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A free-volume hole-filling model for the solubility of liquid molecules in glassy polymers 1: Model derivation

J.C. Arnold *

Materials Research Centre, School of Engineering, Swansea University, Swansea, UK

A R T I C L E I N F O

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The use of hole-filling models is quite common for the sorption of gases into glassy polymers, but these have yet to be explicitly applied to the case of liquid immersion, where extensive use of Flory–Huggins theory dominates. This paper explores how the models based on the idea of sequential filling of a Gaussian distribution of pre-existing free-volume holes within the structure of the glassy polymer can be modified to allow the prediction of the equilibrium solubility of a liquid penetrant. For liquids, the driving force for sorption is more subtle than for gases, with more emphasis on molecular interactions rather than external pressure. For this reason, terms relating to the molecular interactions of a liquid molecule filling a hole were developed, including the effects of elastic constraint for small holes. Consideration of thermal fluctuations show that configurational entropy provides much of the driving force for sorption. Some comparisons with experimental data show a reasonable agreement, and one which is far better than the Flory–Huggins theory.

1. Introduction

The solubility of liquids in glassy polymers is an important process in many fields. For most food packaging applications, gas sorption is critical, but with non-food packaging permeation of liquid components from the inside can be important [1,2], as can the migration of antioxidants [3–5]. Membrane technology relies on controlled permeation through polymers [6,7]. In many applications, chemical and long-term mechanical resistance is affected by liquid solubility. The mechanical behaviour of composites in contact with water is often determined by the solubility into the glassy thermoset resin leading to hydrolysis and swelling [8,9]. Liquid solubility is also fundamental to the process of environmental stress cracking (ESC) in glassy polymers [10–12].

In many cases where there is a need to predict the equilibrium absorption of a liquid into a polymer, the Flory–Huggins lattice approach is used [13]. This is strictly only valid for rubbery polymers, where chains (or specifically chain segments between entanglements) are free to move. Despite this, the use of Flory–Huggins theory is widespread for glassy polymers, especially as a part of a more general ESC model [7,10,11,14–16].

1.1. Lattice-based models

Flory–Huggins theory is derived from considerations of free filling of equal sized lattice sites, and leads to an equation for the Helmholz free energy (ΔF_m) of mixing (per unit volume) of:

$$\Delta F_m = \frac{RT}{V_L}\left[v_L \ln v_L + \frac{v_L}{x}\ln v_P + \chi v_L v_P\right] \tag{1}$$

where V_L is the molar volume of the liquid, v_L and v_P are the volume fractions of liquid and polymer, respectively, χ is the interaction parameter, representing the enthalpy change due to intermolecular bonds and x is the number of lattice sites (of a size equal to the liquid molecule volume) occupied by each polymer chain.

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* Tel.: +44 1792 295749.
E-mail address: j.c.arnold@swansea.ac.uk

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Nomenclature

B	bulk modulus of polymer at T_g
d	separation of molecules
d_{min}	equilibrium separation of molecules
d_L	average liquid molecule separation
d_{Lmin}	minimum liquid molecule separation
d_P	average polymer molecule separation
d_{Pmin}	minimum polymer molecule separation
d_h	hole diameter
E_p	cohesive energy density of polymer
$f(V_h)$	probability of holes of size V_h
f_0	constant
G	energy of higher enthalpy level
G_{el}	shear modulus of polymer
I	total number of holes per unit volume
K	bulk compressibility of liquid
k	Boltzmann constant
P	pressure
R	gas constant
N_A	Avagadro's constant
n	constant
n_1	number of filled holes (per unit volume)
n_2	number of empty holes that could be filled (per unit volume)
S	entropy
T	temperature
T_g	glass transition temperature
V	volume
V_h	hole volume
V_L	liquid molar volume
V_{Lmin}	minimum volume needed for liquid molecule
V_0	average hole volume
v_e	effective number of chain segments per unit volume
v_L	volume fraction of liquid
v_P	volume fraction of polymer
W	width of hole-size distribution
x	number of lattice sites occupied by each polymer chain
z	number of nearest neighbours
β	volumetric thermal expansion coefficient of liquid
χ	interaction parameter
ΔF_m	Helmholz free energy of mixing
ΔG_i	contributions to Gibbs free energy of hole-filling
ΔS_c	configurational entropy change
ΔS_h	entropy change for liquid molecule filling hole
$\delta_{\mathrm{L}}^{\mathrm{d}}$	solubility parameter (L: liquid, P: polymer; d: dispersive, p: polar; h: hydrogen bonding)
ε, σ	constants in Lennard–Jones potential
$\Omega(G)$	probability of occupancy of a hole at energy G

For a network polymer, such as a crosslinked rubber or an entangled glassy polymer, the value of x tends to infinity, and so the second term disappears. There is also a need for a term representing the elastic resistance to swelling. The standard method of doing this for rubbery polymers is to assume that the total volume of the system is the volume of unswollen rubber plus the volume of absorbed liquid, and then to apply standard rubber elasticity theory. This is the basis of the Flory–Rehner theory [17] and leads to an expression for Helmholz free energy of:

$$\Delta F_m = \frac{RT}{V_L}[v_L \ln v_L + \chi v_L v_P] + \frac{kTv_e}{2}\left[\frac{3}{v_P^{2/3}} - 3 - \ln(1/v_P)\right] \tag{2}$$

where v_e is the effective number of chains per unit volume. One simplifying assumption that can be used is that the term kTv_e is equal to the shear modulus G_{el}. For glassy polymers, the magnitude of the shear modulus is such that the Flory–Rehner theory predicts negligible solubility in all cases, so this should only be used for polymers approximating to ideal rubbers.

The interaction parameter, χ, is normally expressed in terms of solubility parameters, and if a three-dimensional approach is used involving Hansen's partial solubility parameters [18] then χ is given by:

$$\chi = 0.3 + \frac{V_L}{RT}[(\delta_L^d - \delta_P^d)^2 + (\delta_L^p - \delta_P^p)^2 + (\delta_L^h - \delta_P^h)^2] \tag{3}$$

With the solubility parameters δ, the subscript L refers to the liquid, P to the polymer and the superscript d refers to dispersive bonding, p to polar bonding and h to hydrogen bonding. The first term represents the typical loss of entropy (mainly of a rotational nature) of a liquid molecule within the polymer network compared to one surrounded by other liquid molecules.

The use of the above theories for liquid absorption into glassy polymers at temperatures well below the glass transition temperature is questionable for two main reasons; firstly it is based on an entropic model where the polymer segments are completely free to move and secondly the elastic resistance term is based on rubber elasticity theory.

1.2. Hole-filling models

A more valid approach is to use the various sorption models, where it is assumed that there are pre-existing sites within the material that can be filled by absorbing molecules. Such models are more common for gas absorption, but are equally applicable to liquid absorption. The most common sorption models are based on the dual-sorption theory [19], which assumes there are two distinct types of sites; those larger than the liquid molecule which can be filled with no expansion of the polymer and smaller sites which lead to volume expansion. An extension to this has been provided by Vrentas and Vrentas which includes a treatment of molecular relaxation to adjust the number of available sites [20]. Another factor that has been considered is the elastic resistance to sorption and Leibler and Sekimoto [21] produced a treatment using the elastic properties of glassy polymers, rather than the more commonly-used rubber elasticity.

An extension to this approach by Kirchheim [22,23] was to use a distribution of site sizes, representing the free-volume holes present in all glassy polymers. His work with absorption of gases extended the dual sorption model quite successfully. In this model, it is assumed that there is a frozen-in distribution of hole sizes, given by a Gaussian function:

$$f(V_h) = f_0 \exp\left[\frac{-B(V_h - V_0)^2}{2V_0RT_g}\right] \tag{4}$$

where f_0 is a pre-factor, B is the bulk modulus at the temperature at which the hole-size distribution is frozen-in (Tg), and V_0 is the average hole size.

The distribution can be simplified to:

$$f(V_h) = \frac{I}{W\sqrt{2\pi}} \exp\left[\frac{-(V_h - V_0)^2}{2W^2}\right] \tag{5}$$

where I is the total number of sites, and W is the width of the Gaussian distribution, given by:

$$W = \sqrt{\frac{V_0RT_g}{B}} \tag{6}$$

In addition, Kirchheim's approach assumed that if a sorbed molecule is in a smaller hole, (i.e. $V_L > V_h$) then the elastic resistance energy is given by:

$$\Delta G = \frac{2}{3} G_{el} \frac{(V_L - V_h)^2}{V_h} \tag{7}$$

The above equations were then combined to give a free energy distribution function, which combined with the external potential of the sorbing gas allowed the sorption isotherms to be predicted.

1.3. Lattice-fluid models

An alternative approach to modelling the sorption of gases into glassy polymers is that of the non-equilibrium lattice fluid (NELF) models of Sarti and co-workers [24,25], based on an original concept of lattice fluids from Sanchez and Lacombe [26]. This model considers the polymer density as a state function and uses continuum thermodynamics to predict the solubility, recognising that glassy polymers are not in equilibrium, but that the gas/polymer mixture reaches a pseudo-equilibrium. These models require PVT data for the sorbing gas and for the polymer. More recent papers [27,28] have used this model to confirm the link between sorption properties and intermolecular attractions between gas molecules (as indicated by boiling point, Lennard–Jones parameters or critical temperature), which does provide a basis for an extension to the case of liquid absorption rather than gases.

A comparison between the hole-filling approach and the NELF model shows that there are advantages and disadvantages to both. The NELF model is arguably more explicit, however, it does rely on a number of approximations and estimated parameters. It cannot predict volume expansion and indeed for any combination that causes swelling, the final swollen volume is needed, making the prediction rather circular. The hole-filling models, however, are dependent on the hole-size distribution for the polymer, which is not completely established. They also assume one liquid molecule per hole, which is also questionable in some cases. Both models can account for changes to the glassy polymer due to physical ageing or different processing histories; the NELF model allows incorporation of the effects of changes to polymer density, while the hole-filling models would require a change to the hole-size distribution.

It would be instructive to perform an analysis of liquid sorption using the NELF model, however, this paper focuses on such an exercise for the hole-filling approach. The main reason for this is that the liquid parameters required for the hole-filling model are generally more readily available than for the NELF model. In order to apply the hole-filling method to liquid absorption at ambient pressures, one important factor is that the driving forces for absorption will be lower without the elevated pressure. In this case, molecular interactions are much more significant, and so an extended model is required. It is the purpose of this paper to develop such a model.

2. Terms contributing to the energy of hole-filling

The basis for the hole-filling model is that the free volume in a glassy polymer exists as a distribution of holes, assumed to be spherical in shape that could each potentially be occupied by one liquid molecule. It is assumed that the network of polymer chains and holes is fixed, approximating to conditions considerably below the glass transition temperature. This approximation would need modifying in future to account for ongoing slow relaxations; however, the current treatment is thought to be a valuable first stage, and mirrors the well-published modelling of gas sorption using a fixed hole-size distribution. There are then various terms that will contribute to the energy of a liquid molecule present in such a free-volume hole.

2.1. Elastic strain energy

For the situation where the liquid molecule is larger than the hole, there will be elastic straining of the polymer, leading to a free energy given essentially by Eq. (7) above. One important difference in this analysis is that it is recognised that the liquid will contain some free volume and so the molecular size determined from the liquid molar volume will be larger than the minimum hole into which a liquid molecule could be fitted without elastic expansion. The solid molar volume (here termed V_{Lmin}) would therefore be a better value, and this is typically 0.8 times the liquid molar volume. The elastic term (per mole of holes) then becomes:

$$\Delta G_1 = \frac{2}{3} G_{el} \frac{(V_{Lmin} - V_h)^2}{V_h} \tag{8}$$

For occupancy of holes larger than this minimum liquid molecular volume, no elastic strain energy is involved.

2.2. Interaction energy between polymer and liquid

There will be secondary bond forces between the liquid and polymer, which will depend on the strength of interaction between the two. For holes that are smaller than the liquid molecule (V_{Lmin}), the polymer will expand to allow the liquid molecule to adopt its equilibrium separation from the polymer chains. For situations where the hole is larger than the liquid molecule, a difference arises as the distance between the liquid molecule and polymer chain segments increases, and so the interaction energy will decrease. In order to model this, it is assumed that the secondary bonds can be treated as a Lennard–Jones potential, where the potential of two molecules separated by a distance d is given by:

$$\text{Potential} = \varepsilon\left[\left(\frac{\sigma}{d}\right)^{12} - \left(\frac{\sigma}{d}\right)^{6}\right] \tag{9}$$

where ε and σ are constants. This potential has a minimum with a value of d_{min} equal to 1.122σ, at which point the potential for a pair of molecules equals $-\varepsilon 4$. The potential can thus be expressed as:

$$\text{Potential} = \varepsilon\left[\left(\frac{0.889 d_{min}}{d}\right)^{12} - \left(\frac{0.889 d_{min}}{d}\right)^{6}\right] \tag{10}$$

The following terms can be specified:

- d_{Lmin} is the minimum liquid molecule separation (corresponding to the volume V_{Lmin});
- d_L is the average liquid molecule separation (corresponding to the liquid molar volume V_L);
- d_{Pmin} is the minimum polymer chain separation;
- d_P is the average polymer chain separation;

The Lennard–Jones potential will be at a minimum when a liquid molecule is in the smallest hole it can occupy without elastic expansion. In this case, the separation (liquid to polymer) is given by $(d_{Lmin} + d_{Pmin})/2$. As this separation will equal 1.122σ, the value of σ can be given by:

$$\sigma = \frac{0.889}{2}(d_{Lmin} + d_{Pmin}) \tag{11}$$

For a liquid molecule in a hole with an average separation equal to $(d_L + d_P)/2$, the total interaction energy can be given by:

$$\Delta G_2 = -V_L[\delta_L \delta_P] \tag{12}$$

which simply represents the average liquid molecule volume multiplied by the averaged cohesive energy density, with δ_L and δ_P being the total solubility parameters of liquid and polymer, respectively. If the three-component Hansen solubility parameters are to be used, then the interaction energy becomes:

$$\Delta G_2 = -V_L[\delta_L^d \delta_P^d + \delta_L^p \delta_P^p + \delta_L^h \delta_P^h] \tag{13}$$

This interaction energy, expressed via the Lennard–Jones potential is:

$$\Delta G_2 = z \cdot \varepsilon\left[\left(\frac{\sigma}{(d_L + d_P)}\right)^{12} - \left(\frac{\sigma}{(d_L + d_P)}\right)^{6}\right] \tag{14}$$

where z is the number of nearest neighbours taking part in the interaction, which is assumed to be independent of hole size.

For a general hole of diameter d_h (with a volume larger than V_{Lmin}), the separation distance between liquid and polymer molecules is given by $d = (d_h + d_{Pmin})/2$. By combining this with the value of $z \cdot \varepsilon$, derived from Eqs. (11), (13), and (14), and the general form of the Lennard–Jones potential, an expression for the interaction energy of a liquid molecule in any hole size is as follows:

For holes of volume larger than V_{Lmin},

$$\Delta G_2 = -V_L\left[\delta_L^d \delta_P^d + \delta_L^p \delta_P^p + \delta_L^h \delta_P^h\right] \times \frac{\left[\left(\frac{0.889(d_{Lmin}+d_{Pmin})}{(d_h+d_{Pmin})}\right)^{12} - \left(\frac{0.889(d_{Lmin}+d_{Pmin})}{(d_h+d_{Pmin})}\right)^{6}\right]}{\left[\left(\frac{0.889(d_{Lmin}+d_{Pmin})}{(d_L+d_P)}\right)^{12} - \left(\frac{0.889(d_{Lmin}+d_{Pmin})}{(d_L+d_P)}\right)^{6}\right]} \tag{15}$$

For holes of volume less than V_{Lmin},

$$\Delta G_2 = \frac{0.25 \cdot V_L[\delta_L^d \delta_P^d + \delta_L^p \delta_P^p + \delta_L^h \delta_P^h]}{\left[\left(\frac{0.889(d_{Lmin}+d_{Pmin})}{(d_L+d_P)}\right)^{12} - \left(\frac{0.889(d_{Lmin}+d_{Pmin})}{(d_L+d_P)}\right)^{6}\right]} \tag{16}$$

It should be noted that this assumes that the number of neighbours remains constant as the hole size increases, which is reasonable as the liquid molecule remains the same size and can only be involved in a fixed number of interactions. The equation for ΔG_2 is independent of the value of z.

2.3. Energy lost by liquid molecule moving out of the liquid phase

The interaction energy of a liquid molecule in the liquid phase, which will be lost when the molecule is removed to the polymer is simply given by the molecular volume of the liquid multiplied by the cohesive energy density of the liquid, i.e.:

$$\Delta G_3 = V_L[(\delta_L^d)^2 + (\delta_L^p)^2 + (\delta_L^h)^2] \tag{17}$$

2.4. The interaction energy across a hole

For a hole in the polymer structure, there will be a certain amount of secondary bonding across the hole, the energy of which will be lost when the hole is filled with a liquid molecule. This factor can be estimated using a Lennard–Jones potential and the cohesive energy density of the polymer, E_p, as follows:

If we assume that the polymer chains have an average molecular separation given by d_P. There will also exist a minimum separation, d_{Pmin}, when the secondary bonding potential is at a minimum, which fixes the value of σ in Eq. (9) above as $0.889 d_{Pmin}$.

If we then consider a ‘segment’ of polymer, represented by a sphere of diameter d_P, which has z nearest neighbour secondary bonds to other chain segments, with an average separation of d_P, then the potential of this segment will be given by:

$$\text{Potential} = z\varepsilon\left[\left(\frac{0.889d_{Pmin}}{d_P}\right)^{12} - \left(\frac{0.889d_{Pmin}}{d_P}\right)^{6}\right] \tag{18}$$

This potential will equal the cohesive energy density multiplied by the segment volume, i.e.:

$$\text{Potential} = -\frac{\pi\cdot d_P^3}{6}[(\delta_P^d)^2 + (\delta_P^p)^2 + (\delta_P^h)^2] \tag{19}$$

If this segment is then removed, it will leave a hole, of the same size as the segment. Importantly, there will now be $z/2$ nearest neighbour interactions across this hole (as each previously interacting part pairs with one on the opposite side of the hole). The separation of each interacting part will now be $2d_P$, and so the potential of this hole can be expressed as:

$$\text{Potential} = \frac{z\varepsilon}{2}\left[\left(\frac{0.889d_{Pmin}}{2d_P}\right)^{12} - \left(\frac{0.889d_{Pmin}}{2d_P}\right)^{6}\right] \tag{20}$$

For holes of different size, the separation will be given by ($d_h + d_{Pmin}$) and the number of interacting nearest neighbours (z') will be proportional to the surface area of the hole as follows:

$$z' = \frac{z}{2}\left(\frac{d_h}{d_P}\right)^2 \tag{21}$$

Therefore the potential of a hole of general size is given by:

$$\text{Potential} = \frac{z\varepsilon}{2}\left(\frac{d_h}{d_P}\right)^2\left[\left(\frac{0.889d_{Pmin}}{d_{Pmin}+d_h}\right)^{12} - \left(\frac{0.889d_{Pmin}}{d_{Pmin}+d_h}\right)^{6}\right] \tag{22}$$

Substituting for $z\cdot\varepsilon$ from Eqs. (18) and (19) above and multiplying by N_A, gives the molar interaction energy of the hole. This energy will be lost when the hole is filled, and so the energy contribution is:

$$\Delta G_4 = \frac{N_A\pi.d_P d_h^2[(\delta_P^d)^2 + (\delta_P^p)^2 + (\delta_P^h)^2]}{12} \times \left[\frac{\left(\frac{0.889d_{Pmin}}{(d_h+d_P)}\right)^{12} - \left(\frac{0.889d_{Pmin}}{(d_h+d_P)}\right)^{6}}{\left(\frac{0.889d_{Pmin}}{d_P}\right)^{12} - \left(\frac{0.889d_{Pmin}}{d_P}\right)^{6}}\right] \tag{23}$$

2.5. *Entropy of liquid molecule in a free-volume hole*

If a liquid molecule is constrained within the smallest free-volume hole possible without elastic straining of the polymer, it occupies less space on average than in the liquid phase. It will therefore have less entropy (due to lost rotational and translational degrees of freedom). Similarly, if a liquid molecule is contained in a larger sized hole, it will have greater freedom to move and hence higher entropy.

The change in entropy with volume at a fixed temperature can be given by one of Maxwell's relationships as:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{24}$$

In the liquid state, for a fixed volume, the second term can be expressed as:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial P}{\partial V}\cdot\frac{\partial V}{\partial T}\right)_V = K\cdot\beta \tag{25}$$

where K is the bulk compressibility of the liquid and β is its volumetric thermal expansion coefficient.

As the volume changes, however, it is reasonable to expect the value of (dP/dT) to change, and as the model considers liquid molecules in holes of different size, this needs to be considered. In the gaseous state, the value of (dP/dT) of an ideal gas is proportional to $1/V$, however, such a variation will not apply when the intermolecular distances are much smaller. For methanol, for instance, the value of (dS/dV) in the liquid state, calculated as βK is close to 1×10^6 J/m^3 K. In the gaseous state, at the boiling point, the value of (dS/dV) has dropped to about 330 J/m^3 K. As the intermediate volumes represent metastable states for which there is no relevant information, a function was chosen that can sensibly accommodate both extremes:

$$\frac{dS}{dV} = \beta K\left(\frac{V_L}{V}\right)^n \tag{26}$$

Therefore the change in entropy in going from the liquid state to a hole of size V_h is given by:

$$\Delta S_h = \frac{\beta K}{(n-1)}\left(V_L - \frac{V_L^n}{V_h^{(n-1)}}\right) \tag{27}$$

The value of n can be found using determined values of β, K and the entropy and molar volume of the gas at the boiling point. For holes smaller than V_{Lmin}, the entropy change is constant at the value for holes of size V_{Lmin}. This lower limit is of a similar size to the entropy change on solidification. The energy due to this entropy change (expressed as free energy per mole) is therefore given by:

$$\Delta G_5 = -T\Delta S_h = -\frac{T\beta K}{(n-1)}\left(V_L - \frac{V_L^n}{V_h^{(n-1)}}\right) \tag{28}$$

3. Overall enthalpy change of hole filling

The total enthalpy change of hole-filling is then given as the sum of each of the five contributions described above. (The term enthalpy is somewhat debatable as it includes an entropic term, but it is used here to distinguish from the configurational entropy term.) In order to examine the relative contributions of each of these terms, typical values for methanol, propan-1-ol, diacetone alcohol and butyl acetate sorbing into polycarbonate have been chosen as examples. These were chosen to explore the different effects of molecular volume and interaction parameter. All the parameters used for the liquids are given in Table 1, with data taken from Barton [18].

The parameters used for Bisphenol A Polycarbonate are as follows:

- Shear modulus: G_{el} = 1 GPa;
- solubility parameters: $\delta_p^d = 17.6$; $\delta_p^p = 3.0$; $\delta_p^h = 6.8$ (J/cm^3)$^{0.5}$;

Table 1
The parameters used for the liquids studied.

	V_L (cm^3/mol)	χ	$K \cdot \beta$ (kJ/m^3 K)	ρ (kg/m^3)	δd (J/cm^3)$^{0.5}$	δp	δh	Mol wt (g/mol)	n
Methanol	40.7	4.32	1000	792	14.5	11.5	21.4	32	1.35
Propanol	74.7	2.87	900	803	15.5	6.6	16.3	60	1.59
Diacetone alcohol	123.6	1.17	1000	938	15.8	8.2	10.8	116	2.3
Butyl acetate	132	1.03	1050	880	15.3	3.7	7.2	116	2.50

- $d_{pmin=}$0.393 nm;
- d_p = 0.411 nm.

The value of d_{pmin} for polycarbonate was estimated from the crystalline unit cell dimensions of polycarbonate. The value of d_p was obtained using the value of d_{pmin}, along with the densities of crystalline and amorphous polycarbonate. The solubility parameters were determined using the group contribution method of Van Krevelen [29].

The total enthalpy of sorption as a function of hole size for methanol in glassy polycarbonate (at 300 K) is shown in Fig. 1. The five different contributions outlined above are also included. The equivalent variation for butyl acetate is shown in Fig. 2.

Various important features can be seen from these graphs. With very small hole sizes, the elastic resistant term dominates and the enthalpy becomes very large. This is more of an effect with the larger molecule of butyl acetate. The hole filling term is negative and slowly decreases once the hole is larger than the liquid molecule. The interaction enthalpy across the hole that is lost on filling is a very small positive contribution, and could arguably be neglected. The liquid entropy term starts as a positive value when the liquid molecule is more constrained in small holes than it is in the liquid, but then becomes negative when there are more degrees of freedom in larger holes.

Overall, the enthalpy decreases to a minimum value for holes of a size slightly larger than the liquid molecule. For methanol, this minimum is very broad and occurs at positive enthalpy, whereas with butyl acetate, it is more pronounced and occurs with a negative enthalpy, due to the greater similarity of solubility parameters for this liquid. The very slight discontinuity of slope is due to the imposed limit to liquid entropy term, but is not critical to the overall results.

The fact that it is possible to get a negative enthalpy may be somewhat surprising to those used to dealing with conventional mixture enthalpies (as used by Flory) as these are always positive. It should be noted that in the conventional case, one liquid molecule is removed from the liquid and replaces a polymer segment and so the polymer–polymer interaction energy is lost. In the situation of hole-filling, one liquid molecule is removed from the liquid and placed in a hole and so only the very small interaction energy across the hole is lost.

Two further examples are shown in Fig. 3. Here, the total hole-filling enthalpy is plotted against hole size for methanol, propan-1-ol, diacetone alcohol and butyl acetate.

4. The total energy change associated with hole filling

In order to determine the overall free energy of sorption via hole filling, it should be recognised that at any finite

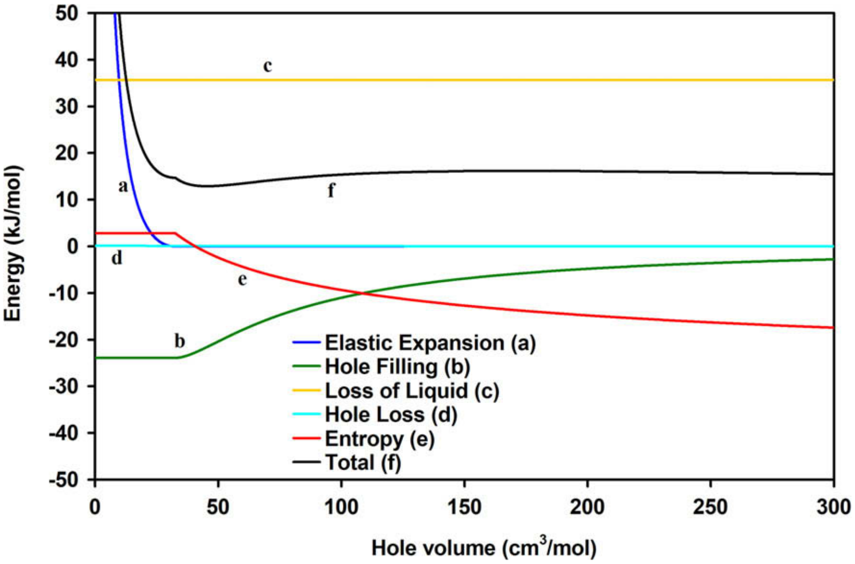

Fig. 1. The contributions to hole-filling energy plotted against hole size for methanol in polycarbonate.

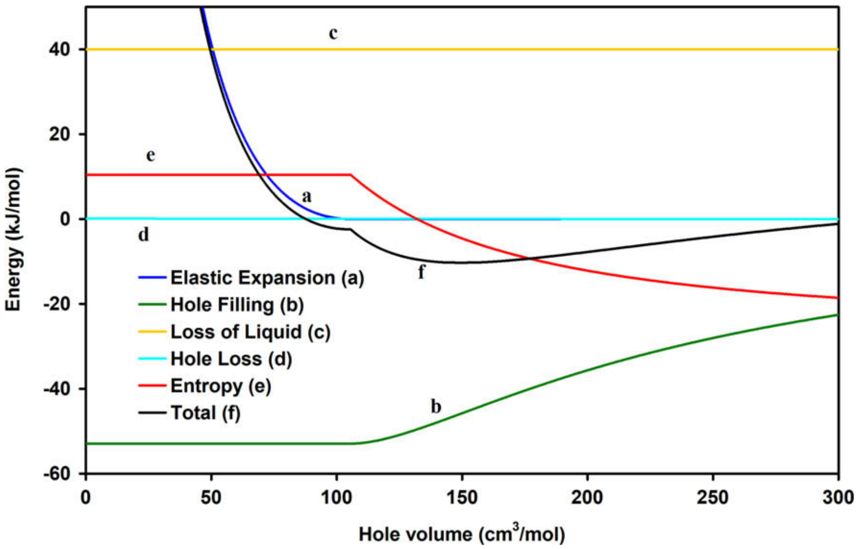

Fig. 2. Butyl acetate in polycarbonate.

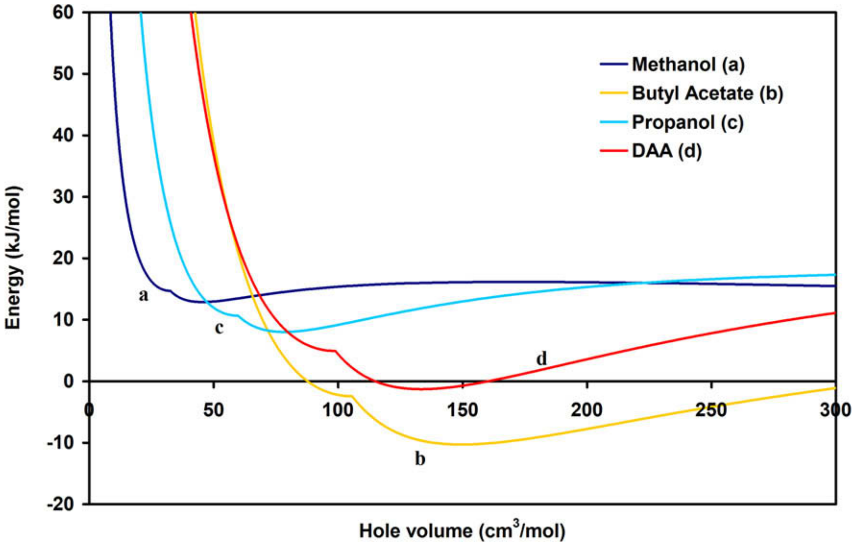

Fig. 3. The overall hole-filling energy plotted against hole size for methanol, butyl acetate, propan-1-ol and diacetone alcohol (DAA) in polycarbonate.

temperature, thermal fluctuations lead to occupancy of higher energy holes, which leads to configurational entropy that also needs to be included. The first stage of this is to combine the enthalpy/hole volume variation with the hole-size distribution function, to give a distribution of enthalpy states (with each state corresponding to one hole).

The hole-size distribution function has been assumed to be a Gaussian of the form given in Eq. (5). One critical aspect of this approach is the exact values of I, the number of holes per unit volume and V_0, the average hole size. Kirchheim [22] presented the following arguments to determine the value of I:

The packing density of small gaseous molecules is about 2×10^{22} cm^{-3}. If it is assumed that there is 15% free volume in a typical glassy polymer, this equates to enough room for 3×10^{21} cm^{-3} molecules. Kirchheim assumed this was an underestimate, as it does not take account of any volume swelling when molecules are absorbed. The number of segments of the polymer is 6×10^{21} cm^{-3}, and he argued that this will be roughly equal to the number of holes. Following these arguments, Kirchheim used a slightly higher value of 6.7×10^{21} cm^{-3}, along with a value of V_0 of 26 cm^3/mol determined by fitting the experimental sorption data. These give a total free volume fraction of 29%, which is much larger than values normally quoted. The average hole size used by Kirchheim is also significantly lower than values derived by other methods such as positron annihilation lifetime spectroscopy (PALS) [30]. PALS studies generally find an average hole size of about 60–66 cm^3/mol for PC, with a free volume fraction of between 8% and 9%. It is interesting to note that for the NELF models of Sarti et al. [27], a free volume of 5.9% was used for PC, though this was defined in a slightly different way to Kirchheim. It is clear that the most debatable issue regarding sorption models is the choice of free volume and related hole sizes. A more extensive discussion of this issue can be found in the following paper.

For this analysis, a value of I of 8.34×10^{20} holes/cm^3 and an average hole size of 65 cm^3/mol were chosen, which gives a free volume of 9%. This combination of values was chosen to give a good agreement with PALS data and PVT data. These values seem more justified than those originally used by Kirchheim, however, this will be discussed more fully in the subsequent paper.

In order to calculate the distribution of enthalpy states $n(G)$, the hole-size distribution is convoluted with the enthalpy/hole volume relationship described above to give the total number of holes as a function of enthalpy. This is not a simple task as the enthalpy curve is generally not singular and two different hole sizes can lead to the same enthalpy. This process needs to sum contributions to a particular enthalpy from both larger and smaller holes. The density of state curves are shown in Figs. 4 and 5 for the examples of butyl acetate and methanol for the hole-size distribution above.

Once the density of states curve has been obtained, the occupancy of holes at any energy can be determined from Fermi–Dirac statistics, based on the derivations of Kirchheim [22,31], and assuming that only one molecule can occupy each hole. This gives the probability of occupancy, $\Omega(G)$, of holes at any energy level (G) as:

$$\Omega(G) = \frac{1}{1 + \exp(\frac{G}{RT})} \qquad (29)$$

It should be noted that only one energy term (G) is needed in Eq. (29), as G (the sum of ΔG_1 to ΔG_5) is the difference in energy for a liquid molecule in a hole compared to being in the liquid. The total sorption (molecules per unit volume) is therefore given by:

$$\text{Sorption} = \int_{-\infty}^{\infty} \frac{n(G)\,dG}{1 + \exp(\frac{G}{RT})} \qquad (30)$$

5. Predicted sorption values

The predicted equilibrium sorption values were then compared with experimentally-determined values. The experimental values were derived from a simple immersion and weighing technique, to be described more fully in the following paper. The comparison of predicted and experimental values is shown in Table 2. In addition to the results of the hole-filling model, predictions using the Flory–Huggins theory (Eq. (1)) are also listed. These use the interaction parameters calculated from solubility parameters using Eq. (3).

The clear conclusions from this are that without any experimentally-derived fitting parameters, the Flory–Huggins theory gives a large underestimate of sorption levels. Successful use of the Flory–Huggins theory generally requires the use of experimentally-derived interaction parameters, which are lower than those calculated from solubility parameters. The predictions of the Flory–Rehner theory are many orders of magnitude too low; the elastic resistance of a glassy polymer swamps all other terms with this analysis which is only applicable to rubbery polymers.

The predictions of the hole-filling model are more encouraging; for propanol, the prediction is quite close to the experimental value. For butyl acetate, there is a moderate underestimate, but it is clear that butyl acetate causes significant swelling and plasticisation which would lead to increased absorption due to chain relaxation, a factor which is not included in this model. The diacetone alcohol

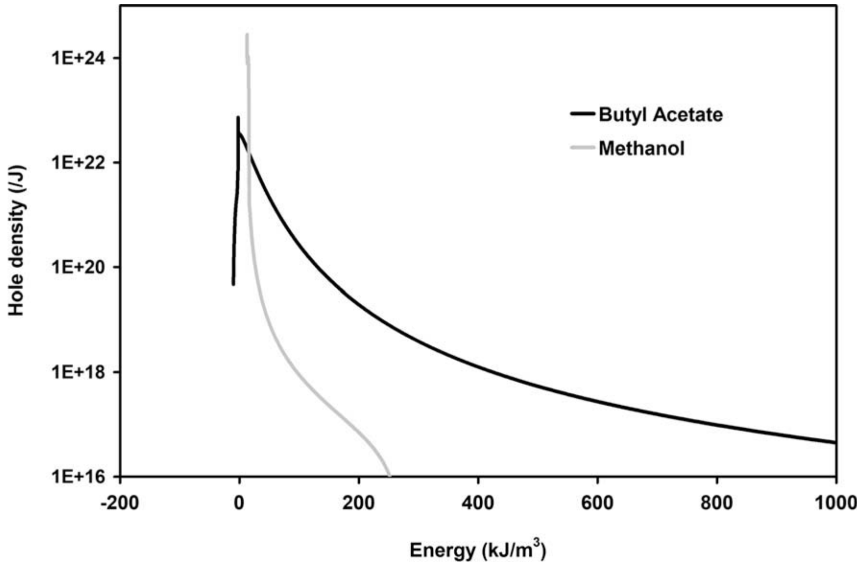

Fig. 4. The density of states, plotted against energy for butyl acetate and methanol in polycarbonate with an average hole size of 65 cm^3/mol and a free volume of 9%.

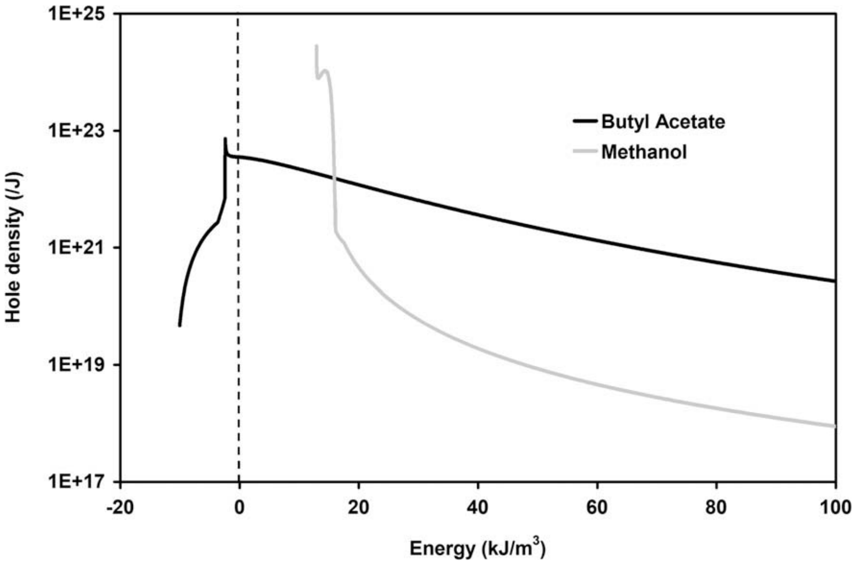

Fig. 5. As Fig. 4 but focussing on the region of lower energies.

Table 2
Comparison of predicted and measured equilibrium solubility of selected liquids into polycarbonate (weight percent liquid absorption).

	Methanol	Propanol	Diacetone alcohol	Butyl acetate
Measured	2.6	0.2	0.2	31
Hole-filling model	4.3×10^{-3}	0.53	0.796	0.775
Flory–Huggins	1.2×10^{-5}	3.5×10^{-4}	2.4×10^{-2}	3.3×10^{-2}

prediction is too high by a factor of about 4. The one case that is not predicted at all well is that of methanol, and reasons for this will be explored more in the following paper. Despite these reservations, it is certainly encouraging that a model using no fitting parameters has predicted to within an order of magnitude.

6. Conclusions

A model has been developed for sorption of liquids into glassy polymers based on the principal of successive filling of pre-existing holes in the polymer. The model uses a Gaussian distribution of hole sizes.

Consideration of the energetics of a liquid molecule entering a hole in a glassy polymer shows that there are several contributing terms, with elastic expansion of the polymer dominating with small holes, and secondary bonding between liquid and polymer being more important for larger holes. The variation of hole-filling enthalpy with hole size shows a minimum when the hole is of a similar size to the liquid molecule. In some cases, the hole-filling enthalpy can be negative due to greater interaction between liquid and polymer than in the liquid state.

Consideration of thermal fluctuations leads to a configurational entropy term, which leads to a finite equilibrium sorption at all finite temperatures. Comparison of the predicted sorption with experimental values shows reasonable agreement, with a limitation where higher sorption and plasticisation leads to a breakdown of the model. Predictions with methanol were not good.

The overall conclusion from this is that the Flory–Huggins theory is not sensible for predicting solubility in glassy polymers; not only does it give significant underestimates of the solubility, but it takes no account of elastic resistance. The hole-filling theory, although it is more complex, does give reasonably good predictions across a range of liquids. The assumption that both holes and liquid molecules are spherical in shape is an approximation that will limit validity, especially with linear molecules. Additionally, the model does not take into account molecular relaxation of the glassy polymer. In this way, it is similar to the well-published accounts of hole-filling by gas molecules. It will lead to an under-prediction of sorption for cases where any significant plasticisation occurs. The model could be extended to include polymer relaxation as an evolution of the hole-size distribution, which would be a sensible next step.

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