Molecular interpretation of Trouton's and Hildebrand's rules for the entropy of vaporization of a liquid

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ABSTRACT

The entropy of vaporization at a liquid's boiling point is well approximated by Trouton's rule and even more accurately by Hildebrand's rule. A cell method is used here to calculate the entropy of vaporization for a range of liquids by subtracting the entropy of the gas from that of the liquid. The liquid's entropy is calculated from the force magnitudes measured in a molecular dynamics simulation based on the harmonic approximation. The change in rotational entropy is not accounted for except in the case of liquid water. The predicted entropies of vaporization agree well with experiment and Trouton's and Hildebrand's rules for most liquids and for water except other liquids with hydrogen bonds. This supports the idea that molecular rotation is close to ideal at a liquid's boiling point if hydrogen bonds are absent; if they are present, then the rotational entropy gain must be included. The method provides a molecular interpretation of those rules by providing an equation in terms of a molecule's free volume in a liquid which depends on the force magnitudes. Free volumes at each liquid's boiling point are calculated to be ~ 1 Å^3 for liquids lacking hydrogen bonds, lower at ~ 0.3 Å^3 for those with hydrogen bonds, and they decrease weakly with increasing molecular size.

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1. Introduction

The structure and entropy of liquids are complex and controversial. Yet one of the simplest observations about liquid entropy is Trouton's rule, made over a century ago. Trouton's rule [1] states that the entropy of vaporization $\Delta S_b^{\circ,pp}$ of pure liquids at their boiling point T_b and standard pressure $p^\circ = 1$ bar is approximately 85–90 J $\cdot$ K^{-1} $\cdot$ mol^{-1}. This also means that the enthalpy of vaporization $\Delta H_b^{\circ,pp}$ divided by T_b has this same value. Much subsequent work has been carried out to understand this universality and the origin of any discrepancies. A more accurate rule was established almost a century ago by Hildebrand [2] that the entropy change of vaporization $\Delta S_b^{\circ,pc}$ to a specific gas-phase concentration is constant. This improves on Trouton's rule because the gas-phase concentration c_g at constant pressure is inversely proportional to T_b via the ideal-gas equation $c_g = p/k_B T_b$. While the choice of standard concentration is arbitrary, Everett [3] suggested it to be that of the ideal gas at $T^\circ = 273.15$ K and $p^\circ = 1$ bar while Shinoda suggested the same but at $T^\circ = 419$ K [4]. The relationship between these two entropy changes is

$$\Delta S_b^{\circ,pc} = \Delta S_b^{\circ,pp} - R \ln \frac{T_b}{T^\circ}. \qquad (1)$$

Alternatively, one can invert this equation to obtain a modified Trouton's rule for $\Delta S_b^{\circ,pp}$ with a logarithmic dependence on T_b [3–5]. Even though Hildebrand's rule is more accurate, it is overshadowed by Trouton's rule which still dominates the textbooks [5]. Similar to how Trouton's constant is obtained, $\Delta S_b^{\circ,pc}$ can be fitted empirically to experimental data, giving values of 83 J $\cdot$ K^{-1} $\cdot$ mol^{-1} [6], 80 J $\cdot$ K^{-1} $\cdot$ mol^{-1}[3], and 84 J $\cdot$ K^{-1} $\cdot$ mol^{-1} [4]. The prediction of either entropy change, however, is another matter. A variety of quantities on which the entropy changes might depend have been proposed: $\Delta H_b^{\circ,pp}$ [7], the critical temperature and volume [8,9], the sum of atomic number [10], T_b [11], molecular mass [11], molecular volume [12–16], symmetry number [17], number of torsions [17], the extent of planarity [17], or type of functional group [18]. None of these, though, have had a firm enough combination of simplicity, accuracy, and a sound theoretical basis to surpass Hildebrand's rule let alone Trouton's rule.

With gas-phase entropy effectively understood when non-ideal behavior is taken into account, the mystery of Trouton's and Hildebrand's rules amounts to understanding liquid-phase entropy. An indirect route to liquid-phase entropy is to subtract the entropy of vaporization from the entropy of an ideal gas obtained either from experiment [19–22], distribution functions [23–27],

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or perturbation calculations [28]. White and Meirovitch use another approach based on the probabilities to insert solvent molecules, one at a time, into a system [29]. However, these approaches give relative rather than explicit information on the liquid phase. A direct approach to quantify liquid-phase entropy is cell theory which expresses it in terms of the free volume of each molecule in the environment of its neighbors [30–34]. Trouton's and Hildebrand's rules amount to the free volume being the same for all liquids at their respective values of T_b. This leaves the questions of what the free volume is and how one calculates it. Most early approaches used approximate, analytical theories [35–37]. More recently a number of computational approaches have been put forward to evaluate the free-volume term which have the advantage that the liquid environment with its diverse range of configurations is modeled more accurately. These methods may be based on Monte Carlo acceptance ratios [38,39], forces [40–46], velocity [47,48], displacements [49], or normal mode analysis of clusters [50]. The purpose of this work is to test our approach to calculate the entropy of liquids based on forces [40–46] by comparing the formulation with other theories, predicting the entropy of vaporization for a range of common liquids, comparing with experiment, examining how the free volumes depend on the liquid, and providing a rationale for Trouton's and Hildebrand's rules.

2. Experimental

The ideal-gas partition function of N of molecules with three rotational degrees of freedom at pressure p and temperature T is [45,44]

$$\Delta_g = \left(e^{-pv_g/k_B T} \frac{k_B T e}{p\Lambda^3} \frac{8\pi^2}{\sigma \prod_{i=x,y,z} \Theta^i} \right)^N, \tag{2}$$

where e is the natural logarithm base, v_g is the volume per molecule, k_B is Boltzmann's constant, σ is the molecule's symmetry number, i is the coordinate x, y or z, $\Lambda = h/(2\pi m k_B T)^{1/2}$ and $\Theta^i = h/(2\pi I^i k_B T)^{1/2}$ are respectively, the translational de Broglie wavelengths and three rotational de Broglie waveangles, h is Planck's constant, m is the molecule's mass, and I^i are the respective moments of inertia along the molecule's principal axes. We neglect the internal partition function because we assume that it does not change between the liquid and gas phases and therefore cancels in the vaporization process. The chemical potential is

$$\mu_g = \left(\frac{\partial}{\partial N}(-k_B T \ln \Delta_g) \right)_{p,T} = -k_B T \ln \frac{k_B T}{p\Lambda^3} \frac{8\pi^2}{\sigma \prod_{i=x,y,z}^3 \Theta^i}. \tag{3}$$

The partial entropy at constant pressure is

$$s_g^p = -\left(\frac{\partial \mu_g}{\partial T} \right)_{p,N} = k_B \ln \frac{k_B T e^{5/2}}{p\Lambda^3} \frac{8\pi^2 e^{3/2}}{\sigma \prod_{i=x,y,z}^3 \Theta^i}. \tag{4}$$

The partial enthalpy is

$$h_g^p = \mu_g + T s_g^p = 4k_B T. \tag{5}$$

The corresponding liquid-phase partition function is given by

$$\Delta_l = \left\{ e^{-(\varphi_l^0 + pv_l)/k_B T} \frac{\Omega_l^{rot}}{\sigma} \prod_{i=x,y,z} \left(\frac{2k_B T}{F_l^i \Lambda} \frac{2k_B T}{\tau_l^i \Theta^i} \right) \right\}^N, \tag{6}$$

where we assume that translational and rotational motion of a molecule may be approximated by a collection of mean-field harmonic potentials [40–46], φ_l^0 is the energy minimum of the mean-field potential, v_l is the volume per molecule, Ω_l^{rot} is the number of orientational minima, and F_l^i and τ_l^i are half the force and torque magnitudes along and about the molecule's principal axes

measured in a molecular dynamics simulation. The halving avoids double-counting of pairwise forces or equivalently shifts the forces into the reference frame of zero net force [40,41]. The chemical potential is

$$\mu_l = \varphi_l^0 - k_B T \ln \left\{ \frac{\Omega_l^{rot}}{\sigma} \prod_{i=x,y,z} \left(\frac{2k_B T}{F_l^i \Lambda} \frac{2k_B T}{\tau_l^i \Theta^i} \right) \right\}, \tag{7}$$

where the small pv_l term may be ignored at ambient pressure. The partial entropy at constant pressure is

$$s_l^p = k_B \ln \left(\frac{\Omega_l^{rot}}{\sigma} \prod_{i=x,y,z} \left\{ \frac{2k_B T e}{F_l^i \Lambda} \frac{2k_B T e}{\tau_l^i \Theta^i} \right\} \right), \tag{8}$$

where we note that F_l^i and τ_l^i have an implicit dependence on the square root of T and that the other derivatives cancel [42]. The partial enthalpy is

$$h_l^p = \mu_l + T s_l^p = \varphi_l^0 + 6k_B T. \tag{9}$$

The standard entropy of vaporization $\Delta S_b^{\circ,pp}$ for a molecule transferring from the pure liquid phase to the gas phase at pressure $p^\circ = 101{,}325$ Pa at the boiling point T_b is obtained using equations (4) and (8):

$$\Delta S_b^{\circ,pp} = s_g^{\circ,p} - s_l^{\circ,p} = k_B \ln \left\{ \frac{k_B T}{p^\circ v_l^{tr1/2}} \frac{8\pi^2}{\Omega_l^{rot} \omega_l^{rot} e^{3/2}} \right\}, \tag{10}$$

observing from the simulations that the moments of inertia change negligibly between the gas and liquid phase, and defining the translational volume $v_l^{tr} = \prod_{i=x,y,z} 2k_B T/F_l^i$ and rotational solid angle $\omega_l^{rot} = \prod_{i=x,y,z} 2k_B T/\tau_l^i$.

In the case of water, we have a theory to calculate Ω_l^{rot} based on the number of ways that a water molecule can form hydrogen bonds with its neighbors [43,45,44,46]

$$\Omega_{water}^{rot} = N_{w1}(N_{w1} - 1) \left(\frac{N_{w1} - 2}{N_{w1}} \right)^2, \tag{11}$$

where N_{w1} is the number of first-shell coordination water molecules and is obtained by integrating water's oxygen–oxygen radial distribution function up to the first minimum which is at 3.4 Å. The expression for Ω_{water}^{rot} omits the symmetry number σ which has already been accounted for in Eqs. (6)–(8). We have since derived a more accurate theory for water's entropy based on a mixture of hydrogen-bond environments [51] but the result is similar so the current theory suffices. Liquid argon requires no rotational partition function because of its spherical symmetry [40]. For the other liquids, we do not yet have a reliable method to calculate Ω_l^{rot}. We explored models involving angular discretization for solutes in liquid water [44]. However, we were not able to achieve improved accuracy relative to the simplicity of entirely neglecting the change in rotational partition function. We found that the approximation of assuming harmonic, non-overlapping minima is poor for rotational motion when the variation in energy is comparable to $k_B T$, particularly for molecules with higher symmetry such as methane and ethane. Even though some confinement exists, as shown by the non-zero values of the torques, an extra contribution comes from the entropy $(1/2)k_B T$ because of the assumed harmonic potential. This problem is analogous to whether torsional motion can be modeled as a set of harmonic potentials or a Fourier series. Consequently, we neglect here the rotational partition function's contribution to $\Delta S_b^{\circ,pp}$ in equation (10) for all liquids except water. This approximation is already commonly made in cell theories [35–37]. Therefore, for all liquids except water $\Delta S_b^{\circ,pp}$ is evaluated with the equation

$$\Delta S_b^{\circ,pp} = k_B \ln \left\{ \frac{k_B T}{p^\circ v_l^{tr} e^{1/2}} \right\}. \tag{12}$$

The results based on this assumption turn out to be remarkably successful for most of the liquids studied here. This suggests that the intermolecular forces of such liquids at their boiling points are weak enough that there is little correlation between the orientations of neighboring molecules. Nonetheless, it points out the need for a general theory to calculate the rotational entropy of liquids with stronger interactions and at lower temperatures. For formic and acetic acid, it is known that the gas-phase species is a dimer because of the two strong hydrogen bonds between the carboxylic acid groups. To account for this, we evaluate $\Delta S_b^{\circ,pp}$ for half a mole of dimer, ignoring its rotational term. Equation (12) contains the expected logarithmic temperature dependence. For a comparison of Trouton's and Hildebrand's rules, we also calculate $\Delta S_b^{\circ,pc}$ using equation (1) and T° = 273.15 K which entails replacing k_BT/p° with v_g° in equation (12). $\Delta H_b^{\circ,pc}$ equals $\Delta H_b^{\circ,pp}$ strictly, the entropy and enthalpy changes to a fixed gas-phase concentration are not what would be measured experimentally but would be lower by k_B and k_BT, respectively [45]. We also note that neither entropy change depends on v_l as advocated by Pitzer [12], consistent with conclusions made elsewhere based on analyses of experimental data [52,53,13]; only if one were to consider vaporization at constant volume in the liquid phase would a v_l dependence arise.

The standard enthalpy of vaporization, derived using equations (5) and (9), is

$$\Delta H_b^{\circ,pp} = h_g^{\circ,p} - h_l^{\circ,p} = k_BT + u_g - u_l, \qquad (13)$$

where $k_BT = pv_g$ is the work term of expansion, u_g and u_l are the potential energies per molecule in the gas and liquid phases, respectively as measured in a computer simulation, and we note in the harmonic approximation for N degrees of freedom that $u_l = \varphi_l^0 + Nk_BT/2$.

Thermodynamic quantities of solvation are calculated for the 16 liquids listed in table 1 which are argon, five hydrocarbons, two arenes, chloroform, water, three alcohols, acetone, and two carboxylic acids. We chose these molecules to give a diversity of polarity and chain length while keeping their size small to stay within the approximation that the change in internal entropy can be neglected. For each molecule, molecular dynamics simulations using the AMBER 9 software package [54] are performed on a single molecule in the gas phase and on a box of 375 molecules in the liquid phase. The OPLS [55] all-atom force field is used for the molecules and TIP4P-2005 for water [56]. To equilibrate each system, 500 steps of steepest-descent minimization are carried out followed by a molecular dynamics simulation at each liquid's T_b in the NVT ensemble using a Langevin thermostat with a time constant of 1 ps. Further molecular dynamics for 2 ns is done in the NPT ensemble at a pressure of 1 bar using a Berendsen barostat with a time constant of 2 ps. The AMBER 9 simulation program was modified to print out the average magnitudes of the forces and torques for all molecules and the coordination number of water. These are collected in a further 1 ns NPT molecular simulation. Simulations have SHAKE on all bonds involving hydrogen atoms, a 2 fs time step, periodic boundary conditions, 8 Å cutoff and particle mesh Ewald with default AMBER parameters. An inspection of the densities during the simulation showed that none of the liquids started to expand and vaporize during the few nanoseconds of simulation.

3. Results and discussion

The results for the predicted molar entropies $\Delta S_b^{\circ,pp}$ and $\Delta S_b^{\circ,pc}$ and molar enthalpy $\Delta H_b^{\circ,pp}$ of vaporization of each liquid are listed together with their experimental counterparts and T_b at 1 bar in table 1. We do not include sampling errors in the predicted values because they are negligible relative to the errors in the theory's approximations which cannot be estimated reliably. $\Delta H_b^{\circ,pp}$ and T_b values from experiment [57,58] were converted into $\Delta S_b^{\circ,pp}$ using the relationship at the boiling point $\Delta S_b^{\circ,pp} = \Delta H_b^{\circ,pp}/T_b$. The $\Delta S_b^{\circ,pp}$ values for all liquids compare well between simulation and experiment, with none deviating by more than 5 J · K^{-1} · mol^{-1} except the alcohols whose $\Delta S_b^{\circ,pp}$ values are 11–16 J · K^{-1} · mol^{-1} too small. Like water, alcohols are associated liquids with strong hydrogen bonds which reduce the entropy of the liquid, which we have ignored here. Concerning Trouton's rule, $\Delta S_b^{\circ,pp}$ values lie in the range 74–114 J · K^{-1} · mol^{-1} which spans Trouton's constant of 85–90 J · K^{-1} · mol^{-1}. The main deviations are either because of the influence of T_b on the concentration in the gas phase as already discussed [2,6,3–5] or the presence of hydrogen bonds which reduce the liquid's rotational partition function relative to that in the gas-phase. The dependence on T_b can be removed by considering $\Delta S_b^{\circ,pc}$ which is clearly more constant, demonstrating that Hildebrand's rule is more accurate than Trouton's. Taking the average of $\Delta S_b^{\circ,pc}$ for the first ten of liquids listed in table 1, which excludes the hydrogen-bonded liquids of water, alcohols and carboxylic acids, one obtains $\Delta S_b^{\circ,pc} = 85$ J · K^{-1} · mol^{-1}, similar to values obtained elsewhere [6,3,4]. $\Delta H_b^{\circ,pp}$ values are mostly within a few kJ mol^{-1} of experiment which supports the accuracy of the OPLS force field; those liquids deviating the most are benzene being too small by 3.9 kJ mol^{-1}, the alcohols too large by 3.4–4.6 kJ mol^{-1}, and the carboxylic acids too large by ∼17 kJ mol^{-1}, a large discrepancy which can be explained by the presence of two intact hydrogen bonds in the gas-phase dimer. This implies that the boiling points of the modeled liquids would deviate slightly from experiment but the effect on the results would be small. The effects of hydrogen bonds on rotational entropy may be seen for water whose $\Delta S_b^{\circ,pp}$ value agrees well with experiment; hydrogen bonds reduce water's rotational entropy by 15.6 J · K^{-1} · mol^{-1} in the liquid phase because of its low

TABLE 1

Simulation and experimental vaporization entropy to constant pressure $\Delta S_b^{\circ,pp}$ and to constant concentration $\Delta S_b^{\circ,pc}$ and enthalpy to constant pressure $\Delta H_b^{\circ,pp}$ at the boiling temperature T_b.

Liquid	T_b/K	$\Delta S_b^{\circ,pp}$/(J · K^{-1} · mol^{-1})		$\Delta S_b^{\circ,pc}$/(J · K^{-1} · mol^{-1})		$\Delta H_b^{\circ,pp}$/(kJ · mol^{-1})	
		Sim.	Expt.	Sim.	Expt.	Sim.	Expt.
Argon	87	74.2	74.5	83.7	84.0	7.0	6.5
Methane	112	77.5	73.1	84.9	80.6	8.3	8.2
Ethane	184	81.4	79.9	84.7	83.1	13.8	14.7
Propane	231	84.3	82.4	85.7	83.8	18.7	19.0
Butane	272	85.8	82.3	85.8	82.3	23.1	22.4
Cyclohexane	354	89.3	84.7	87.1	82.5	32.3	30.0
Benzene	353	84.4	87.0	82.3	84.8	26.8	30.7
Toluene	384	85.9	86.5	83.1	83.6	30.3	33.2
Chloroform	334	87.6	87.5	85.9	85.8	34.2	29.2
Acetone	330	86.8	88.4	85.2	86.8	31.6	29.2
Water[a]	373	113.0	109.1	110.4	106.5	41.4	40.7
Methanol	338	93.9	104.3	92.1	102.5	39.0	35.2
Ethanol	352	95.6	109.7	93.5	107.6	43.2	38.6
Propanol	370	95.5	111.9	93.0	109.4	44.8	41.4
Formic acid[b]	374	55.5	60.7	52.9	58.1	39.0	22.7
Acetic acid[b]	391	55.7	60.6	52.7	57.6	41.4	23.7

[a] Rotational partition function included.
[b] ΔS°_b is evaluated assuming that the molecule dimerizes in the liquid and gas-phases.

TABLE 2
Forces F, torques τ, free volume v_l^{tr} and solid angle ω_l^{rot} in the liquid phase.

Liquid	$F^x/10^{-10}$ N	$F^y/10^{-10}$ N	$F^z/10^{-10}$ N	$\tau^x/10^{-20}$ (N · m)	$\tau^y/10^{-20}$ (N · m)	$\tau^z/10^{-20}$ (N · m)	$v_l^{tr}/\text{Å}^3$	$\omega_l^{rot}/\text{rad}^3$
Argon	0.24	0.24	0.24	0.00	0.00	0.00	0.96	
Methane	0.33	0.33	0.33	0.19	0.19	0.20	0.83	4.12
Ethane	0.49	0.56	0.56	0.38	0.57	0.57	0.85	1.04
Propane	0.62	0.73	0.76	0.61	0.92	0.93	0.76	0.50
Butane	0.70	0.89	0.93	0.79	1.42	1.37	0.74	0.28
Cyclohexane	1.07	1.08	1.27	1.49	1.54	1.65	0.63	0.25
Benzene	0.81	0.82	1.23	1.51	1.55	1.19	1.14	0.33
Toluene	0.85	0.98	1.38	1.63	2.28	1.64	1.03	0.20
Chloroform	0.94	0.96	1.18	1.19	1.26	1.56	0.74	0.33
Acetone	0.87	0.99	1.11	1.18	1.29	1.43	0.79	0.35
Water	1.69	1.82	1.42	1.12	1.28	1.52	0.25	0.50
Methanol	1.19	1.67	1.18	1.12	1.13	1.77	0.35	0.36
Ethanol	1.36	1.46	1.56	1.28	2.12	2.10	0.30	0.16
Propanol	1.39	1.51	1.64	1.48	2.69	2.59	0.31	0.10
Formic acid	1.33	1.58	1.33	0.96	1.35	2.04	0.39	0.42
Acetic acid	1.55	1.45	1.44	1.42	1.69	2.52	0.39	0.21

first-shell coordination number N_{w1} of 4.63 compared to 6–12 for a typical liquid and because of the correlations between hydrogen bond donor and acceptors. Similar but smaller effects would be expected for the alcohols but cannot be better understood without a more exact theory for the rotational entropy in the liquid phase, as well as for the internal entropy. For the carboxylic acids, the dimer treatment performs well but slightly underestimates experiment by $5 \, J \cdot K^{-1} \cdot mol^{-1}$, presumably because the dimer has more rotational and internal entropy in the gas-phase than in the liquid.

Additional insight is given from the free volumes and solid angles in table 2, together with the force and torque magnitudes used to calculate them, already halved. Force and torque magnitudes, representing interaction strengths, are seen to increase with T_b as expected. The free volumes v_l^{tr} of liquids without hydrogen-bonds lie around 1 Å^3 while those of liquids with hydrogen bonds are much smaller at 0.25 Å^3 for water and 0.35–0.31 Å^3 for the alcohols methanol, ethanol, and propanol. There is a weak decrease in v_l^{tr} with molecular size: it is 0.83–0.74 Å^3 for the series of alkanes, 0.35–0.31 Å^3 for the series of alcohols, and 1.14–1.03 Å^3 for benzene and toluene; the planar arenes have the largest value of $v_l^{tr} = 1.14$ and 1.03 Å^3 for benzene and toluene, consistent with their poorer packing; cyclohexane, the largest molecule without hydrogen bonds, has $v_l^{tr} = 0.63 \, \text{Å}^3$. There is a greater sensitivity of ω_l^{rot} to the number or strength of the interactions; the respective quantities are 4.12–0.28 rad^3 for the alkane series, 0.36–0.10 rad^3 for the alcohol series, and 0.33 and 0.22 rad^3 for benzene and toluene. Neither of these trends, though, has much effect on $\Delta S_b^{\circ,pc}$ because v_l^{tr} contributes logarithmically and because our data suggest that the rotational contribution is small. Thus constancy of $\Delta S_b^{\circ,pc}$ remains. In comparison with other works, the weak decreasing of v_l^{tr} with molecular size that we observe runs counter to the corresponding states idea advocated by Pitzer [12] that larger molecules would have larger values of v_l^{tr}. Everett determined an averaged value [3] of $v_l^{tr} = 2.2 \, \text{Å}^3$ which is slightly larger; part of the reason for this is that he has no $e^{1/2}$ term because he assumes both that the molecules have a square-well-shaped free volume in the liquid phase rather than a harmonic one and that the molecules in a liquid possess communal entropy k_B which cancels with that in the gas phase. Whether a liquid possesses communal entropy has long been a point of dispute [59,60,33,34,40], but the high density of liquids relative to gases at ambient pressures, even at the boiling point, means that little volume is likely to be shared by molecules. Moreover, the free volume that we calculate exceeds that expected based on the atomic volume and liquid density [40], similar to what Hildebrand found for two chlorofluorocarbons [61]. This indicates that our approach to calculate v_l^{tr} implicitly captures the sharing of volume in the liquid phase as molecules continually move out of each other's way.

4. Conclusions

A cell method is used to calculate the entropy of vaporization to a fixed pressure or fixed concentration for 16 liquids. For non-hydrogen-bonded liquids, we obtain good agreement with experiment and see that Hildebrand's rule, that the entropy of vaporization is constant to constant concentration, is more accurate than Trouton's rule to constant pressure for which the concentration depends on T_b. Our approach lets us calculate the liquid-phase free volume from the force magnitudes measured in a molecular dynamics simulation for any liquid. The free volumes are ~1 Å^3 for liquids without hydrogen bonds and ~0.3 Å^3 for liquids with hydrogen bonds. They show a weak decrease with molecular size

but not enough to affect the entropy of vaporization. Our results support the view that the rotational entropy gain must be included for liquids with hydrogen bonds, as we demonstrate for water, but can be ignored for those without. This indicates that a more general theory is required for other hydrogen-bonded liquids whose rotational term we do not calculate, and for all liquids in general at lower temperatures and lower densities. This development would require moving beyond the harmonic approximation and a more precise accounting for of the communal entropy. Possible approaches include having a combination of harmonic and free volume entropy terms [48] or softer, trigonometric periodic potentials. The internal entropy change should also be included. Such investigations are the subject of future work.

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