Generalizing Solubility Parameter Theory to Apply to One- and Two-Dimensional Solutes and to Incorporate Dipolar Interactions

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ABSTRACT: Hildebrand and Hansen solubility parameters are commonly used to identify suitable solvents for the dispersion or dissolution of a range of solutes, from small molecules to graphene. This practice is based on a number of equations, which predict the enthalpy of mixing to be minimized when the solubility parameters of solvent and solute match. However, such equations have only been rigorously derived for mixtures of small molecules, which interact only via dispersive forces. Herein, we derive a general expression for the enthalpy of mixing in terms of the dimensionality of the solute, where small molecules are considered zero-dimensional, materials such as polymers or nanotubes are one-dimensional (1D) and platelets such as graphene are two-dimensional (2D). We explicitly include contributions due to dispersive, dipole–dipole, and dipole-induced dipole interactions. We find equations very similar to those of Hildebrand and Hansen so long as the solubility parameters of the solute are defined in a manner which reflects their dimensionality. In addition, the equations for 1D and 2D systems are equivalent to known expressions for the enthalpy of mixing of rods and platelets, respectively, as a function of surface energy. This agreement between our expressions and those commonly used shows that the concept of solubility parameters can be rigorously applied to extended solutes such as polymers, nanotubes, and graphene. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Mixtures of two components in the liquid phase are very important in many areas of science and technology. Such mixtures cover a wide spectrum: from simple liquid–liquid mixtures such as alcohol and water through to dissolved solids, for example polymer solutions or even complex dispersions of nanomaterials in solvents. In general, it is important to understand what governs the miscibility of liquid–liquid mixtures or the solubility of solids in liquids. For nonelectrolytic systems, this is generally understood via the free energy of mixing, ΔG_{Mix}.[1] This quantity represents the difference in free energy between a mixture of two components and the two components in their unmixed form and is usually written as

$$\Delta G_{\text{Mix}} = \Delta H_{\text{Mix}} - T\Delta S_{\text{Mix}} \tag{1}$$

where ΔH_{Mix} is the enthalpy of mixing and ΔS_{Mix} is the entropy of mixing. If ΔG_{Mix} is negative, mixing is favorable. The entropy of mixing is generally calculated statistically for a random mixture and can be very large for mixtures of small molecules.[2] In such a situation, ΔH_{Mix} can be relatively large without prohibit-

ing mixing. However, for solutions of macromolecules such as polymers in solvents, ΔS_{Mix} is much smaller.[2] This means that for mixing to occur, ΔH_{Mix} must be below a critical value, which is relatively small. In this scenario, it is very important to understand what determines ΔH_{Mix} for a given solute–solvent combination. Such understanding would allow solvents to be chosen to minimize ΔH_{Mix} and so facilitate dissolution.

It has been known for a long time that ΔH_{Mix} can be approximated by the Hildebrand–Scatchard equation:[1–3]

$$\left(\frac{\Delta H_{\text{Mix}}}{V_{\text{Mix}}}\right) = \phi(1 - \phi)\left(\delta_{T,S} - \delta_{T,N}\right)^2 \tag{2}$$

where $\Delta H_{\text{Mix}}/V_{\text{Mix}}$ is the enthalpy of mixing per volume of mixture, ϕ is the solute volume fraction, and $\delta_{T,S}$ and $\delta_{T,N}$ are the Hildebrand solubility parameters of solvent (S) and solute (N). The Hildebrand solubility parameter of a given material is generally taken as the square root of the cohesive energy density of the material. Equation (2) predicts that the enthalpy of mixing will be minimized and so mixing will be favored when $\delta_{T,S} \approx \delta_{T,N}$. Thus, this expression represents a simple guide for choosing a

Additional Supporting Information may be found in the online version of this article.

solvent for a given solute. This approach, which can be traced back at least as far as the 1930s,[4,5] has been very successful. Today, publications such as the Polymer Handbook[6] contain listings of the solubility parameters of hundreds of solvents. The ubiquity of this approach can be gauged by the fact that the use of solubility parameters to understand complex systems such as dispersions of nanoparticles in solvents is becoming common.[7–17] In fact, it has recently been shown that graphite and a range of other layered compounds can be exfoliated only in solvents which have the correct solubility parameters.[11,14,18]

However, for such a well-known and widely used framework, solubility parameter theory has some notable gaps. Equation (2) was originally derived for mixtures of small molecules. Therefore, although this expression is widely used to describe polymer solutions, this is not strictly correct as the derivation effectively considers monomers which are disconnected from each other.[2,3] To the authors' knowledge, an equation analogous to eq. (2) has not been derived specifically for polymer solutions. Most current theoretical research into solubility parameters in polymer physics involves assuming eq. (2) (or related expressions, see below) to apply and then calculating solubility parameters for different polymers using techniques such as the group contribution approach.[3]

In addition, as previously mentioned, a number of articles have described using Hildebrand (and related) solubility parameters to describe the dispersion of both one-dimensional (1D) nanomaterials such as nanotubes[9] and two-dimensional (2D) nanomaterials such as graphene[14] in solvents. In these cases, eq. (2) has been used in an entirely empirical fashion. That is, while the data were consistent with eq. (2), there is no theoretical evidence to suggest that eq. (2) should hold for such extended structures. Given the usefulness of this method, it is surprising that variations of eq. (2) have not been derived for extended solutes. It is worth noting that equations have been reported that state the enthalpy of mixing for dispersions of rods[8] and platelets[14] in solvents in terms of the surface energies of the components. However, it is not clear how these expressions relate to more traditional solubility parameter equations (i.e., those based on Hildebrand parameters).

There are also other difficulties. It is known that eq. (2) works best for systems of molecules that interact predominately through the dispersion interaction. Where dipolar interactions or hydrogen bonding are present, Hansen et al.[19–23] have proposed expressions which are similar to eq. (2) but include extra terms to describe the additional interactions. For example, Hansen proposed that the enthalpy of mixing could be written as

$$\frac{\Delta H_{\text{Mix}}}{V_{\text{Mix}}} \approx \phi(1-\phi)\left[\left(\delta_{D,S}-\delta_{D,N}\right)^2 + \frac{1}{4}\left(\delta_{P,S}-\delta_{P,N}\right)^2 + \frac{1}{4}\left(\delta_{H,S}-\delta_{H,N}\right)^2\right] \quad (3)$$

where δ_D, δ_P, and δ_H are the Hansen solubility parameters describing dispersive, polar, and hydrogen bonding interactions, respectively, and where the subscripts S and N represent solvent and dispersed phase (solute), respectively.[20] This extension of Hildebrand's method works extremely well and is widely used. However, eq. (3) is empirical. The terms describing the dipole

and hydrogen bonding interactions were added by analogy with the dispersion term and the factor of $1/4$ added to provide better agreement with experiment. Given the practical importance of Hansen parameters, an explicit derivation of the first two terms in eq. (3) would be of interest (it is impossible to derive such an expression for hydrogen bonding).[21] Moreover, other interactions such as dipole-induced dipole effects should be incorporated.

In this article, we use simple models to derive just this set of equations. We use a lattice model to derive variants of eq. (2) for both 1D and 2D solute. We then show the equivalence of using either surface energy-based solubility parameters or Hildebrand parameters in these variants. Finally, we derive a variant of eq. (3) that includes the first two terms (dispersion and dipolar interactions) and an additional term describing dipole-induced dipole interactions.

RESULTS AND DISCUSSION

Extending Hildebrand's Expression for 1D and 2D Solutes

We can adapt the concept of Hildebrand solubility parameters to apply to both 1D and 2D solutes, i.e., rods and platelets. The simplest way to do this theoretically is to use a lattice model.[2,24,25] Such models arrange the molecules of the liquid on a cubic lattice and consider only nearest neighbor interactions. The latter approximation has been shown to work extremely well because of the rapid fall-off of the van der Waals intermolecular interaction with distance.[26] In fact, it can be shown that lattice models can predict properties of liquids just as well as more sophisticated analytical techniques (see Supporting Information). Thus, we believe the simplicity of lattice models justifies their use here. Specifically, we have adapted the methodology described in Ref. 2 and follow the same procedure for both rods and platelets (a detailed derivation is given in the Supporting Information). We use a lattice model, where all components of the system (i.e., the solvent and either rods or platelets) are placed on a cubic lattice. Each solvent molecule occupies one site, whilst a rod occupies a linear array of n lattice sites and a platelet occupies a square array of $n \times n$ sites.

We consider the rods or platelets as initially packed together (i.e., before dissolution) in the form of a crystal (the rods in a cubic close packed bundle and the platelets in a stack). The solvent molecules are initially condensed in a cubic array of lattice sites. Mixing the solute with the solvent leads to the final state, where the solvent and solute molecules are randomly arranged on the lattice to form a uniform mixture.

We label the nearest neighbor binding energy between adjacent lattice sites as ε_{S-S}, ε_{1D-1D}, ε_{2D-2D}, ε_{S-2D}, and ε_{S-1D} depending on whether the sites are occupied by solvent (S), 2D platelets (2D), or 1D rods (1D). We define all such intersite interaction energies as positive. We compute the enthalpy of mixing as the sum of two terms. The first is effectively the enthalpy of vaporization of the initial state, i.e., the sum of energies required to separate both solvent molecules from the condensed phase and solutes from their parent crystal to infinite separation. However, we note that neither the individual rods nor platelets are broken up in this procedure. It is worth

noting that we ignore the effect of the melting enthalpy of the rod/platelet crystal.[1] This can be done because it is known that the effects of melting enthalpy and solubility parameters can be separated into independent terms in equations expressing dispersed concentration.[27,28]

The second term is effectively the enthalpy of condensation of these separated molecules to the mixed state. This is computed by summing the interaction energy of all solvent and solute molecules with their surroundings in the mixed state. A key part of this derivation involves the realization that for infinitely long rods or infinitely large platelets, no solvent site can be surrounded by more than four rods or two platelets (see Supporting Information).

This derivation is given in detail in the Supporting Information. The enthalpy of mixing per volume of mixture for a dispersion of rods (1D) or platelets (2D) is found to be

$$\left(\frac{\Delta H_{\mathrm{Mix}}}{V_{\mathrm{Mix}}}\right)_{2D} = \frac{z_{2D}}{2}\frac{\phi(1-\phi)}{v_S}\left(\varepsilon_{S-S} + \varepsilon_{2D-2D} - 2\varepsilon_{S-2D}\right) \quad (4)$$

$$\left(\frac{\Delta H_{\mathrm{Mix}}}{V_{\mathrm{Mix}}}\right)_{1D} = \frac{z_{1D}}{2}\frac{\phi(1-\phi)}{v_S}\left(\varepsilon_{S-S} + \varepsilon_{1D-1D} - 2\varepsilon_{S-1D}\right) \quad (5)$$

where z_{2D} and z_{1D} are the number of nearest neighbors which platelets and rods have in a crystal, respectively (i.e., 2 and 4 in a cubic lattice). Also, ϕ is the volume fraction of the dispersed phase and v_S is the volume of a lattice site (taken physically as the volume of a solvent molecule).

We note these equations are similar to the enthalpy of mixing for small molecular solutes, where we make the approximation that solvent and solute volumes are equal:[2]

$$\frac{\Delta H_{\mathrm{Mix}}}{V_{\mathrm{Mix}}} = \frac{z_{0D}}{2}\frac{\phi(1-\phi)}{v_S}\left(\varepsilon_{S-S} + \varepsilon_{N-N} - 2\varepsilon_{S-N}\right) \quad (6)$$

In this instance, the subscript N represents a small molecule solute and z_{0D} is generally considered to be the number of nearest neighbors per lattice site (i.e., 6 in a cubic lattice for both solvent and solute). However, it is worth noting that by comparison to the derivation of eqs. (4) and (5), it is clear that z_{0D} actually refers to the solute, rather than the solvent. Standard derivations usually do not distinguish between z_{0D} and the number of nearest neighbours per solvent molecule, z_S, simply because $z_S = z_{0D} = 6$. However, because this work considers zero-dimensional (0D), 1D, and 2D solutes, differentiation between z_{0D}, z_{1D}, z_{2D}, and z_S will be critical. By comparison of eqs. (4)–(6), it is apparent that all the information on the dimensionality of the solute is contained in the quantities z_{0D}, z_{1D}, and z_{2D}.

Equations (4)–(6) are interesting but of limited practical use. It would be more valuable to recast these equations in terms of properties that are intrinsic to solvent and solute. This can be done by using the cohesive energy density of the materials to define solubility parameters. Although Hansen solubility parameters are of most practical use, we will initially work in terms of Hildebrand solubility parameters for the sake of clarity and simplicity. Later, we will extend this to Hansen solubility parameters.

For the solvent, using a lattice model, we can write the cohesive energy density as[2]

$$E_{C,S} = \frac{z_S}{2}\frac{\varepsilon_{S-S}}{v_S} = \delta_{T,S}^2 \quad (7)$$

where $\delta_{T,S}$ is the Hildebrand solubility parameter of the solvent, and z_S the number of nearest neighbors a solvent molecule has in the bulk solvent. For rods or platelets, Hildebrand parameters have not been properly defined, which allows us to do so using expressions for cohesive energy of the rod and platelet crystals (see Supporting Information)

$$E_{C,2D} = \frac{z_{2D}}{2}\frac{\varepsilon_{2D-2D}}{v_S} = \frac{z_{2D}}{z_S}\delta_{T,2D}^2 \quad (8)$$

$$E_{C,1D} = \frac{z_{1D}}{2}\frac{\varepsilon_{1D-1D}}{v_S} = \frac{z_{1D}}{z_S}\delta_{T,1D}^2 \quad (9)$$

In addition, we initially make the approximation that only London (dispersive) interactions are important. This allows us to use the geometric mean expression[1] (see Supporting Information and also below):

$$\varepsilon_{S-2D} = \sqrt{\varepsilon_{S-S}\varepsilon_{2D-2D}} = \frac{2v_S}{z_S}\delta_{T,S}\delta_{T,2D} \quad (10)$$

$$\varepsilon_{S-1D} = \sqrt{\varepsilon_{S-S}\varepsilon_{1D-1D}} = \frac{2v_S}{z_S}\delta_{T,S}\delta_{T,1D} \quad (11)$$

We note that only z_S (rather than z_{1D} or z_{2D}) appears in eqs. (10) and (11) specifically because of the form of our derivation of the Hildebrand parameters in eqs. (8) and (9).

Combining eqs. (7)–(11) with (4) and (5), respectively, gives

$$\left(\frac{\Delta H_{\mathrm{Mix}}}{V}\right)_{2D} = \frac{z_{2D}}{z_S}\phi(1-\phi)\left(\delta_{T,S} - \delta_{T,2D}\right)^2$$

$$= \tfrac{1}{3}\phi(1-\phi)\left(\delta_{T,S} - \delta_{T,2D}\right)^2 \quad (12)$$

$$\left(\frac{\Delta H_{\mathrm{Mix}}}{V}\right)_{1D} = \frac{z_{1D}}{z_S}\phi(1-\phi)\left(\delta_{T,S} - \delta_{T,1D}\right)^2$$

$$= \tfrac{2}{3}\phi(1-\phi)\left(\delta_{T,S} - \delta_{T,1D}\right)^2 \quad (13)$$

Again, these expressions are almost identical both to each other and to the standard expression [i.e. eq. (2)]. We note that because these equations contain ratios of z_S, z_{1D}, and z_{2D}, these final equations are independent of the type of lattice under consideration (e.g., a cubic lattice). These ratios (i.e., $\tfrac{1}{3}$ and $\tfrac{2}{3}$) are the only differences between eqs. (2), (12), and (13). Their values can be understood intuitively as follows. To dissolve 0D molecules (assuming a cubic lattice), all six bonds to nearest neighbors must be broken. However, for a 1D material to be dissolved, each lattice site only has to have four bonds to nearest neighbors broken (the other two are covalently bound to neighboring sites on the same 1D object). This is the origin of the factor of $\tfrac{2}{3}$ ($\tfrac{4}{6} = \tfrac{2}{3}$). A similar argument can be applied to the platelets.

We note that these factors (i.e., $\tfrac{1}{3}$ and $\tfrac{2}{3}$) originate in the values of $z_S = z_{0D} = 6$, $z_{1D} = 4$, and $z_{2D} = 2$, which depend on the

dimensionality (d) of the dispersed phase, i.e., $d = 0$ for a small molecule, $d = 1$ for a rod, and $d = 2$ for a platelet. This allows us to write the general expression for the enthalpy of mixing of low-dimensional nanomaterials in solvents:

$$\left(\frac{\Delta H_{\text{Mix}}}{V_{\text{Mix}}}\right)_d = \left(1 - \frac{d}{3}\right)\phi(1-\phi)(\delta_{T,S} - \delta_{T,N})^2 \quad (14)$$

where $\delta_{T,N}$ represents the Hildebrand parameter of the dispersed nanomaterial of dimensionality d.

We believe that this expression will prove useful for a number of reasons. First, it generalizes the well-known relationship between enthalpy of mixing and Hildebrand solubility parameters. Second, it shows that Hildebrand solubility parameter theory is appropriate not just for use with systems of small molecules, but for solutes which are larger than one lattice site. We note that the mathematical derivation does not require either rods or plates to be rigid. Thus, in the case of 1D solutes, this analysis is applicable to flexible polymers. This puts the common practice of using eq. (2) to describe solutions of polymers in solvents on a firm theoretical footing. In addition, this work implies that Hildebrand solubility parameters are also appropriate for more exotic solutes, for example nanomaterials such as nanotubes or graphene.

Relationship to Surface Energy
We can use eqs. (7–9) to note that, independent of dimensionality, the intercell binding energy can be related to solubility parameter by

$$\varepsilon_{i-i} = \frac{2v_S}{z_S}\delta_{T,i}^2 \quad (15)$$

where i can represent solvent, $0D$, $1D$, or $2D$ material depending on the situation. Again, we note that only z_S (rather than z_{1D} or z_{2D}) appears in eq. (15) specifically because of the form of our definition of the Hildebrand parameters in eqs. (8) and (9).

Using this, we can relate the solubility parameter to the surface energy by considering splitting the lattice into two portions along a plane. If the split breaks n intersite bonds, then the energy cost will be $n\varepsilon_{i-i}$ and the amount of new surface created will be $2nv_S^{2/3}$, where the factor of 2 describes the fact that two new surfaces are created and $v_S^{2/3}$ is the surface area of one face of a cube of volume v_s. This means the surface energy is given by

$$E_{\text{Sur},i} = \frac{n\varepsilon_{i-i}}{2nv_S^{2/3}} = \frac{v_S^{1/3}\delta_{T,i}^2}{z_S} \quad (16)$$

an expression that is similar to the empirical relationship reported by Koenhen and Smolders.[29]

Hernandez et al.[14] have published an expression for the enthalpy of mixing per volume of platelets in a solvent to be:

$$\frac{\Delta H_{\text{Mix}}}{V} \approx \frac{2}{T_{2D}}\left(\sqrt{E_{\text{Sur},S}} - \sqrt{E_{\text{Sur},2D}}\right)^2\phi \quad (17)$$

where $E_{\text{Sur},S}$ and $E_{\text{Sur},2D}$ are the total surface energies of solvent and platelet, respectively, and T_{2D} is the platelet thickness. If we

use eq. (16) to replace the solubility parameters in eq. (12), remembering that $z_{2D} = 2$, we find

$$\frac{\Delta H_{\text{Mix}}}{V} \approx \frac{2}{v_S^{1/3}}\left(\sqrt{E_{\text{Sur},S}} - \sqrt{E_{\text{Sur},2D}}\right)^2\phi(1-\phi) \quad (18)$$

In our model, the platelets have thickness equal to one cell width, i.e., $T_{2D} = v_S^{1/3}$. This means that in the limit of low volume fraction, as considered by Hernandez et al., eq. (17) is identical to eq. (12). It can also be shown that Bergin's expression for the enthalpy of mixing of rods, written in terms of surface energy,[8] can be found from eqs. (16) and (13). This clearly demonstrates that surface energy-based solubility parameters are analogous to Hildebrand parameters.

Incorporating Nondispersive Interactions
However, it is known that Hildebrand solubility parameters are not ideal for describing the dispersion of polar materials. This is because of the approximation described above that considers only the dispersion interaction. To resolve this issue, Hansen[20] suggested that additional solubility parameters be introduced. These are the square roots of the dispersive, polar, and hydrogen bonding components of the cohesive energy density of a material and are denoted $\delta_{D,N}$, $\delta_{P,N}$ and $\delta_{H,N}$, respectively.[3,20,30] Hansen proposed that the enthalpy of mixing could then be written as eq. (3). (We note that in line with the notation used above, N can represent 0D, 1D, or 2D, depending on the nature of the solute, i.e., small molecule, rod, or platelet.)

However, there are a number of problems with this analysis as described in the introduction. The first is that eq. (3) was not derived but written down by comparison with Hildebrand's expression. Second, other important interactions such as dipole-induced dipole effects are ignored. Finally, the factor of 4 is included only because it gives better agreement with experimental results.

To attempt to clarify these issues, we now derive an expression for the enthalpy of mixing from first principles, considering London and dipolar interactions. We do not consider H-bonding interactions, as simple expressions do not exist to relate the intermolecular H-bonding energy to molecular properties.

Deriving Mixing Enthalpy from First Principles as a Function of Dispersive and Polar Solubility Parameters
Derivation of an expression for the enthalpy of mixing within a lattice model involves the calculation of the bracketed energetic term in eq. (6). For simplicity, we will label this as

$$\Delta E = (\varepsilon_{S-S} + \varepsilon_{N-N} - 2\varepsilon_{S-N}) \quad (19)$$

To calculate ΔE, it is necessary to calculate ε_{S-S}, ε_{N-N}, and ε_{S-N}. We will assume that each of these interaction energies is the sum of a dispersive and a dipolar term. Considering two lattice sites A and B, we write the intersite interaction energy in the general form

$$\varepsilon_{A-B} = \varepsilon_{D,A-B} + \varepsilon_{P,A-B} \quad (20)$$

where the subscripts D and P represent dispersive and dipolar interactions, respectively. For the dispersion interaction, the

intersite interaction energy is proportional to the product of the polarizabilities of the lattice sites (i.e., α_A and α_B, see Supporting Information)[31]

$$\varepsilon_{D,A-B} = k_1 \alpha_A \alpha_B \qquad (21a)$$

where k_1 is a constant. Similarly, for two lattice sites interacting by dipolar interactions, the energy of interaction is proportional to the square of the product of the dipole moments associated with the lattice sites (i.e., μ_A and μ_B, see Supporting Information)[31]

$$\varepsilon_{P,A-B} = k_2 \mu_A^2 \mu_B^2 \qquad (21b)$$

where k_2 is a constant. In the Supporting Information, we derive ΔE using these specific expressions. There is, however, a more general method. These expressions can be thought of as special cases of the general form:

$$\varepsilon_{A-B} = a(x_A x_B)^n \qquad (21c)$$

where x_A and x_B are intrinsic parameters associated with sites (molecules) A and B and a and n are arbitrary constants. In the case where A and B are identical, i.e., ε_{A-A} and ε_{B-B}, we can arrange eq. (21c) to give $x_A = (\varepsilon_{A-A}/a)^{1/2n}$ and $x_B = (\varepsilon_{B-B}/a)^{1/2n}$. Substituting these back into (21c) gives

$$\varepsilon_{A-B} = (\varepsilon_{A-A}\varepsilon_{B-B})^{1/2} \qquad (22)$$

This is the geometric mean approximation which this argument shows to be generally true for any intersite interactions with energy dependence such as that given by (21c). This means, of course, that the geometric mean approximation can be applied to dipole–dipole interactions as well as dispersive interactions.

When considering both dispersive and dipole–dipole interactions, we can then write eq. (19) as

$$\Delta E = \varepsilon_{D,S-S} + \varepsilon_{D,N-N} - 2(\varepsilon_{D,S-S}\varepsilon_{D,N-N})^{1/2} + \varepsilon_{P,S-S}$$
$$+ \varepsilon_{P,N-N} - 2(\varepsilon_{P,S-S}\varepsilon_{P,N-N})^{1/2} \qquad (23)$$

Extending eq. (7) to represent the cohesive energy density of the solvent, where both dispersive and dipole interactions are present gives:

$$E_{C,S} = \frac{z_S}{2v_S}(\varepsilon_{D,S-S} + \varepsilon_{P,S-S}) = \delta_{D,S}^2 + \delta_{P,S}^2 \qquad (24a)$$

where $\delta_{D,S}$ and $\delta_{P,S}$ are the dispersive and polar Hansen parameters, respectively, of the solute. From eq. (24a), we can see that $\varepsilon_{D,S-S} = 2v_S\delta_{D,S}^2/z_S$ and $\varepsilon_{P,S-S} = 2v_S\delta_{P,S}^2/z_S$. By comparison with eqs. (8) and (9), we can write a similar equation for the solute giving

$$E_{C,N} = \frac{z_N}{2v_S}(\varepsilon_{D,N-N} + \varepsilon_{P,N-N}) = \frac{z_N}{z_S}\left(\delta_{D,N}^2 + \delta_{P,N}^2\right) \qquad (24b)$$

Herein, $\delta_{D,N}$ and $\delta_{P,N}$ are the dispersive and polar Hansen parameters, respectively, of the solute. Also, note that z_N represents

the number of van der Waals bonded neighbors per solute lattice site. Thus, z_N could represent z_{0D}, z_{1D}, or z_{2D} depending on the situation. Equation (24b) shows that $\varepsilon_{D,N-N} = 2v_S\delta_{D,N}^2/z_S$ and $\varepsilon_{P,N-N} = 2v_S\delta_{P,N}^2/z_S$. Note that z_N has disappeared due to cancellation. Substituting these expressions into eq. (23) gives

$$\Delta E \approx \frac{2v_S}{z_S}\left[(\delta_{D,S} - \delta_{D,N})^2 + (\delta_{P,S} - \delta_{P,N})^2\right] \qquad (25)$$

Herein, $\delta_{D,i}$ and $\delta_{P,i}$ are Hansen's dispersive and polar parameters for material i. Converting this to the enthalpy of mixing for a mixture of solvent and solute with dimensionality d, [i.e., comparing eqs. (4), (5), and (14) and using (25)] gives

$$\left(\frac{\Delta H_{\text{Mix}}}{V_{\text{Mix}}}\right)_d = \left(1 - \frac{d}{3}\right)\phi(1 - \phi)\left[(\delta_{D,S} - \delta_{D,N})^2 + (\delta_{P,S} - \delta_{P,N})^2\right] \qquad (26a)$$

It is important to note that, unlike the specific derivation presented in the Supporting Information, the general derivation described above does not depend on the exact forms of eqs. (21a) and (21b), but holds so long as a general energy equation such as (21c) applies. This is an important result. Among other things, it shows that simply applying a weighting factor to the dipole interaction term in eq. (20) cannot result in Hansen's factor of $1/4$.

Comparing eq. (26a) to Hansen's expression given above [eq. (3)], we see that the form is identical, except for the dimensionality term, the presence in Hansen's equation of an empirically obtained hydrogen-bonding term, and the factor of $1/4$ in the P and H terms. It also resembles the expressions proposed by van Arkel,[22] Blanks and Prausnitz,[19] Small,[21] and Chen.[32]

However, an extremely important distinction to make between the derivation presented here and the latter formulae is that this expression was derived from first principles by considering the interactions relevant to dispersion, whereas those previously reported in the literature were arrived at purely by comparison with Hildebrand's expression for the enthalpy of mixing. In other words, our approach produces a similar result to Hansen's but gives it a solid theoretical basis. It is worth noting that our model is somewhat simplistic, as it seems to assume that each lattice site can be associated with a well-defined dipole moment, but due to the use of eq. (21c), this is not necessarily so. As long as the energy associated with the dipolar interaction scales with the product of terms intrinsic to each material, eq. (26) will be valid. This seems reasonable, even if the Keesom potential [eq. (21b)] does not hold exactly.

It is also worth emphasizing that in deriving eq. (26a), we do not conclude that Hansen's hydrogen-bonding term [eq. (3)] is invalid or somewhat unnecessary. Many years of experience have shown that when choosing solvents, the correct value of the hydrogen-bonding Hansen parameter is necessary to ensure solubility.[20] However, the analysis presented here relies on the ability to express the components of the cohesive energy density in terms of parameters intrinsic to the material in question [eq. (21c)]. This simply cannot be done for hydrogen-bonding.

Toward Hansen's Factor of $^1/_4$?

An important motivating factor behind this work was to find theoretical evidence to support the factor of $^1/_4$ preceding the polar term in eq. (3). This factor is wholly empirical and was included by Hansen to improve the agreement with experimental data.[20] Unfortunately, we have been unsuccessful in this goal. As described above, it is impossible to include a weighting factor in eq. (20) that results in the required fraction. In addition, it is impossible to introduce a weighting factor into eq. (24) without destroying the relationship between solubility parameters and cohesive energy density. However, while we have not found a mechanism to introduce a factor of $^1/_4$ in the appropriate position in eq. (3), we can introduce some asymmetry between the dispersive and polar terms in eq. (26).

To do this, we note that the dispersion interaction is spatially isotropic, while the dipole–dipole interaction is directional. This means that for any given molecule, the number of neighbors with which it interacts via the dispersion interaction may be different to the number interacting via dipole–dipole interactions. This implies that parameter z_S in eq. (25) should really have two values, one for dispersive interactions and one for dipole–dipole interactions. This applies equally well to the solute such that in eqs. (4–6), the parameters z_{0D}, z_{1D}, and z_{2D} should also have two values. For clarity, in this section, we will introduce slightly modified notation; the number of nearest neighbors interacting via dispersive interactions will be $z_{S,D}$ and $z_{N,D}$ for solvents and solutes, respectively. Similarly, the number of nearest neighbors interacting via dipole–dipole interactions will be $z_{S,P}$ and $z_{N,P}$ for solvents and solutes, respectively. With this in mind and rewriting the entire calculation, we find

$$\left(\frac{\Delta H_{\mathrm{mix}}}{V}\right)_{\mathrm{total}} = \phi(1-\phi)\left[\frac{z_{N,D}}{z_{S,D}}\left(\delta_{D,N}-\delta_{D,\mathrm{Sol}}\right)^2 + \frac{z_{N,P}}{z_{S,P}}\left(\delta_{P,N}-\delta_{P,\mathrm{Sol}}\right)^2\right] \tag{26b}$$

Noting that the solute can be 0D, 1D, or 2D and all neighbors interact via the dispersion interaction, we can divide across by $z_{N,D}/z_{S,D}$. Applying the methodology described above, eq. (26b) becomes

$$\left(\frac{\Delta H_{\mathrm{mix}}}{V}\right)_{\mathrm{total}} = \left(1-\frac{d}{3}\right)\phi(1-\phi)\left[\left(\delta_{D,N}-\delta_{D,\mathrm{Sol}}\right)^2 \right.$$
$$\left. + \frac{z_{N,P}}{z_{N,D}}\frac{z_{S,D}}{z_{S,P}}\left(\delta_{P,N}-\delta_{P,\mathrm{Sol}}\right)^2\right] \tag{26C}$$

From this equation, we see a clear asymmetry between the dispersive and dipole–dipole terms as expressed by the factor $z_{N,P}z_{S,D}/z_{N,D}z_{S,P}$. In general, this factor will depend on both solvent and solute and will usually be close to 1. It may, however, be likely that circumstances will occur where this factor deviates significantly from 1. This equation does not explain the inclusion of Hansen's factor of $^1/_4$ in all cases. However, we believe its significance is to show that alternate mechanisms exist leading to asymmetry between the dispersive and dipole–dipole terms and a theoretical prediction of the factor of $^1/_4$ found in eq. (3). We hope this will spur further theoretical work, leading to the solution of this long-standing problem.

The Effect of Dipole-Induced Dipole Effects

Of course, this model is still quite limited; for example, it ignores at least one potentially important interaction: the dipole-induced dipole interaction. In this section, we will include this interaction. However, for simplicity, we will assume the number of nearest neighbors interacting via dispersive and dipole interactions to be equal. Dipole-induced dipole interactions may be described by an intersite interaction energy:[21,31]

$$\varepsilon_{\mathrm{DID},A-B} = k_3\mu_A^2\alpha_B \tag{27}$$

We see that such an interaction is controlled by the permanent dipole moment of one site and the molecular polarizability of the other, and that the full description of such an interaction must then include a term describing site A acting on B and site B acting on A.

Thus, adding a term of type $\varepsilon_{\mathrm{DID},A-B} = k_3\mu_A^2\alpha_B + k_3\mu_B^2\alpha_A$ into the expression for ΔE to represent the dipole-induced dipole interaction, the resulting ΔE leads to (see Supporting Information)

$$\Delta E \approx \frac{2v_S}{z_S}\left[\left(\delta_{D,A}-\delta_{D,B}\right)^2 + \left(\delta_{P,A}-\delta_{P,B}\right)^2\right.$$
$$\left. +2A(\delta_{D,A}-\delta_{D,B})(\delta_{P,A}-\delta_{P,B})\right] \tag{28}$$

where $A = k_3/\sqrt{k_1k_2}$ is essentially a combination of physical constants (see Supporting Information). As before, we can use this to express the enthalpy of mixing for a solute of dimension d:

$$\left(\frac{\Delta H_{\mathrm{Mix}}}{V_{\mathrm{Mix}}}\right)_d = \left(1-\frac{d}{3}\right)\phi(1-\phi)\left[\left(\delta_{D,S}-\delta_{D,N}\right)^2 + \left(\delta_{P,S}-\delta_{P,N}\right)^2\right.$$
$$\left. +2A(\delta_{D,S}-\delta_{D,N})(\delta_{P,S}-\delta_{P,N})\right] \tag{29}$$

To our knowledge, this is the most general analytical expression of its kind yet presented.

However, it is worth noting that eq. (28) and so eq. (29) cannot be complete. Analysis of eq. (28) shows that ΔE must always be positive as long as $A < 1$ (see Supporting Information). It can be shown (see Supporting Information) that $A < 1$ for all molecules, meaning that this model predicts universally positive enthalpy of mixing. Yet, it has been shown experimentally that some mixtures have a negative enthalpy of mixing.[33] Because eq. (29) cannot give negative values, such experimental results cannot be explained by any combination of dispersive, dipole, and dipole-induced dipole interactions. It is probable that other types of interaction, most likely specific interactions, must be present for the enthalpy of mixing to be negative. This suggests that hydrogen-bonding terms such as that included in eq. (3) are critical if models such as these are to be realistic. Addition of the hydrogen-bonding term in eq. (3) to eq. (29) will not result in an equation that can predict negative heats of mixing. One reason for this may be the empirical nature of the hydrogen-bonding term in question. However, a number of authors have proposed different terms for the hydrogen bonding contribution to the enthalpy of mixing.[34,35] Some such terms allow a negative contribution to the enthalpy of mixing, which in certain circumstances may lead to an overall negative heat of mixing.
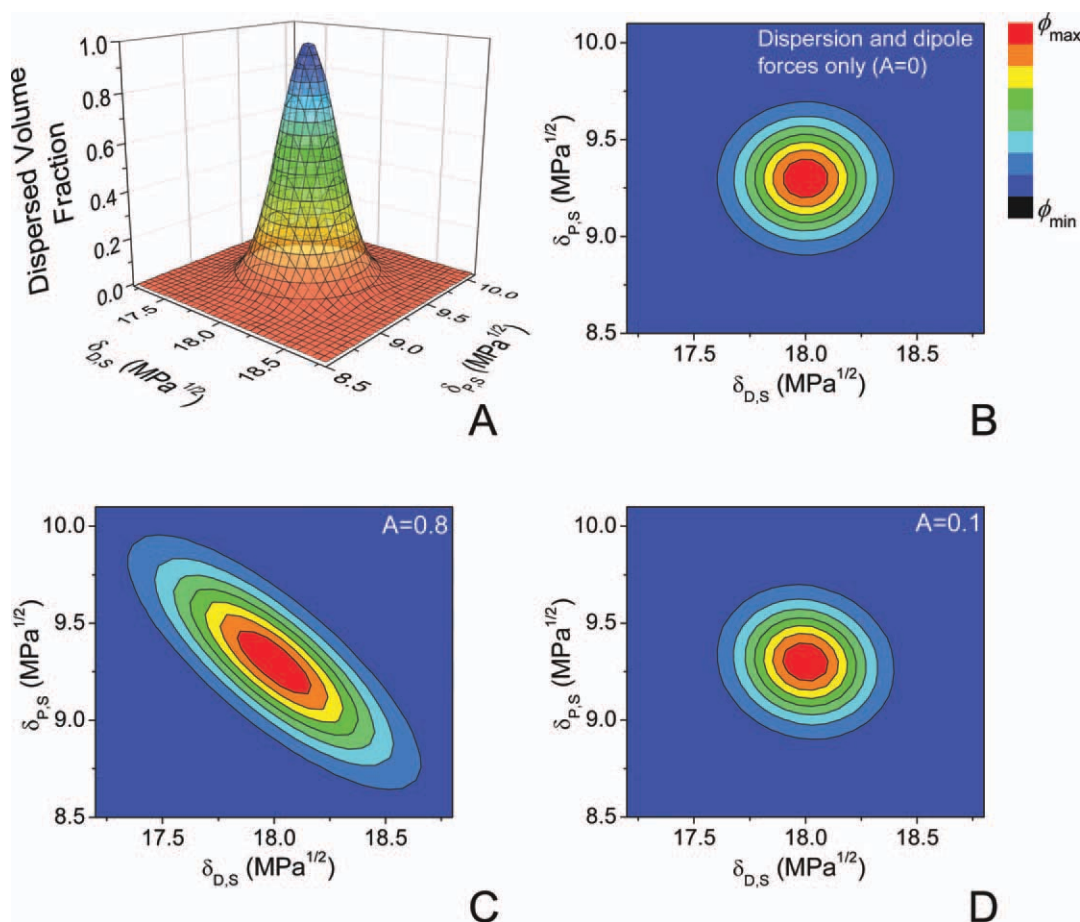
Figure 1. (A) Dispersed volume fraction of rods (in arbitrary units) in the case where only dispersive and dipole–dipole interactions are present [eq. (29)]. (B) A contour plot of the surface illustrated in A. (C) A contour plot plotted from eq. (30), where dispersive, dipole–dipole, and dipole-induced dipole interactions are present. Here, a nonphysical value of $A = 0.8$ is used in the dipole-induced dipole term. (D) A contour plot plotted from eq. (30) with a realistic estimate of $A = 0.1$. Note its similarity to the case where only dispersive and dipolar interactions are considered (B). In all four graphs, $d = 1$, $v_N = 50$ L/mol (i.e., 50,000 g/mol assuming a density of 1000 kg/m³), $\delta_{D,S} = 18$ MPa$^{1/2}$, and $\delta_{P,S} = 9.3$ MPa$^{1/2}$ were used. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

There is one other interesting possibility to explain the fact that eq. (29) does not allow negative heats of mixing. Delmas et al.[36] suggested that equations such as (2) [and so (23)] do not actually give the enthalpy of mixing but more properly the non-combinatorial free energy of mixing. If this is the case, the Gibbs-Helmholtz equation can be used to calculate the actual enthalpy of mixing. This results in an expression which can be positive or negative.

Relating the Dispersed Concentration to Enthalpy of Mixing

We can use the expressions derived above to find the dispersed concentration of solute, using recent work that has shown that for small molecules and rod-like solutes the maximum dispersed volume fraction is given by:[37]

$$\phi_N \propto \exp\left[-\frac{\bar{v}_N}{RT}\frac{\partial(\Delta H_{\text{Mix}}/V_{\text{Mix}})}{\partial\phi}\right] \quad (30)$$

where $\bar{v}_N$ is the volume per mole of the dispersed phase. Assuming we can model a platelet as a very low aspect ratio

rod, we can apply eq. (30) to 0D, 1D, and 2D solutes. For simplicity, we will illustrate this first in the case where we consider only dispersive and dipole–dipole interactions. Thus, inserting eq. (26a) into eq. (30), and making the approximation of low volume fraction ($1 - \phi \approx 1$), we obtain an expression for the maximum dispersed solute volume fraction:

$$\phi_N \propto \exp\left[-\left(1-\frac{d}{3}\right)\frac{\bar{v}_N}{RT}\left[(\delta_{D,S}-\delta_{D,N})^2+(\delta_{P,S}-\delta_{P,N})^2\right]\right] \quad (31)$$

This predicts that the dispersed volume fraction will behave as a 2D Gaussian function in $\delta_{D,S}$ and $\delta_{P,S}$ space, i.e., the product of two individual Gaussians of equal width, one a function of $\delta_{D,S}$ and the other a function of $\delta_{P,S}$. We illustrate this in Figure 1(A) for a hypothetical polymer (i.e., $d = 1$) with $\bar{v}_N = 50$ L/mol (equivalent to a molecular weight of 50,000 g/mol assuming a density of 1000 kg/m³, $\delta_{D,N} = 18$ MPa$^{1/2}$, and $\delta_{P,N} = 9.3$ MPa$^{1/2}$. This graph clearly shows the polymer concentration to depend on dispersive and polar solubility parameters as a 2D

bell-shaped curve. The data are also plotted as a contour plot in Figure 1(B) to illustrate the symmetry between $\delta_{D,S}$ and $\delta_{P,S}$.

We can follow the same procedure for the case where we also consider dipole-induced dipole interactions. Using eqs. (29) and (30), the dispersed volume fraction is given by

$$\phi_N \propto \exp\left[-\left(1 - \frac{d}{3}\right)\frac{\bar{v}_N}{RT}\left[(\delta_{D,S} - \delta_{D,N})^2 + (\delta_{P,S} - \delta_{P,N})^2 \right.\right.$$
$$\left.\left. + 2A(\delta_{D,S} - \delta_{D,N})(\delta_{P,S} - \delta_{P,N})\right]\right] \quad (32)$$

At first glance, it would seem as though the last term, a product of the two different parameters, would significantly change the behavior compared with eq. (31). In fact, this expression simply describes a specific case of a 2D elliptical Gaussian function, i.e., a Gaussian broadened in one dimension, narrowed in the other, and rotated by $\pi/4$ in the $\delta_{D,S}, \delta_{P,S}$ plane. We initially thought that this narrowing might explain Hansen's factor of $^1/_4$ [eq. (3)]. However, the rotation by $\pi/4$ means that the width of the function projected onto both $\delta_{D,S}$ and $\delta_{P,S}$ axes is equal so no net asymmetry is introduced. We illustrate this by plotting the dispersed volume fraction for a hypothetical polymer with $\bar{v}_N = 50$ L/mol, $\delta_{D,S} = 18$ MPa$^{1/2}$, and $\delta_{P,S} = 9.3$ MPa$^{1/2}$ and $A = 0.8$ as a contour plot in Figure 1(C). Herein, the narrowing and rotation can be clearly seen.

Realistically, we can estimate that for real molecules $A \leq 0.1$ (see Supporting Information), suggesting the narrowing is very small. We can check this by replotting eq. (32) for $A = 0.1$ in Figure 1(D). The observed narrowing is so small that the resultant contour plot is virtually indistinguishable from that in Figure 1(B), where the dipole-induced dipole interaction was not included. This suggested that eq. (29), although strictly speaking more correct, is not necessarily more accurate. This means that for any normal circumstances, eq. (26a) can be used to represent the enthalpy of mixing.

Finally, we note that the inclusion of the dimensionality factor $(1 - d/3)$ in eqs. (31) and (32) has one important effect. For example, for 2D solutes, $(1 - d/3) = 1/3$. Inclusion of this factor means that the full width at half maximum of the Gaussian peaks shown in Figure 1 will be a factor of $\sqrt{3} \approx 1.73$ larger than that which would be expected without taking account of dimensionality (a factor of 1.22 for 1D solutes). This may partly explain the fact that experimental studies have shown such curves to be ~3 times broader than expected.[18,37]

CONCLUSIONS

By considering separately the cases of both rod-like and planar solutes, we have derived a general expression for the enthalpy of mixing of solutes of dimensionality d (where $d = 0$, 1, or 2). When $d = 0$, the expression reverts to the well-known Hildebrand–Scatchard expression. For $d = 1$ and 2, the expression differs from the Hildebrand–Scatchard expression only by a numerical constant, which depends on the solute dimensionality. Such an expression is applicable to solutes such as polymers or materials such as carbon nanotubes or graphene.

Second, we have demonstrated that the enthalpy of mixing so derived may be equivalently written in terms of either Hildebrand parameters or surface energy-based solubility parameters.

Finally, by considering the equations governing dipole–dipole, induced dipole-induced dipole, and dipole-induced dipole interactions, we have derived an expression for the enthalpy of mixing for a solute of dimensionality, d, that matches reasonably to Hansen's empirical expression but is considerably more general:

$$\left(\frac{\Delta H_{\text{Mix}}}{V_{\text{Mix}}}\right)_d = \left(1 - \frac{d}{3}\right)\phi(1 - \phi)\left[(\delta_{D,S} - \delta_{D,N})^2 + (\delta_{P,S} - \delta_{P,N})^2\right.$$
$$\left. + 2A(\delta_{D,S} - \delta_{D,N})(\delta_{P,S} - \delta_{P,N})\right]$$

We can use this to show that solute concentration will behave as a 2D Gaussian, which is the product of Gaussian curves in $\delta_{D,S}$ and $\delta_{P,S}$, respectively. In practice, however, A is so small that virtually identical results are found without the need to include the dipole-induced dipole term.

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