Size Range of Solid−Liquid Interface Energy of Organic Crystals

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Received: January 24, 2002

In light of our thermodynamic model, which is applied for organic molecules through a suitable consideration of diameter of the molecules, the size and size dependence of excess Gibbs free energy at the solid−liquid interface of different kinds of organic crystals are predicted. The predicted values are within the size range of the interface energy, considering nature of the interface energy, and correspond to the latest experimental data. Moreover, the known experimental results for the interface energy of chain molecules are discussed.

1. Introduction

In view of the obvious importance of the solidification transition, where a liquid undergoes processes of nucleation and growth, it is desirable to have a quantitative knowledge of excess Gibbs free energies at the solid−liquid interface γ_{sl} and the corresponding size dependence $\gamma_{sl}(D)$, with D being the size of the crystals, which is work required to form or to extend a unit area of interface between liquid and crystal plastically.[1−4] It is known that γ_{sl} is not easy to measure even for pure elements; γ_{sl} values obtained by the same or different methods have large differences.[1−9] This is especially true for organic crystals due to their lower thermal conductivity and their lower γ_{sl} values, which have the same size of wall−liquid interface energy where the wall must exist during the measurements as shown in Table 1.[2] Both evidently increase measuring error.[2,5−9] Note also that in Table 1 the γ_{sl} values of organic molecules determined by the latest measurements[3] are smaller than other data, partly due to technique improvement to solve the above problems. In light of this observation, it is plausible that as the measuring technique is further amended, still smaller γ_{sl} values are expected.

Owing to the difficulty of measuring γ_{sl} values, some theoretical attempts have been carried out.[1−4] Among many models, an empirical relationship for metallic elements in terms of Turnbull's classic nucleation theory is as follows:[1−4]

$$\gamma_{sl} = khH_m/V_m \tag{1}$$

where k is a material constant between 0.32 and 0.53,[1] h is the atomic diameter, H_m is the gram-atom melting enthalpy, and V_m is the gram-atom volume. However, approximations made in eq 1, that melting entropy is temperature-independent and that γ_{sl} is size- and temperature-independent, need to be improved.[1]

To determine k value in eq 1 with a clear physical background, a γ_{sl} function has been deduced by use of the Gibbs−Thomson equation and our model for the size-dependent melting temperature in the following form:[4,16]

$$\gamma_{sl} = 2hS_{vib}H_m/(3V_mR) \tag{2}$$

where R is the ideal gas constant and S_{vib} is the vibrational part of the overall gram-atom melting entropy S_m. Since the

vibrational contribution to S_m is essential for metallic and organic molecular crystals, $S_{vib} \approx S_m$ is taken.[4,16] When $k = 2S_m/3R$, eq 2 shows the same result as eq 1. Equation 2 suggests that not only the energetic (chemical bond strength) difference in molecules between crystal and liquid (H_m) but also the structural (coordinate number) difference in molecules between them (S_m) affects the size of γ_{sl}. The prediction of eq 2 has been found to be consistent with experimental results for metallic elements.[4] Note that eq 2 is temperature-dependent because H_m is temperature-dependent.[17,18] Because we here discuss γ_{sl} value at or near melting temperature, this dependence is neglected in the following and H_m is taken as melting enthalpy at the melting temperature. Note also that eq 2 has better suitability for different kinds of crystals than eq 1 does, since only for metallic elements is $S_m/R \approx 1$ and thus k may be expressed as a constant as shown in eq 1. Otherwise, k is a function of melting entropy indicated in eq 2.

Because there is no suitable model to calculate γ_{sl} values of organic crystals, eq 1 has been extended to organic crystals.[2−4] Through comparing the known experimental data, it is found that eq 1 with a lower limit for the k value of 0.32 (this adoption is understandable since S_m of organic crystals is usually only half to one-fourth that of metallic elements) may be applied for organic crystals composed of spherical molecules but failed for those consisting of chain molecules.[2,3] Although measured γ_{sl} values of the latter are in question (see the later text), an issue still arises whether eq 2 or 1 is universal for all kinds of crystals.

In this paper, the nature of γ_{sl} and $\gamma_{sl}(D)$ functions of organic molecular crystals are discussed, which brings out determination of the size range of γ_{sl} in organic crystals. On the basis of this discussion, proper consideration of molecule diameter, and recent experimental results,[3] we argue that eqs 2 and 4 may predict γ_{sl} and $\gamma_{sl}(D)$ values correctly.

2. Size Range of γ_{sl} of Organic Crystals and Model Extension of γ_{sl} and $\gamma_{sl}(D)$ Functions to Organic Crystals

Organic crystals as molecular crystals differ from metallic and ionic ones, whose chemical bonds are covalent within molecules but consist of van der Waals forces or hydrogen bonds among molecules. The former, being responsible for stability of individual molecules, are much stronger than the latter, being primarily responsible for bulk properties of matter, such as γ_{sl}. Because bond strengths of van der Waals forces or hydrogen

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TABLE 1: Comparison between γ_{sl} Values Determined from Eq 2 and Experimental Results for Organic Crystals and Related Parameters[a]

	γ_{sl} (mJ m^{-2})	γ_{sl}' (mJ m^{-2})	γ_{lv}	n	h^b (nm)	V_m^c (cm^3 g-atom^{-1})	S_m^d (J g-atom^{-1} K^{-1})	H_m^d (J g-atom^{-1})
benzene	19.8[2] 44 ± 10[2] 15.7[3] 22 ± 2[8]	15.4	28.9[13]	1	0.5034	6.40	2.95	829
naphthalene	27.2[2] 61 ± 11[2] 8.2[3] 69[9]	18.6	28.8[12]	2	0.4534	6.18	2.98	1062
chlorobenzene	14.1[3]	15.7	33.6[12]	1	0.5344	7.66	3.50	801
cyclohexane	4.6[3]	0.62	25.5[12]	1	0.5465	5.46	0.532	146
heptane	17.1[3]	9.9	20.1[12]	7	0.3018	5.04	3.34	616
diphenyl	24.0[2] 50 ± 10[2]	13.2	34.5[13]	2	0.4756	5.89	2.47	846
cis-decalin	11.6[3]	4.08	32.2[14]	2	0.4771	6.91[14]	1.47[14]	339[14]
trans-decalin	18.4[3]	8.82	29.9[14]	2	0.4818	6.49[14]	2.13[14]	516[14]
carbon tetrabromide	10−20[2]	3.81		1	0.5481	4.81	2.18[15]	790[15]
succinonitrile	28 ± 4[2]	1.94	47[14]	2	0.4021	6.20	1.20	392
ethylene dibromide	19.5[3] 35 ± 7[2]	19.7	38.4[14]	2	0.4156	19.83	4.72	1355
stearic acid[e]	106−151[6] 151 ± 10[7]	14.3	28.9[10]	18	0.2936	7.83	2.95	1010
myristic acid[e]	81[6] 59[5]	16.0	28.6[10]	14	0.2918	10.8	3.15	1031
lauric acid[e]	70 ± 5[7] 71 ± 15[7]	13.9	28.5[10]	12	0.2988	4.90	3.05	964

[a] Experimental results are shown in column 2 as γ_{sl}; results determined by eq 2 are shown in column 3 as γ_{sl}'. [b] h is determined from eq 3. [c] V_m is determined by M/ρ, with M being the molecular weight and ρ the solid density cited from ref 11 unless otherwise specified. [d] S_m and H_m values are obtained from ref 12 unless otherwise specified. [e] For the three fatty acids, a part of the original data[6,7] is solid−vapor interface energy γ_{sv}. Let $\gamma_{sl} \approx \gamma_{sv} - \gamma_{lv}$, and the data listed in the table are obtained.

bonds are weaker than those of metallic or ionic bonds, γ_{sl} values of organic crystals are smaller than those of metallic and ionic crystals, such as Pb with $\gamma_{sl} \approx 40-60$ mJ m^{-2} (γ_{sl} values of Pb in fact is one of the smallest γ_{sl} values among metallic or ionic crystals because its values of S_m and H_m are small, which leads to a small γ_{sl} value of Pb in terms of eq 2).[2] Moreover, γ_{sl} values of compounds composed of full hydrogen bonds, such as H_2O with $\gamma_{sl} \approx 25-45$ mJ m^{-2}, should also be larger than those of organic crystals since molecules of organic crystals have only partly hydrogen bonds while the others are van der Waals forces.[2] Thus, γ_{sl} values for organic crystals could be not more than 30−40 mJ m^{-2}.

It is known that organic molecules mostly consist of C−H bonds with intermolecular dispersion forces caused by relative movement between electrons and the atomic nucleus. Their relative movements change electron density within the molecule. Generally, the larger the number of electrons and the more diffuse the electron cloud in the molecule, the greater its dispersion forces. However, the forces hardly affect the net attraction applied to a unit area of interface, so the size difference of γ_{sl} values for organic molecules thus is smaller than those of metallic and ionic crystals (for other two kinds of intermolecular forces, orientation forces and induced forces, a similar discussion may be carried out).

Although measured γ_{sl} values of organic crystals composed of chain molecules are much larger than the above limits shown in Table 1,[5−7] their real values should be similar to that composed of spherical molecules since γ_{sl} denotes excess energy of unit area where molecular weight has negligible effect on it. Even if chain molecules may contain one or more hydrogen bonds, γ_{sl} values still vary little since most bonds of the molecules are van der Waals forces. This result also implies that anisotropy of γ_{sl} of organic crystals is small, although this issue up to now is still debated.[2−4]

Moreover, for a typical fcc crystal, the coordinate number (bond number) decrease of molecules on a solid−liquid interface

is usually 1−2, while that on a liquid−vapor interface is 3−4. If this bond number is proportional to the corresponding interface energy, with the note that the bond strength difference of molecules between solid and liquid states is only several percent, γ_{sl} must be smaller than the excess Gibbs free energy of liquid−vapor interfaces γ_{lv}, which is easy to measure with better measuring accuracy. Thus, the γ_{lv} value of the same substance is a good reference as an upper limit on γ_{sv}. For organic crystals, the γ_{sl} value may be around half γ_{lv} as a rough estimation. Since $\gamma_{lv} \approx 20-40$ mJ m^{-2} shown in Table 1, γ_{sl} < 20 mJ m^{-2}, which is also smaller than the above-stated limits in terms of consideration of the bond strength of metallic, ionic, and hydrogen bonds.

On the basis of the above consideration, it is known that γ_{sl} values of organic molecules must be smaller than those of the other types of crystals. Thus, literature values for organic crystals in a size of γ_{sl} > 20 mJ m^{-2} may be questionable.

Before we determine the γ_{sl} value by use of eq 2, the parameter h, defined as the atomic diameter of metallic elements in eq 2, must be redefined to adapt to the case of molecular crystals. For organic spherical molecules, h can be an averaged diameter of the molecules since the molecule for molecule crystals has a similar effect as atoms for metallic elements. For chain molecules, considering that the γ_{sl} value states excess energy of interface molecules in a unit area, the h value for chain molecules thus may be defined as the mean size of a segment of chain molecules (note that this definition is only meaningful for eq 2 and do not imply any generalization for the definition of molecule diameters):

$$h = [V_m/(nN_0)]^{1/3} \qquad (3)$$

where n denotes the segment number of the chain and N_0 is Avogadro's constant.

Since any nucleus during solidification is in the nanometer size range, $\gamma_{sl}(D)$, not γ_{sl}, has to be considered for theoretical

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prediction of actual nucleation and growth processes. This relationship for metallic elements has been established as follows:[17−18]

$$\gamma_{sl}(D)/\gamma_{sl} = [1 - D_0/D]/[1 \pm (8\kappa\gamma_{sl}D_0/3)^{1/2}/D] \quad (4)$$

where κ shows the compressibility. The sign in the denominator is positive for crystals having free surface and is negative for those having a coherent or semicoherent interface with surrounding solid matrix.[18] D_0 denotes a critical diameter at which almost all molecules of a nanocrystal are located on its surface, where the crystal is indistinguishable from the surrounding liquid and the solid−liquid interface is therefore at all diffuse. Thus, $\gamma_{sl}(D \rightarrow D_0) = 0$, where D_0 depends on the existence of curvature of crystals, with $D_0 = 3h$ for a particle or a wire having curved surfaces and $D_0 = 2h$ for a film having plane surfaces.[17,18] The physical background of eq 4 is that the surface/volume ratio increases as D decreases, while $\gamma_{sl}(D)$ follows the same size dependence. This essential principle should also be applicable for organic crystals. This is also the reason eq 4 is utilized to calculate the $\gamma_{sl}(D)$ function of organic crystals.

3. Results and Discussion

Table 1 shows a comparison between γ_{sl} values determined by eq 2 and the corresponding experimental results [2−3,5−9] for 14 different organic molecular crystals. The corresponding γ_{lv} values of the crystals are also listed in the table as reference. The predictions of eq 2 are in agreement with the principles of $\gamma_{sl} < \gamma_{lv}$ and the upper size limit of γ_{sl} values. In addition, the predictions partly correspond to the latest experimental results but are smaller than the early experimental results. Since the early measured γ_{sl} values, especially the data for chain molecule crystals, are evidently larger than the possible size of the contribution of van der Waals forces on γ_{sl} values, this disagreement between the prediction of eq 2 and experimental results for the chain molecules may hardly illustrate the incorrectness of eq 2. In terms of the above discussion, we believe that our predictions are at least qualitatively correct in size range.

In Table 1, although $\gamma_{sl} < 20$ mJ m^{-2} as analyzed in the above discussion, γ_{sl} values of different organic crystals change from 0.62 mJ m^{-2} for cyclohexane to 19.7 mJ m^{-2} for ethylene dibromide or about 30 times. This difference can be found in eq 2. The variants of γ_{sl} in eq 2 are h, S_m/R, and H_m/V_m. Since h for different substances varies a little, the essential contributions to differences in γ_{sl} values are H_m/V_m, denoting the energetic difference between crystal and liquid, and S_m/R, showing the corresponding structural difference. The cited data in Table 1 for H_m/V_m values are between 27 and 172 J cm^{-3}, while those for S_m/R values are between 0.064 and 0.568. Since H_m/V_m and S_m/R for one substance do not simultaneously take the largest values induced by different melting temperatures of different substances T_m, with the known fact that $H_m = T_m S_m$, the real differences in γ_{sl} values are smaller than the largest possible difference.

$\gamma_{sl}(D)$ values of five organic nanocrystals have been calculated with eq 4 and are shown in Table 2. The model predictions are consistent with the experimental observation[3] with the note that there exists a size distribution of nanocrystals. As the size of crystals decreases, $\gamma_{sl}(D)$ decreases. At $D = 4$ nm, the decrease of $\gamma_{sl}(D)$ for different substances is different, which is induced by different D_0 or D_0/D values. The drop of $\gamma_{sl}(D)$ values in comparison with the corresponding bulk values reaches 20−40% where the critical size of a nucleus may be near 4 nm.

TABLE 2: $\gamma_{sl}(D)/\gamma_{sl}$ Value Comparison between the Predicted Values and the Corresponding Experimental Results

	$\gamma_{sl}(D)/\gamma_{sl}$	$[\gamma_{sl}(D)/\gamma_{sl}]'$	κ^b (MPa^{-1} × 10^{-5})
benzene	0.67	0.66	87
naphthalene	0.68	0.69	≈87
chlorobenzene	0.89	0.63	67
heptane	0.63	0.80	134
trans-decalin	0.60	0.68	≈87

[a] Experimental results are shown in column 2 as $\gamma_{sl}(D)/\gamma_{sl}$; predicted values in terms of eq 4 are shown in column 3 as $[\gamma_{sl}(D)/\gamma_{sl}]'$. The experimental $\gamma_{sl}(D = 4$ nm) values are obtained by measuring the slope of experimental data of melting temperature versus $1/D$ with two points of $D = 4$ nm and $D = 8.5$ nm in terms of the Gibbs−Thomson equation. [b] Related κ values at $D = 4$ nm. Since κ values of crystals are not found, κ values of the corresponding liquid are used, which leads to minor error.[14] Note that κ values of naphthalene and *trans*-decalin have been estimated as that of benzene.

Thus, the energetic resistance for the nucleation process in liquid may be smaller than what the classic theory has estimated.[18]

The above agreement between eq 4 and experiments denotes that the energetic and structural differences between crystal and liquid [$H_m(D)$ and $S_m(D)$] decrease with decreasing size, which is proportional to surface/volume ratio with a $1/D$ relationship.[16] The success of model prediction for $\gamma_{sl}(D)$ values in return confirms again that H_m and S_m, not H_m itself, determine the sizes of γ_{sl} values as shown in eq 2.[4]

4. Conclusion

In summary, after a suitable definition of molecular diameter given by eq 3, γ_{sl} and $\gamma_{sl}(D)$ values of organic crystals with different geometric shapes are estimated in terms of our thermodynamic model of eqs 2 and 4, where γ_{sl} and $\gamma_{sl}(D)$ are functions of H_m and S_m. Agreement among our model prediction, the latest experimental results, and the discussed size range based on consideration of the nature of γ_{sl} have been found.

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