$$\tilde{A}(V, N_1, N_2, \dots, M_{12}, \dots) = A_{\text{ref}}(T, V - \sum_{ij} M_{ij} V_{ij}^H, N_1, N_2, \dots) + \tilde{A}_{\text{HB}}(T, V, N_1, N_2, \dots, M_{12}, \dots) \quad (9)$$

and, differentiating it

$$P(T, V, N_1, N_2, \dots) = P_{\text{ref}}(T, V - \sum_{ij} M_{ij} V_{ij}^H, N_1, N_2, \dots) - kT \sum_{ij} M_{ij}/V \quad (10)$$

This is a very simple and elegant equation. One should keep

in mind, however, that  $M_{ij}$  might have a very complicated dependence on temperature, volume, and concentration owing to eq 1.

Let us discuss the limits of validity of eq 10. First, as any mean field result, it works when fluctuations are small, i.e., far from critical points. Actually the validity region of this approach is the same as that of the acting mass law in chemical kinetics, and sometimes these equations work well surprisingly close to critical points.<sup>11</sup> We did not specify the state of the reference system, so eq 10 should work for liquids, gases or solids—as long as the reference system is well-defined. The hydrogen bonds in this model could be “simple” or cooperative; the latter means that formation of the subsequent bonds with the same molecule could be enhanced by the formation of the first bond.<sup>14,15</sup> The only situation when eq 10 does *not* work is when the formation of a hydrogen bond influences formation of another hydrogen bond between *the same* molecules. Then our basic premise  $p_{ij} \sim 1/V$  does not work, and eq 10 is not valid. This is the usual case with molecules having carboxylic groups: usually there are two bonds in each pair of  $-\text{COOH}$  groups. However, in this situation we can often treat each pair of bonds as one “superbond” with double energy.<sup>16</sup> In this situation  $M_{ij}$  in eq 10 is the number of such pairs.

Let us now discuss the physical meaning of eq 10. The first term is obvious: it describes a reference system in an “effective volume” obtained by the incorporation of volume change upon formation of hydrogen bonds. What is the physical meaning of the second term? It is tempting to interpret it as the loss of translational entropy upon formation of hydrogen bonds. Indeed, let us imagine hydrogen bonds in the gas phase, where  $P_{\text{ref}} = kT N/V$ ,  $N$  being the number of particles. Suppose for simplicity that the volume change upon bond formation is zero. Equation 10 predicts that such system collapses if the average number of hydrogen bonds per molecule exceeds 1. This corresponds to the well-known effect in the polymerization theory: formation of infinite chains leading to infinite average molecular weight and, as the result, drop in osmotic pressure.<sup>17</sup> However, in fluid and solid phase the number of hydrogen bonds per molecule can be greater than one, and eq 10 does not have such simple interpretation.

Equation 10 is quite a powerful tool for determining the equation of state of hydrogen-bonding systems. Indeed, since it works with any reference system equation of state  $P_{\text{ref}}(T, V, N_1, \dots)$ , we can use the vast apparatus of the thermodynamics of systems without hydrogen bonds. All we need to write down the equation of state of a hydrogen-bonded system is to choose a suitable equation of state of a reference system, solve eq 1, and substitute them into eq 10.

Moreover, since eq 10 is so simple, we can easily obtain qualitative understanding of the effects of hydrogen bonds on the equation of state. For example, let us discuss whether hydrogen bonds can lead to a negative coefficient of thermal expansion. This question is relevant to the famous anomaly of liquid water and is important to many applications ranging from biology to industry. From the equation

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \quad (11)$$

and the fact that  $(\partial V/\partial P)_T$  is always negative<sup>18</sup> follows that the sign of the thermal expansion coefficient is determined by the sign of  $(\partial P/\partial T)_V$ . Differentiating eq 10 and using the chain rule, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P_{\text{ref}}}{\partial T}\right)_V - \sum_{ij} \left(\frac{\partial M_{ij}}{\partial T}\right)_V \left[ \left(\frac{\partial P_{\text{ref}}}{\partial V}\right)_T V_{ij}^H + \frac{kT}{V} \right] - k \sum_{ij} \frac{M_{ij}}{V} \quad (12)$$

The constants of hydrogen bond formation have the temperature dependence  $K \sim \exp(-\Delta A/kT)$ , where  $\Delta A < 0$  is the free energy of bond formation. At the temperatures lower than the characteristic energy scale  $\Delta A/k$  the constants are large, and the numbers  $M_{ij}$  do not strongly depend on the temperature (unless there is a strong competition between hydrogen bonds of different kinds<sup>19</sup>). Therefore the contribution of hydrogen bonds in eq 12 is represented mostly by the last term, which is negative. It means that for a sufficiently large degree of hydrogen bonding the sum 12 becomes negative, causing an anomaly of the thermal expansion coefficient.

The trick that we used to obtain eq 4 is not restricted to pressure only. Instead we could differentiate free energy with respect to other thermodynamic quantities and obtain, for example, for entropy and chemical potential

$$S = \frac{\partial \tilde{A}}{\partial T}, \quad \mu_i = \frac{\partial \tilde{A}}{\partial N_i} \quad (13)$$

where all derivatives are taken *at constant values* of the numbers of hydrogen bonds  $M_{ij}$ .

The value of  $N$  in formula 6 does not depend on temperature. Differentiating eq 9 by  $T$ , we obtain therefore

$$S = S_{\text{ref}} + \sum_{ij} M_{ij} \left[ \frac{\Delta A_{ij}}{T} - \frac{\partial \Delta A_{ij}}{\partial T} \right] - \frac{A_{\text{HB}}}{T} \quad (14)$$

The chemical potential  $\mu_1$  of the particles of kind 1 actually depends on the form of the function  $\mathcal{N}(N_1, N_2, \dots)$ . In the case of cooperative hydrogen bonding, this dependence can be quite complicated.<sup>12,15</sup> Therefore, we will discuss here only the simplest case when all the bonds are *not* cooperative. Suppose that each molecule of the kind 1 has  $d_i^{(1)}$  donor functional groups of the sort  $i$  and  $a_j^{(1)}$  acceptor functional groups of the sort  $j$  ( $i, j = 1, 2, \dots$ ). Then  $N$  is proportional to the factors<sup>1</sup>

$$\prod_i \frac{(N_1 d_i^{(1)})!}{(N_1 d_i^{(1)} - \sum_j M_{ij})!} \prod_j \frac{(N_1 a_j^{(1)})!}{(N_1 a_j^{(1)} - \sum_i M_{ij})!} \quad (15)$$

Substituting these expressions in eq 6 and using eqs 9 and 10, we obtain

$$\mu_1 = \mu_{\text{ref}}^{(1)} + kT \sum_i \left( \frac{N_1 d_i^{(1)} - \sum_j M_{ij}}{N_1 d_i^{(1)}} \right) + kT \sum_j \ln \left( \frac{N_1 a_j^{(1)} - \sum_i M_{ij}}{N_1 a_j^{(1)}} \right) \quad (16)$$

where  $\mu_{\text{ref}}^{(1)}$  refers to the reference system.

In conclusion, we obtained simple and elegant formulae that allow one to calculate equation of state and other thermodynamic variables of a hydrogen-bonded system once they are known for a reference system without hydrogen bonds.

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## References and Notes

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