Free volume in condensed phases: Separation of contributions

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Free volume present in condensed phases is either divided among the atoms present, or treated as independent holes. If a distribution of hole sizes is assumed, both approaches can be reconciled: smaller holes (interstitials) can be considered as being attached to atoms, while holes larger than a critical size (e.g. atomic) can be treated as independent. The distribution obtained depends on the choice of a free volume model. The model of Landau and Lifshits is studied in detail as an example. Numerical calculations are reported for liquid toluene in the 220–370K range. Temperature increase produces an increase in the number of independant holes which continually coalesce. Initially, interstitial holes grow slightly with a temperature increase, but then their size tends asymptotically to a limit.

INTRODUCTION AND SCOPE

Free volume represents a key to the understanding of the properties of liquid and amorphous solid phases. The most successful theory of the equilibrium properties of liquids developed by Flory[1,2] is based on the introduction of a free volume term into the partition function. A modification of the same approach by Simha and collaborators[3,4] was applied to liquid as well as solid phases. Transport properties of liquid phases have been dealt with by the theory of rate processes (Eyring, Glasstone and Laidler[5]) and its various modifications. A working theory of diffusion in polymer-containing systems has been formulated by Vrentas and Duda[6–8].

In most of the theories featuring free volume one of the two extreme approaches is used. In one such approach, the free volume is divided between solvent molecules, polymer segments, ions, etc. (theory of the liquid state, Flory[1,2]). This approach is similar to that when the physical space is represented by a set of Voronoi polyhedra[9], where each entity 'owns' one polyhedron. In the opposite extreme, the free volume is 'liberated'; the independent holes become entities constituting a physical system. The Eyring theory[5] is formulated in terms of holes, and holes are also important in the developments of Simha *et al.*[3,4].

An intermediate approach is also possible. Vrentas and Duda[7] recognize four contributions to the volume of a polymeric system: (1) occupied volume, which resembles the hard-core volume of Flory[1,2]; (2) extra free volume of glass, a non-equilibrium contribution, with its magnitude depending on the cooling rate; (3) interstitial free volume, which can be divided among molecular (i.e., non-hole) entities constituting the system; and (4) independent holes, corresponding to an equilibrium liquid. Confining our attention to liquid systems, we are left with three contributions to volume. Putting aside the hard-core or occupied volume v^*, we have two contributions to free volume. Vrentas and Duda leave open the question of how the free volume can be divided into interstitials and independent holes.

A further step can be taken if we recognize that we have a distribution of hole sizes. Some holes, which have the volume v_h bigger than a critical or cut-off volume v_c, are large enough to be independent (this includes in particular the independence of motions). At the same time, we have what Vrentas and Duda call interstitials, with volumes $v_i < v_c$. The problem is in the separation of the free volume v_f into v_i and v_h contributions.

The existence of holes as a class of entities constituting the system should not be taken literally. Statistical mechanics suggest a slight fluctuation of density around an equilibrium value. At a given moment we might have a distance between two neighbouring liquid molecules large enough to accommodate a hole of molecular size. Various hole theories are trying to seize this effect in various ways, but for any particular pair of molecules the situation described is short-lived. While we can discuss averages and distributions of hole sizes, the lifetime of a single individual hole is found to be negligible from both experiment and from theoretical considerations of statistical mechanics. Permanent holes would scatter electromagnetic radiation, (X-rays in particular) in a way which is not observed on pure liquids.

MODELS

To obtain the desired relations, we assume a model for v_f. Two such models have been used by Golikov and Chalykh[10] in their work on separation of the Gibbs function of activation for diffusion into energetic and entropic contributions. In the first model, Frenkel[11], the energy of formation of a hole of diameter R is:

$$u = \pi \gamma R^2 \tag{1}$$

where γ is the surface tension. In the second model due to Landau and Lifshits[12] we have:

$$u = \frac{\pi R^3}{12 \kappa_T} \tag{2}$$

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where κ_T is the isothermal compressibility

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \tag{3}$$

Numerical values depend on the model, but the character of contributions involved does not. We use the model (2), applicable to liquids as well as solids.

Since we are interested in volumes rather than diameters, we write

$$v = \mu R^3 \tag{4}$$

where μ is a geometric parameter[13,14]. Equation (4) is deceptively simple, but μ depends on the coordination number z, and the limits of z values in liquids are[15]:

$$4 \leqslant z \leqslant 11 \tag{5}$$

The lower limit corresponds to the liquid–vapour critical point, and the upper limit to the triple point. The fact that the primary effect of a temperature increase is a reduction of the coordination number has been discussed earlier by Simha and Somcynsky[3]. Therefore μ depends on the temperature T.

Over a large part of existence of the liquid state, changes of z and therefore of $\mu(z)$, are small (a paper discussing this is in preparation). Drastic changes takes place in the vicinity of the critical point. For solids, changes in z are very small. Thus, as an approximation we shall 'freeze' μ. We can take the value $\mu(8) = 0.7698$, and rewrite (2), introducing equation (4), as:

$$u = Ev, \tag{6}$$

i.e. $E = \pi/(12\mu\kappa_T)$.

DISTRIBUTION OF HOLE SIZES

Given (6), the probability $p(v)$ of having a hole of volume v (to be more accurate, in the interval from v to $v + \mathrm{d}v$) takes the Boltzmann form:

$$p(v)\mathrm{d}v = \frac{E}{kT}\mathrm{e}^{-Ev/kT}\mathrm{d}v \tag{7}$$

The pre-exponential factor is the normalization, and

$$\int_0^\infty p(v)\mathrm{d}v = 1 \tag{8}$$

as expected. The hole size can be anything from zero to infinity, so that for the time being we have lumped the interstitials and independent holes together.

Given (7), the average hole size $\bar{v}$ is

$$\bar{v} = \int_0^\infty vp(v)\mathrm{d}v = \frac{kT}{E} \tag{9}$$

and we can now proceed to disentangle interstitials (index i) from independent holes (index h). In terms of average volumes we have

$$\bar{v} = p_i\bar{v}_i + p_h\bar{v}_h \tag{10}$$

The problem at hand consists in the evaluation of $\bar{v}_i$, $\bar{v}_h$ and, say, p_h (we have $p_i = 1 - p_h$). Firstly:

$$p_h = \int_{v_c}^\infty p(v)\mathrm{d}v = \mathrm{e}^{-Ev_c/kT} \tag{11}$$

We now obtain, by making use of (9):

$$\bar{v}_h = \frac{\int_{v_c}^\infty vp(v)\mathrm{d}v}{p_h} = \bar{v} + v_c \tag{12}$$

while

$$\bar{v}_i = \frac{\int_0^{v_c} vp(v)\mathrm{d}v}{1 - p_h} = \frac{\bar{v} - \bar{v}_h\mathrm{e}^{-v_c/\bar{v}}}{1 - \mathrm{e}^{-v_c/\bar{v}}} \tag{13}$$

A NUMERICAL EXAMPLE

To acquire an understanding of relative roles of interstitial and independent holes (more quantitatively: to evaluate parameters featured in equation (10)) we have made calculations for an exemplary liquid. Toluene was chosen, since accurate volumetric data including κ_T values are available, it is a fairly often used polymeric solvent, and has a reasonable range of existence as a liquid[16]: $T_m = 178.0\mathrm{K}$ and $T_{cr} = 594.0\mathrm{K}$.

The temperature dependence of the isothermal compressibility of liquids is given by[17]

$$\frac{\kappa_T}{(\mathrm{J \cdot cm^{-3}})} = \exp\left[c_i + \frac{c_2}{T/\mathrm{K}} + c_3 \ln\left(\frac{T}{\mathrm{K}}\right)\right] \tag{14}$$

Equation (14) works equally well for elements, inorganic and organic compounds, and polymeric materials. We have used in (14) the dimensionless calculus, so as to indicate units and to avoid expressions such as 'ln T'. Parameters for toluene, based on the best experimental data, are listed in ref. 17; to obtain $10^6\ \kappa_T$, these are: $C_1 = -33.4110$; $C_2 = 642.807$; and $C_3 = 4.2609$. Reasons why $\mathrm{J \cdot cm^{-3}}$ is the pressure unit are given in ref. 18.

For calculations we have taken a temperature interval of 150 K. For reasons discussed above, the interval is relatively far from the critical point; it does not include the melting point, but it does include the usual ambient temperatures. Values of κ_T obtained from equation (14) and of $\bar{v}$ from (9) are given in the second and third columns of the *Table* .

To obtain $\bar{v}_i$ and $\bar{v}_h$, we need the cut-off volume v_c. It can be defined in a number of ways. For instance, it can be related to $\hat{V}^*$, the specific critical hole volume required for a jump in the theory of diffusion of Vrentas and Duda[6–8] (note that a polymer + solvent system involves two such parameters). Independent holes correspond to the vacancies in the quasi-lattice in the theory of Simha[3,4]. For the present essential illustrative purposes the exact choice of v_c is not particularly important. Therefore we assume arbitrarily that at the melting point the liquid phase contains one half of interstitial and one half of independent holes. The substitution $p_h(T_m) = 0.5$ into equation (11) produces $v_c = 2.2218 \cdot 10^{-24}\ \mathrm{cm^3}$. Equations (11–13)

Table 1 Parameters characterizing the free volume in toluene

T (K)	$10^4\,\kappa_T$ (J·cm^{-3})$^{-1}$	$10^{24}\,\bar{v}$ (cm^3)	p_h	$10^{24}\,\bar{v}_i$ (cm^3)	$10^{24}\,\bar{v}_h$ (cm^3)
220	5.490	4.903	0.6356	1.028	7.125
230	5.843	5.456	0.6655	1.036	7.678
240	6.235	6.075	0.6937	1.043	8.297
250	6.666	6.765	0.7201	1.049	8.987
260	7.136	7.533	0.7446	1.055	9.754
270	7.648	8.383	0.7672	1.061	10.605
280	8.202	9.323	0.7880	1.065	11.545
290	8.800	10.360	0.8070	1.070	12.582
300	9.443	11.501	0.8243	1.077	13.723
310	10.134	12.754	0.8401	1.080	14.975
320	10.874	14.126	0.8545	1.080	16.348
330	11.665	15.628	0.8675	1.081	17.850
340	12.510	17.267	0.8793	1.081	19.489
350	13.410	19.054	0.8899	1.096	21.276
360	14.368	20.999	0.8996	1.091	23.221
370	15.387	23.112	0.9083	1.105	25.334

then lead to the values of p_h, $\bar{v}_i$ and $\bar{v}_h$ listed in the last three columns of the *Table* .

DISCUSSION

As expected from the above equations, the data in the *Table* show that both p_h and $\bar{v}_h$ go symbatically with the temperature. However, at lower temperatures $\bar{v}_i$ is symbatic with T, but then tapers off, apparently towards an asymptotic value.

There is a flat level of $\bar{v}_i$ around 320K — an artifact resulting from frozen μ. As discussed in an earlier paper[14], μ increases when z decreases. Therefore, μ increases with T, and the flat part of the $\bar{v}_i(T)$ curve is premature, while the phenomenon of tapering off $\bar{v}_i$ is real.

We conclude that the thermal expansion, in the sense of growth of total volume (and of total free volume) produced by a temperature increase, produces more independent holes. At the same time, these holes coalesce. However, the interstitials, which at first were also growing, subsequently tend to a certain size limit. This means that there is only so much free volume that a molecule (or a polymer segment) can tie to itself. From the very nature of the interstitial and the independent-hole components of the free volume, one can draw a qualitative picture as to the respective roles played by these components. Once we have performed the quantitative separation of the components, the picture formulated earlier is confirmed (*Table* 1).

The free volume is also important in other classes of properties of polymeric and non-polymeric materials, especially in calculation of the temperature shift factor for mechanical properties, usually calculated via the W–L–F equation[19]. Therefore, the shift factor is important in the impact transition temperature defined for polymers by Zewi and Corneliussen[20]. We shall study the shift factor in a separate paper.

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