

# Consistent Application of the Boltzmann Distribution to Residual Entropy in Crystals

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“Residual” entropy ( $3\text{--}12\text{ J mol}^{-1}\text{ K}^{-1}$ ) is present near 0 K in some crystals composed of nonsymmetric molecules, for example, CO,  $\text{N}_2\text{O}$ ,  $\text{FClO}_3$ , and  $\text{H}_2\text{O}$ . It is detected only by the difference between spectroscopic calculations of the absolute entropy of the gaseous chemical and calorimetric measurements of its heat capacity (and phase changes) from 0 K to the temperature of the gas. Calorimetry, like any thermodynamic measurement, yields a difference, and thus gives  $\Delta S$  rather than absolute entropy values. Unlike the corresponding energy or enthalpy, entropy is normally set equal to zero at 0 K in accord with the third law of thermodynamics thereby allowing for the calculation of its absolute values at any given temperature. I shall show that residual entropy can be estimated by four different approaches to entropy (methods 1–4). Because they are applied to the same system, they should yield the same result and they do; therefore, confirming the utility of the informational, thermodynamic, stochastic, and statistical–probabilistic aspects of entropy. The assumptions, limitations, and constraints of this thesis will be stated.

## Method 1: Informational or Combinatoric

Informational or combinatoric method, derived using the coin tossing model, is traditionally used in textbooks (1–3). It applies the Boltzmann–Planck formula:

$$\begin{aligned}\Delta S_{\text{residual}} &= \lim_{T \rightarrow 0} \left( S_{\text{crystal}}^{\text{random}} - S_{\text{crystal}}^{\text{perfect}} \right) \\ &= k_B \ln \left[ \frac{W_2(\text{random})}{W_1(\text{perfect})} \right] \quad (1)\end{aligned}$$

where  $W_2$  and  $W_1$  correspond to the numbers of microstates of the real and perfect crystals, respectively. The ratio of  $W_2/W_1$  available per molecule is often viewed as the static number of configurationally nonequivalent arrangements,  $m$ . Then, each molecule will have  $m$  times the number of positions in the randomized crystal containing  $N$  molecules as compared to the perfect one

$$\frac{W_2}{W_1} = W_2 = m^N \quad (2a)$$

and thus

$$\ln W_2 = N \ln m \quad (2b)$$

For instance, CO has two possible configurations, “head-to-head” and “head-to-tail”, Figure 1A (the OC–CO arrangement is not independent, so it is not counted separately).  $N = N_A$  for 1 mole in eqs 1 and 2;  $W_1 = 1^N = 1$  because it represents the perfectly ordered crystal obeying the third law. Therefore, based on eq 2,  $\Delta S_{\text{residual/mole}} = k_B N_A \ln m = R \ln m$ .

Note that eqs 1–2 are usually applied without any reference to the energy of intermolecular interactions ( $\epsilon$ ); that is, they calculate *informational*, configurational values of residual entropy. Even though this is phenomenologically correct, this approach does not fully represent the *thermodynamic* significance of entropy because the fundamental equation

$$dS = \frac{dq_{\text{rev}}}{T} \quad (3)$$

involves  $dq_{\text{rev}}$ , an energy exchange in the form of heat under conditions of thermal equilibrium with the surroundings. To reconcile eqs 1–3, I suggest using an approach that is based on a consistent application of the Boltzmann distribution whose role as a link between the classical and statistical thermodynamics was stressed earlier (4).<sup>1</sup>

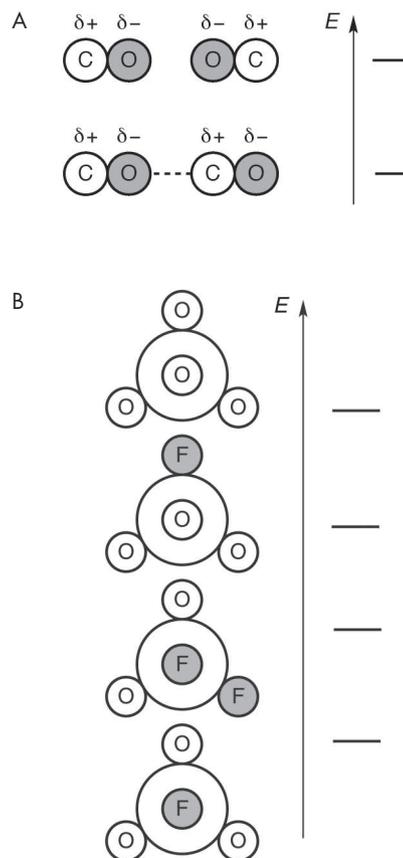


Figure 1. Possible molecular arrangements in crystals and related energy levels for the resulting intermolecular interactions: (A) CO (B)  $\text{FClO}_3$ , the central atom in each structure belongs to a different (adjacent) molecule; the large unlabeled atom behind the central atom is chlorine. The qualitative assignment of energy levels is based on the difference in electronegativity for O and F atoms.

## Method 2: Thermodynamic

Let us consider freezing a polar diatomic molecular compound like CO or ICl. At a thermodynamic melting point, both the liquid and solid are at thermal equilibrium with the surroundings. The molecules of the solid may be lined up “head-to-tail” to maximize the dipole–dipole interactions or be randomly dispersed (Figure 1A). The fraction of the aligned molecules in the solid phase depends on the result of the conflict between their thermal motion, indicated by the  $T_{\text{fusion}}$ , and the strength of intermolecular forces. This is quantitatively described by the Boltzmann distribution of particles on two levels,  $E$  and  $E + \epsilon$ , where  $\epsilon$  is the energy difference between the low (“head-to-tail”) and higher energy (“head-to-head”) aligned molecules (eq 4).

$$\frac{N_1}{N_1 + N_2} = \frac{e^{\frac{-E}{k_B T}}}{e^{\frac{-E}{k_B T}} + e^{\frac{-(E + \epsilon)}{k_B T}}} \quad (4a)$$

(lower energy level population fraction)

$$\frac{N_2}{N_1 + N_2} = \frac{e^{\frac{-(E + \epsilon)}{k_B T}}}{e^{\frac{-E}{k_B T}} + e^{\frac{-(E + \epsilon)}{k_B T}}} \quad (4b)$$

(higher energy level population fraction)

$$\frac{N_2}{N_1} = e^{\frac{-\epsilon}{k_B T}} \quad (4c)$$

If the dipole–dipole interactions between the oppositely charged ends of the molecules are strong and the temperature at the melting point is low enough ( $\epsilon \gg k_B T_{\text{fusion}}$ , eq 4c), the crystal freezes as an organized molecular array ( $N_1 \gg N_2$ ), an “ordered” or perfect crystal, as in ICl (5). Therefore, the maximal quantity of intermolecular potential energy in the system is released to the surroundings at the freezing temperature.

Conversely, if the dipole–dipole forces are weak relative to the  $k_B T$  heat bath ( $\epsilon \ll k_B T_{\text{fusion}}$ , eq 4c),  $N_2/N_1$  is close to 1, as in CO. As a result, when the crystal freezes with nearly random molecular orientation, only about half of the aligned dipole–dipole interactions have formed (and only the corresponding quantity of intermolecular potential energy is released from the crystal). Note that the difference between the observed energy released from this real crystal,  $\Delta_{\text{fusion}} H_{\text{observed}}$ , and that from the theoretical perfect (aligned) crystal yields the value of the energy gap ( $\epsilon$ , per pair of molecules, or  $N_A \epsilon/2$  per mole):

$$\Delta_{\text{fusion}} H_{\text{observed}} - \Delta_{\text{fusion}} H_{\text{perfect}} = q_{\text{latent}} = \frac{N_A \epsilon}{2} \quad (5)$$

This potential energy in the real CO crystal that “should have been released” at the solidification temperature (as would the hypothetical perfect crystal) was “frozen-in” when the liquid solidified with about half of the possible intermolecular head-to-tail interactions not effected. The corresponding en-

tropy can be defined as  $\Delta S_{\text{latent}}$  or, indicating the temperature of the reversible process,  $\Delta S_{\text{latent}}(T_{\text{fusion}})$ . However, the same crystal cannot freeze in a reversible process in both perfect and randomized forms at the same temperature. Therefore, no simple equation like eq 3 involving  $T_{\text{fusion}}$  could be written to connect  $\Delta H_{\text{latent}}(q_{\text{rev}})$  and  $\Delta S_{\text{latent}}$  if one wants to use true, that is, reversible, thermodynamic values of the heat involved.

Upon further cooling of the randomly-aligned CO solid, the increase in the difference between the values of  $\epsilon$  and  $k_B T$  (eq 4c) favors alignment of the opposite ends of the molecules. If the CO were a liquid, the realignment would take place as a reversible process as the system progresses toward the structure of a perfect crystal (6). However, in its solid form, rotation of molecules in the real crystal to become aligned is impossible for kinetic reasons, that is, high “activation energy” (6). So, at any temperature between 0 K and the solid’s melting point the CO or  $\text{FCIO}_3$  crystal is not at equilibrium with the surroundings—unlike a crystal with its  $N_2/N_1$  ratio corresponding to the surroundings’ temperature. In this respect, the situation is similar to supercooled liquids (2a).

To define the value of  $\Delta S_{\text{latent}}$ , the Boltzmann–Planck equation can be used. But eq 1 has to be modified to refer the numbers of microstates to the temperatures corresponding to the thermal equilibrium that is inherent for the Boltzmann distribution:

$$\begin{aligned} \Delta S_{\text{latent}}(T_{\text{fusion}}) &= S_{\text{random}}(T_{\text{fusion}}) - S_{\text{perfect}}(0) \\ &= k_B \ln \left[ \frac{W_2(T_{\text{fusion}})}{W_1(0 \text{ K})} \right] \end{aligned} \quad (6a)$$

$W(T)$  can be counted from the population of the energy levels using the following formula for distinct permutations (7a), which is consistent and inherently connected with eqs 3–5 because it yields the  $W$  values for the most probable (Boltzmann) distribution (2c, 4, 7c):

$$W(T) = \frac{N_{\text{total}}!}{N_1! N_2! \dots N_m!} \quad (6b)$$

$W_1(0 \text{ K}) = 1$  based on eq 4c. For  $W_2$ , a nearly equal population of all the available energy levels ( $m$ ) for  $m$  types of dipole–dipole interactions should be postulated, assuming  $T \gg \epsilon/k_B$  in eq 4, thus reducing the denominator of eq 6b to  $[(N/m)!]^m$  ( $m = 2$  for CO, Figure 1A). This allows for the new method of calculation of the  $W_2(T_{\text{fusion}})$  and  $\Delta S_{\text{residual}}$  values using Stirling’s approximation for factorials,  $\ln N! = N \ln N - N$ :

$$W_2 = \frac{N!}{\left[ \left( \frac{N}{m} \right)! \right]^m}$$

hence,

$$\ln W_2 = N \ln N - N - \frac{mN}{m} \ln \left( \frac{N}{m} \right) + N = N \ln m \quad (6c)$$

where  $W_2$  and  $W_1$  correspond to the numbers of microstates of the real and perfect crystals, respectively, at two points of thermal equilibrium,  $T_2 = T_{\text{fusion}}$  and  $T_1 = 0$ , accounting for only the energy of intermolecular interactions defined in eqs 4 and 5.

As one can see, method 2 (eq 6c) yields the same value as method 1 (eq 2), that is,  $\Delta S_{\text{residual}} = \Delta S_{\text{latent}}(T_{\text{fusion}})$ . From the standpoint of *mathematics*, eq 2 appears to be consistent with the Boltzmann distribution because, just like eq 6c, it calculates the total number of permutations under no energy constraints ( $\epsilon \ll k_B T_{\text{fusion}}$ ). Note that method 2 counts the same arrangements as method 1 in virtually the same way because they become energetically equivalent under such conditions. However, the equivalence of two such strikingly different methods requires further validation from the standpoint of *physics*. I shall show that this can be done considering the classical entropy of mixing.

### Method 3: Stochastic or Mixing

The stochastic or mixing method is based on the following well-known equation

$$\Delta_{\text{mixing}}S = -R \sum_{i=1}^m (n_i \ln \chi_i) \quad (7a)$$

where  $n_i$  is the number of moles of each component (for 1 mole of the mixture it is numerically equal to the mole fraction,  $\chi_i$ ). Equation 7a can be derived by applying the Stirling's approximation to eq 6b (7a). Note that an intermediate step in this derivation is eq 7b, so-called Gibbs entropy (2c)

$$S = k_B \sum_{i=1}^m (p_i \ln p_i) \quad (7b)$$

where  $p_i$  is the probability of a microscopic state with a certain energy. Equation 7b bridges probability (which is supposed to be temperature-dependent, based on eq 4) and seemingly temperature-independent random spatial distribution of molecules, that is, combinatorics. How can it be *both*?

Note that eqs 2 and 6b–6c are applicable for *distinguishable* arrangements, and in crystals all particles are distinguished by their specific location in the network of intermolecular forces. However, eqs 7a and 7b are used for ideal gases or solutions, that is, for indistinguishable molecules with no intermolecular interactions ( $\epsilon = 0$ ). This apparent contradiction was successfully addressed by Noggle who showed that the derivation of eq 7a from eq 6a does not require the *lack* of intermolecular interactions but rather assumes no preference in them (7a). This is applicable to crystals only at the melting point (as it is “frozen-in” the crystal with residual entropy) and only when the molecular orientations are absolutely random—exactly the case of our interest, when  $N_1 = N_2 = \dots = N_m$ , that is, when an “infinitely” high temperature for this particular Boltzmann distribution is achieved. Then, there is no preference for any molecular orientation and no energy constraint; one can say that the *effective* energy gap is zero because  $\epsilon$  is totally overpowered by  $k_B T$ .<sup>2</sup> Thus, the ideal solution assumption is equivalent to

that of infinitely high temperature [ $\epsilon \ll k_B T$  or  $\Delta_{\text{mixing}}H(\text{per mole}) = (N_A \epsilon)/2 \ll RT$ ]. This condition reconciles methods 1–3 and provides the physical basis for the connection of eqs 7a and 7b with the Boltzmann distribution at  $T_{\text{fusion}}$ .

Equations 4a and 4b provide the formulas for mole fractions of  $N_1$  and  $N_2$  to be used in eq 7a, that is,  $\chi_1$  and  $\chi_2$ , respectively. Expanding this to  $m$  species and assuming an equal population of  $m$  energy levels, one would obtain:

$$\begin{aligned} \Delta S_{\text{residual}} &= -R \sum_{i=1}^m \left(\frac{1}{m}\right) \ln \left(\frac{1}{m}\right) \\ &= -R m \left(\frac{1}{m}\right) (-\ln m) = R \ln m \end{aligned} \quad (8)$$

This approach (method 3) may be interpreted as stochastic, probability-based “mixing” of either  $m$  different spatial, positional domains (eq 2; ref 2b) (at “infinitely” high  $T = T_{\text{fusion}}$ ) or  $m$  parallel sets of Boltzmann distributions (in electronic energies and vibration for crystals) that are different only in the energy of intermolecular interactions or vibrations (eq 6c). The only problem with this method is that, unlike the other two, it does not calculate the values of  $W_2$ . However, this problem can be addressed as follows.

### Method 4: Statistical or Probabilistic

The statistical or probabilistic method for the calculation of  $W_2(T_{\text{fusion}})$  can be derived by combining eqs 4a or 4b with eq 7b (instead of 7a). It uses the partition function of the system,  $Q$  (applied only to intermolecular interactions), connected to the partition function of a single molecule ( $q$ )<sup>4</sup> that, in turn, equals  $1/p_i$ , the inverse probability of equiprobable different species with different energies valid for “infinitely” high  $T$ ,  $\epsilon \ll k_B T$  (2c)

$$W_2 = T_{\text{fusion}} = Q = q^N = \left(\frac{1}{p_i}\right)^N \quad (9)$$

where  $N$  is the number of molecules in the system. Assuming  $N_1 = N_2$  at the freezing point, the single-molecule partition function,  $q$ , equals exactly 2 for a totally random CO crystal [ $1/p_i = 1/(1/2)$ ;  $q = 1/(1/m) = m$  in general]. In combination with eq 7b, method 4 provides the final statistical mechanical validation for the use of eq 6c for the calculations of  $W_2$  (then,  $\Delta S_{\text{residual}}$ ) and also defines its limits. Similar mathematics is used in methods 1, 2, and 4 because both the coin tossing and Boltzmann distribution are based on maximum probability. Yet, method 4, just like method 3, is applicable only to separate species. As shown above, this is true *only* when  $\epsilon \ll k_B T$ . This, in turn, leads to  $N_1 = N_2 = \dots = N_m$ , so the general formula for permutations ( $W$ , eq 6b) yields the same result as eqs 2 and 6c (unconstrained permutations) as stressed in eq 9.

This is the reason why all four methods yield the same value of residual entropy,  $R \ln m$ ; the only difference is that the “infinitely” high temperature assumption for  $W_2$  is explicit in method 2 but *implicit* in methods 1, 3, and 4 (this, along with the potential energy difference between the real

and perfect crystals should always be stated). However, if the value of  $\epsilon$  is comparable with  $k_B T_{\text{fusion}}$ , the “solution” is not ideal (i.e., method 3 is not applicable), the probabilities of two possible orientations are not equal in method 4 and the “informational” entropy (method 1) overestimates the values of  $W_2$  and the corresponding entropy unless the fractions of each form are calculated using either eq 6b or the system partition function (eq 9). Thus, the criterion for the appearance of residual entropy equal to  $R \ln m$  is that  $\epsilon \ll k_B T$  at the melting point, so the system behaves as if  $\epsilon = 0$  at  $T_{\text{fusion}}^2$ .

The use of eqs 3–5 does not imply that either the appearance or value of residual entropy depends on the value of  $\epsilon$ ; it is the number of different energy levels,  $m$ , resulting from different ways to arrange the molecules in a crystal that determines the value of  $\Delta S_{\text{residual}} = R \ln m$ .

## Applications

The molar residual entropy of CO can be calculated in four ways, based on eqs 2, 6c, 8, and 9 (methods 1–4), respectively:

$$\begin{aligned} \Delta S_{\text{residual}} &= k_B \ln \left( \frac{W_2}{W_1} \right) = k_B \ln \left( \frac{2^N}{1} \right) \\ &= k_B N_A \ln \left( \frac{2}{1} \right) = R \ln 2 = 5.76 \text{ J/K mol} \end{aligned} \quad (10a)$$

$$\begin{aligned} \Delta S_{\text{residual}} &= k_B \ln \left[ \frac{N_A!}{\left( \frac{N_A}{2} \right)! \left( \frac{N_A}{2} \right)!} \right] = k_B N_A \ln 2 \\ &= R \ln 2 = 5.76 \text{ J/K mol} \end{aligned} \quad (10b)$$

$$\begin{aligned} \Delta S_{\text{residual}} &= -R \left[ \frac{1}{2} \ln \left( \frac{1}{2} \right) + \frac{1}{2} \ln \left( \frac{1}{2} \right) \right] \\ &= -R \ln \left( \frac{1}{2} \right) = R \ln 2 = 5.76 \text{ J/K mol} \end{aligned} \quad (10c)$$

$$\begin{aligned} \Delta S_{\text{residual}} &= k_B \ln \left[ \frac{\left( \frac{1}{p_2} \right)^N}{\left( \frac{1}{p_1} \right)^N} \right] = k_B \ln \left[ \frac{\left[ \frac{1}{\left( \frac{1}{2} \right)} \right]^N}{1^N} \right] \\ &= R \ln 2 = 5.76 \text{ J/K mol} \end{aligned} \quad (10d)$$

The same residual entropy value, based on the occupation of two different energy levels, can be obtained for linear NNO, para-substituted benzenes, or crystals of metal cyanides. For nonlinear molecules, more than two energy levels

could be occupied. For instance, for tetrahedral  $\text{FCIO}_3$  (or  $\text{CH}_3\text{D}$ ), there are four possible dipole arrangements in a tightly packed crystal (Figure 1B). Therefore, considering the electrostatic interactions between the dipoles, there are four different energy levels: this results in the presence of  $[(N/4)!]^4$  in the denominator of eq 6c yielding the  $\Delta S$  value of  $R \ln 4 = 11.52 \text{ J K}^{-1} \text{ mol}^{-1}$ . Equations 2 (9) and 8 would be adjusted as  $\Delta S_{\text{residual}} = k_B \ln(W_2/W_1) = k_B \ln(4^N/1) = k_B N_A \ln(4/1) = R \ln 4$  and  $\Delta S_{\text{residual}} = -4R[(1/4)\ln(1/4)] = -R \ln(1/4) = R \ln 4$ , respectively—yielding the same number as expected.

In real crystals, the value of  $W_2$  could be lower or higher than predicted. The experimental values of molar residual entropy for CO, RbCN,  $\text{N}_2\text{O}$ , *p*-bromochlorobenzene,  $\text{CH}_3\text{D}$ ,  $\text{FCIO}_3$  are 4.6, 5.43, 5.8, 5.7, 11.6, and 10.1  $\text{J K}^{-1}$ , respectively (1e, 2a, 7d, 8, 9). In addition to possible partial rearrangements in the solid state (“freezing-in” is not always perfect; also, the condition  $\epsilon \ll k_B T_{\text{fusion}}$  may not be met precisely), the differences between the predicted and real values underscore the limitation of the “head-to-tail” model, which is valid only for a simplified explanation that assumes the averaging of real molecular orientations.<sup>3</sup> The real crystal lattice formation occurs at short intermolecular distances and, thus, is dominated by repulsive rather than attractive potentials that force the system into a certain type of packing (10). To account for the deviations from the simple model used in this study, molecular alignment in the real crystal lattice and the related energy levels would have to be considered.

The advantages of using method 2 can be illustrated by finding the value of residual entropy for ice crystals. The configurational disorder in ice is caused by 16 possible alignments of which only 6 can be realized because water molecules cannot attain any “head-to-head” (O–O or H–H) configurations (11). The combinatoric calculation by Pauling (11a) requires visualizing all possible alignments that is, by far, not as obvious as in CO or  $\text{FCIO}_3$ :

$$\begin{aligned} \Delta S &= k_B \ln \frac{W_2}{W_1} = k_B \ln \left[ \frac{6^N \left( \frac{1}{2} \right)^{2N}}{1} \right] \\ &= k_B \ln \left[ 6^N \left( \frac{1}{4} \right)^N \right] = k_B N_A \ln \left( \frac{3}{2} \right) = R \ln \left( \frac{3}{2} \right) \end{aligned} \quad (11)$$

In contrast, method 2 is based on experimental evidence of the number of available energy levels and molecular geometry: If common ice Ih is converted to “ordered” ice XI, based on X-ray data, the crystal’s unit cell is slightly compressed in two out of three spatial dimensions by 0.23% and 0.78% (11b, c). This can be illustrated by considering an  $\text{H}_2\text{O}$  molecule located in the orthogonal  $x, y, z$  Cartesian space (Figure 2A). Compression along the  $z$  direction would not alter the hydrogen bond length whereas pressing along either  $x$  or  $y$  coordinate would. The  $x$  and  $y$  dimensions of the molecule are slightly nonequivalent because of the H–O–H bond angle of  $105\text{--}109^\circ$  (11c); pressure on the molecule in the  $x$  direction results in a greater impact in shortening the

hydrogen bonds (Figure 2A). In turn, this results in creating small differences ( $\epsilon$ ) between the energy levels for hydrogen bonds of different strength (eq 4c) and consequently leads to the occurrence of residual entropy with three different forms ( $m = 3$  including the ground state, which corresponds to the uniform ice XI, Figure 2B).

This leads to the appearance of three  $(N/3)!$  terms in the denominator of eq 6c. The lack of “head-to-head” alignment has to be accounted for by subtracting the corresponding entropy,  $\Delta S_{\text{“head-to-head”}} = R \ln 2$  (eqs 10a–d):

$$\begin{aligned} \Delta S &= k_B \ln \frac{N_A!}{\left(\frac{N_A}{3}\right)! \left(\frac{N_A}{3}\right)! \left(\frac{N_A}{3}\right)!} - R \ln 2 \\ &= k_B N_A \ln 3 - R \ln 2 = R \ln \left(\frac{3}{2}\right) \end{aligned} \quad (12a)$$

If one assumes  $m = 3$  based on Figure 2B and method 2, then methods 1 and 4 lead to the same answer given no “head-to-head” or “head-to-tail” randomness:

$$\begin{aligned} \Delta S &= k_B \ln 3^N - k_B \ln 2^N = k_B \ln \left[ \frac{1}{\left(\frac{1}{3}\right)} \right]^N - k_B \ln 2^N \\ &= R \ln 3 - R \ln 2 = R \ln \left(\frac{3}{2}\right) \end{aligned} \quad (12b)$$

This assumption ( $m = 3$ ) is consistent with eq 11. The value of  $m$  in eq 11 is hidden, but it can be made more visible if the number of ways the system can be configured,  $6^N(1/2)^{2N}$ , is rewritten as  $[(6/2)(1/2)]^N$ : there are 6 different arrangements of molecular pairs, that is, 3 per one molecule (this is  $m$ ), and only half of them are realized for  $N$  molecules of  $\text{H}_2\text{O}$  accounting for the lack of the “head-to-head” alignment. Thus, method 2 may be viewed as a “shortcut” for method 1 applicable to complex systems in which the number of energy levels for  $\epsilon$  can be determined more easily than the number of molecular arrangements.

Entropy of mixing of three different forms (method 3) yields the same value as expected:

$$\begin{aligned} \Delta S &= \Delta S_{\text{maximum}} - \Delta S_{\text{“head-to-head”}} \\ &= -3R \left[ \frac{1}{3} \ln \left(\frac{1}{3}\right) \right] - R \ln 2 \\ &= R \ln 3 - R \ln 2 = R \ln \left(\frac{3}{2}\right) \end{aligned} \quad (12c)$$

## Conclusions

Non-aligned molecular arrangements of molecular arrangements in polar crystals are caused by weak molecular dipoles ( $\epsilon \ll k_B T_{\text{fusion}}$ ) at the thermodynamic freezing point. This “infinitely” high temperature assumption is implicit in calculations of configurational entropy and is equivalent to

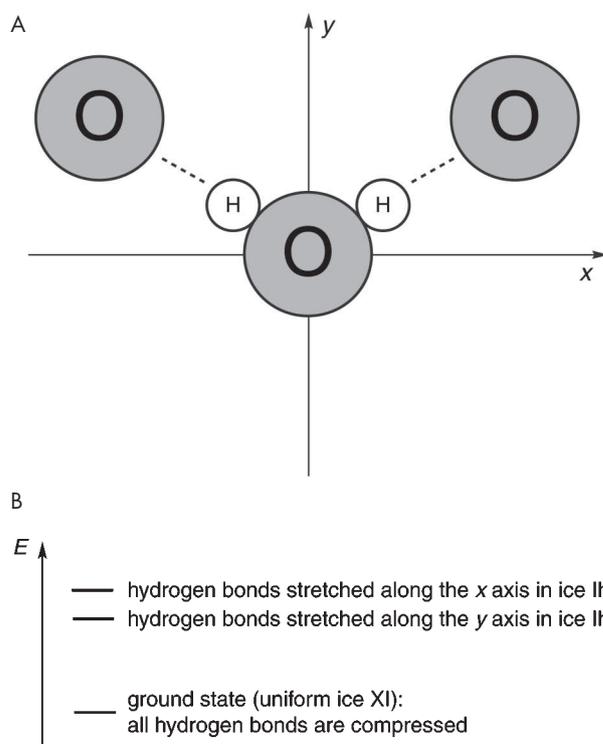


Figure 2. Illustration of the presence of three energy levels for intermolecular interactions in ice crystals. (A) The molecule of water spatial alignment that illustrates how compressing the crystal in  $x$  and  $y$  directions results in shortening the hydrogen bonds in two nonidentical ways. (B) The resulting splitting of the energy levels for intermolecular O–H bonds

the ideal solution assumption in calculations of entropy of mixing. This leads, in turn, to the same numerical answers in calculating the residual entropy using different methods thus showing the convergence of the configurational–informational, thermodynamic (energy distribution), stochastic (mixing), and statistical–probabilistic aspects of entropy.

## Acknowledgments

I thank Norman C. Craig (Oberlin College) for helpful comments, Mark R. Hoffmann (UND) for critical reading of the manuscript, and Frank L. Lambert for productive arguments. The comments of *JCE* reviewers were truly substantial in improving the article.

## Notes

1. The Boltzmann distribution and difference in energies between different molecular alignments are mentioned in covering residual entropy by Levine and Noggle (6, 7b); however, no detailed derivation has been provided.

2. The equal population of energy levels may also be obtained when  $\epsilon = 0$ , regardless of temperature. However, this would imply that freezing a liquid comprised of symmetrical molecules, like  $\text{N}_2$ , would also result in creating residual entropy equal to  $R \ln 2$ , that

is, a well-known Gibbs paradox. Of course, since  $\epsilon = 0$  at any temperature, no energy of intermolecular interactions is “frozen in” solid  $N_2$ . Therefore, the intermolecular energy difference, as a marker, appears to be essential for the experimental manifestation of residual entropy.

3. For instance, “ordered” ICl packs in a crystal as a puckered zigzag chain in which not only the I–Cl but also I–I intermolecular interactions are significant. The “head-tail” alignment is observed using X-ray crystallography; however, while viewed under a different angle, the Cl–I–I–Cl–I–I atomic order may be seen (5a, b).

4. Note that  $q$  used in eq 9 refers to the partition function of a single molecule and should not be confused with the  $q$  used in eq 3 to represent heat.

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