The solid–liquid interface energy of organic crystals

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ABSTRACT: A simple thermodynamic model, originally developed for metals based on the Gibbs–Thomson equation and related considerations for homogeneous nucleation, has been extended to predict the solid–liquid interface energy γ_{sl} of organic crystals. The model predictions correspond to available experimental and other theoretical results for 38 organic crystals. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: solid–liquid interface energy; organic crystals

INTRODUCTION

The solid–liquid interface energy γ_{sl}, which is defined as the reversible work required to form or to extend a unit area of interface between a crystal and its coexisting fluid plastically, is one of the most fundamental materials properties.[1–6] It plays a key role in many practically important physical processes and phenomena like homogeneous nucleation, crystal growth from the melt, surface melting, and roughening transition, etc. Thus, a quantitative knowledge of γ_{sl} value is necessary. However, direct measurements for γ_{sl} are not at all easy even for elements in contrast to the case of liquid–vapor interface energy γ_{lv}.[1–4] This is especially true for organic crystals because of their lower thermal conductivity and smaller γ_{sl} values, which have the same size of wall–liquid interface energy where the wall must exist during the measurements.[2] Both evidently increase measuring error.[2] On the other hand, a theoretical method to determine γ_{sl} values of organic crystals does not exist to the best of our knowledge. Therefore, it is necessary and important to develop a thermodynamic prediction method to calculate γ_{sl} values of organic crystals.

Due to the difficulty of measuring γ_{sl} values, some theoretical attempts have been carried out.[1,2,4,6] Based on the nucleation experiments and the classical nucleation theory (CNT), Turnbull proposed an empirical relationship that γ_{sl} is proportional to its g-atom melting enthalpy ΔH_m,[1]

$$\gamma_{sl} = \frac{\tau \Delta H_m}{V_g^{2/3} N_a^{1/3}} \tag{1}$$

where the coefficient τ is considered to be 0.45 for metals (especially closely packed metals) and 0.34 for non-metallic elements at about 20% of undercooling below the melting point T_m,[1] V_g is the g-atom volume of the crystal at T_m, and N_a is the Avogadro constant. The γ_{sl} values measured by Turnbull are recognized now to be lower than real ones for metals.[7,8] According to the review papers of Eustathopoulos or Kelton,[3,5] $\tau = 0.55$ or $\tau = 0.49 \pm 0.08$ for metals while τ value increases noticeably for molecules having more asymmetry.[2,6] Undoubtedly, Eqn (1) overlooks some important pieces of physics,[2,6] and the existence of τ to be determined also weakens the theoretical meaning of this equation.

Singh[9] predicted that τ lies between 0.30 and 0.35 for organic crystals. Similarly, τ was also predicted to be 0.30 for water and some organic compounds[10] when ΔH_m and V_g are measured in units of $J\,mol^{-1}$ and $cm^3\,mol^{-1}$ rather than $J\,(g\text{-atom})^{-1}$ and $cm^3\,(g\text{-atom})^{-1}$, respectively. However, this has not been strictly examined. Thus, γ_{sl} function of organic crystals needs to be further considered.

In this contribution, a thermodynamic model for γ_{sl} of organic crystals is established on the basis of the Gibbs–Thomson equation and some considerations for homogeneous nucleation of elements.[2,8] It is found that the model predictions correspond to available experimental or other theoretical results for 38 organic crystals.

MODEL

The most powerful method available for theoretically estimating γ_{sl} is to make direct use of the so-called Gibbs–Thomson equation (known also as the Kelvin equation),[2] which describes the equilibrium between

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small spherical solid nucleus and the infinite amount of its liquid,

$$\gamma_{sl} = \frac{r_n \Delta H_m}{2V_g}\left(1 - \frac{T_n}{T_m}\right) \quad (2)$$

where r_n and T_n are the critical radius of the solid nucleus and the nucleation temperature, respectively. The physical meaning of Eqn (2) is that the growth of the solid phase will be thermodynamically more favourable than its dissolution for solid nucleus with size larger than r_n at T_n. Thus, the γ_{sl} value can be determined in terms of Eqn (2) as long as the r_n value at T_n is known.

In the CNT, when spherical elemental nucleus with a radius r is formed from the corresponding liquid phase at a temperature T below the bulk T_m, the Gibbs free energy change $\Delta G(r,T)$ can be expressed as,[8]

$$\Delta G(r,T) = -(4/3)\pi r^3 g_m(T)/V_g + 4\pi R^2 \gamma_{sl}(r,T) \quad (3)$$

where g_m is the Gibbs free energy difference function between crystal and liquid, which is given as,[11]

$$g_m(T) = \frac{7\Delta H_m T(T_m - T)}{T_m(T_m + 6T)} \quad (4)$$

Recently, through combining Eqn (2) and a model for the size-dependent melting temperature, γ_{sl} is read as,[6]

$$\gamma_{sl}(T) = \frac{2hS_{vib}\Delta H_m(T)}{3RV_g} \quad (5)$$

where R is the ideal gas constant and S_{vib} is the vibrational part of the overall melting entropy S_m. Although Eqn (5) has been applied to determine γ_{sl} values of organic crystals and gained a certain success,[12] the assumption of $S_{vib} \approx S_m$ will result in significant deviation for organic crystals with larger volume change on melting and thus larger positional entropy S_{pos} noted that $S_{vib} \approx S_m - S_{pos}$.[8]

In terms of the Helmholtz function $\Delta H_m(T) = g_m(T) - Tdg_m(T)/dT$ with Eqn (4), $\Delta H_m(T)$ can be determined as,

$$\Delta H_m(T) = \frac{49\Delta H_m T^2}{(T_m + 6T)^2} \quad (6)$$

On the other hand, solid–liquid interface energy should be size-dependent.[6] $\gamma_{sl}(r)$ function for particles has been established and simplified as,[6]

$$\frac{\gamma_{sl}(r)}{\gamma_{sl}} \approx 1 - 3h/2r \quad (7)$$

Substituting Eqns (4)–(7) into Eqn (3) and letting $\partial \Delta G(r,T)/\partial r = 0$, r_n can be determined as,

$$\frac{r_n\theta}{h} = A + \sqrt{A^2 - 3A\theta/2} \quad (8)$$

where $\theta = 1 - T_n/T_m$ is the degree of undercooling and $A = \frac{14S_{vib}}{3R}\left(\frac{1-\theta}{7-6\theta}\right)$.

Since the average value of θ of 37 elements (except for Hg, Ga, and Te) is about 0.21[13] and the average value of

S_{vib}/R of concerned elements in Table 1 of Ref. 8 is about 0.95,[8] there is,

$$\frac{r_n\theta}{h} \approx 1.04 \quad (9)$$

For any pure, isotropic, spherical, condensed material, h in Eqn (9) can be estimated from the known value of V_g and the packing density η of the solid crystals as,

$$h = \left[\frac{6\eta V_g}{\pi N_a}\right]^{1/3} \quad (10)$$

Taking the $V_g^{1/3}$ value from Eqn (10) and substituting it and Eqn (9) into Eqn (2), there is,

$$\gamma_{sl} = \frac{\beta\Delta H_m}{V_g^{2/3}N_a^{1/3}} \quad (11)$$

with $\beta \approx [27\eta/(32\pi)]^{1/3}$

Table 1 gives comparisons of γ_{sl} of 17 metals among the model predictions γ_0 by Eqn (11), available experimental data γ_{exp},[2,4,14–17] and MD results γ_{MD}[18–20] where the related parameters are also listed.[21,22] Because many of the elements, that is, those with asterisk in column 1 of Table 1, can transform from one crystalline form to another on heating from 0 K to T_m while γ_{sl} is calculated at $T = T_m$, the η values of the high temperature allotropic forms are employed. In case of hexagonal close-packed (hcp) elements, the ideal hcp structure (all the atomic distances are uniform and $\eta = 0.74$) has been employed for simplification. It can be found that γ_0 corresponds to γ_{exp} and γ_{MD} except for Sb and Tl. The γ_{exp} value of Tl was determined by a similar method in estimating $\gamma_{exp}(Pb) = 76 \, mJ \, m^{-2}$,[15] which is considerably higher than the result from other experiment.[2]

Although Eqn (11) is deduced in terms of the Gibbs–Thomson equation and related discussions for homogeneous nucleation of metallic elements, this equation should be also applicable to other types of materials, for example, organic crystals. Although $\theta \approx 0.21$ and $S_{vib}/R \approx 0.95$ are not suitable for organic crystals, the equation $r_n\theta/h \approx 1.04$ is reasonable for organic crystals. Because θ values of organic crystals are unavailable to us, and since water consists of full hydrogen bonds, water is taken as the example. Using $\theta \approx 0.143$,[1] $S_{vib}/R \approx 0.89$, and $h \approx 0.096$,[6] Eqn (9) can also be obtained. Note that η is 1 in this case since the correlation between molecular diameter h and V_g is unrelated to η for spherical organic crystals.

RESULTS AND DISCUSSION

Table 2 shows a comparison of $\gamma_{sl}(T_m)$ for 38 different organic molecular crystals between the model predictions γ_0 and available experimental data γ_{exp}[2,4,23–26] where the related parameters are also listed.[27–30] It is found that γ_0 corresponds to the late experimental data[2,4,25,26] which

Table 1. Comparisons of $\gamma_{sl}(T_m)$ of metals among the model predictions γ_0 by Eqn (11), available experimental data γ_{exp}, and MD results γ_{MD}

	γ_0	γ_{exp}	γ_{MD}	ΔH_m	V_g	η[a]
Ag	163	172[15]		11.3	10.3	0.74
Al	159	158 ± 30[16]	149[20]	10.8	10	0.74
Au	180	156[15], 190[16]		12.5	10.2	0.74
Bi	81	55 ∼ 80[2], 82[15]		10.9	21.3	0.44
Cd	75	87[15]		6.1	13.1	0.74
Co[b]	308	328[15]		16.1	6.7	0.74
Cu	239	232[15], 237 ± 26[16]		13	7.1	0.74
Fe[b]	247	336[15]	221[18]	13.8	7.1	0.68
Li[b]	35	30[17]		3	13.1	0.68
Na[b]	21	20[17]		2.6	23.7	0.68
Ni	333	364[15]	326[19]	17.2	6.6	0.74
Pb	47	40 ± 7[2], 76[15]		4.8	18.2	0.74
Pt	306	323[15]		19.6	9.1	0.74
Sb	163	80 ∼ 130[15]		19.7	18.2	0.44
Sn[b]	66	62 ± 10[2]		7	16.7	0.54
Tl[b]	41	67[15]		4.2	17.2	0.68
Zn	113	132[14], 87 ∼ 123[15]		7.3	9.2	0.74

γ, ΔH_m[21], and V_g[21] are measured in units of mJ m^{-2}, kJ (g-atom)$^{-1}$, and cm^3 (g-atom)$^{-1}$, respectively, which have the same units as those in Table 2.
[a] From Ref. 22.
[b] These metals have allotropic forms.

are evidently smaller than the early experimental ones for lauric, myristic, and stearic acids.[23,24] Moreover, other theoretical results γ_1 calculated by Rai *et al.*,[31–48] γ_2, and γ_3 determined in terms of Eqn (1) with $\tau = 0.30$ and 0.35 are also listed for comparison; note that in this case the units of $\Delta H_m'$ and V' are taken as J mol^{-1} and cm^3 mol^{-1} rather than J (g-atom)$^{-1}$ and cm^3 (g-atom)$^{-1}$, respectively, listed in Table 2.[10] Note that $\Delta H_m' = n\Delta H_m$ and $V' = nV_g$ with n being the number of atoms in a molecule. Thus, although β is larger than τ, γ_0 may be larger or smaller than γ_2 and γ_3 because of the existence of n. Generally, γ_0 is in good agreement with γ_2 while is smaller than γ_1. Although γ_1 was claimed to be calculated in terms of Eqn (1) with τ lying between 0.30 and 0.35 (τ value was not definitely mentioned),[31–33,36–42,44–48] γ_1 values of 15 organic crystals are larger than γ_3, which is determined by Eqn (1) with $\tau = 0.35$. Since γ_0 corresponds to γ_2 with $\tau = 0.30$, the case that γ_0 is smaller than γ_1 is obvious and may hardly illustrate the incorrectness of Eqn (11).

It is known that organic crystals as molecular crystals differ from metallic ones, whose chemical bonds are covalent within molecules, while molecules are bound by van der Waals forces or hydrogen bonds. The former, being responsible for stability of individual molecules, is much stronger than the latter, being primarily responsible for bulk properties of matter, such as γ_{sl}. Since bond strengths of van der Waals forces or hydrogen bonds are weaker than those of metallic bonds, γ_{sl} values of organic crystals should be smaller than those of metallic crystals, such as $\gamma_{sl} \approx 40 \pm 7$ mJ m^{-2} of Pb,[2] which is one of the smallest γ_{sl} values among metallic crystals except for alkali metals where abnormally small γ_{sl} values (≤ 30 mJ m^{-2}) result from smaller ΔH_m and unnaturally larger V_g as shown in Table 1. As shown in Table 2, γ_0

values of all 38 organic crystals are smaller than the upper limit of 47 mJ m^{-2}.

Although some measured γ_{sl} values of organic crystals composed of chain molecules are much larger than the above limits as shown in Table 2,[23,24] their real values should be similar to those 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 analysis also implies that anisotropy of γ_{sl} of organic crystals is small, although this issue is still debated up to now.[2,4,6]

Moreover, for a typical fcc crystal, the bond number decrease of molecules on a solid–liquid interface is usually 1–2, while that on a liquid–vapor interface is 3–4. Since the 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 of the bond strength, γ_{sl} should be always smaller than γ_{lv} where γ_{lv} is easy to measure with better accuracy. Although the above analysis is made in terms of the relation between interface energy and bond number for metals, this relation should also be applicable to organic crystals. Thus, the γ_{lv} value of the same substance is a good reference as an upper limit on γ_{sl}. The available γ_{lv} values of these crystals are also listed in Table 2 from references.[27–29] The model predictions in terms of Eqn (11) are in good agreement with the principle of $\gamma_{sl} < \gamma_{lv}$. Since the early measured γ_{sl} values for lauric, myristic, and stearic acids[23,24] are evidently larger than the corresponding γ_{lv} values,[2] the disagreement between γ_0 and early γ_{exp} for these three kinds of acids may also hardly illustrate the incorrectness of

Table 2. Comparisons of $\gamma_{sl}(T_m)$ of organic crystals among the model predictions γ_0 by Eqn (11), available experimental data γ_{exp}, and other theoretical results γ_1, γ_2, and γ_3

	γ_0	γ_{exp}	γ_1	γ_2	γ_3	γ_{lv}	ΔH_m^a	V_g^a
Acenaphthene	23.2		29.7[31]	29.9	35.1		0.979	5.88
Acetanilide	27.2		33.2[31]	33.4	39.2	35.7	1.140	5.82
Benzene	16.9	19.8[2], 15.7[4]		17.8	20.8	28.9	0.829	7.39
Benzil	20.2		34[32]	27.5	32.2		0.915	6.57
Benzoic acid	27.8		40.7[33]	31.3	36.7		1.210	6.16
Camphene	2.6	4.4 ± 0.5[34]		3.5	4.1		0.110	6.10
Camphor	6.2	10.8 ± 1.1[35]		8.6	10.1		0.254	5.60
Carbontetrabromide	8.5	10–20[2]	6.8[36]	6.7	7.8		0.790	19.4
Chlorobenzene	14.8	14.1[4]		15.6	18.3	33.6	0.796	8.48
p-Chloronitrobenzene	25.0		29.4[37]	27.7	32.4	37.0	1.288	7.97
Cis-decalin	8.4	11.6[4]		11.8	13.8	32.2	0.339	5.48
Cyclohexane	3.5	4.6[4]		4.2	4.9	25.5	0.149	5.98
p-Dibromobenzene	17.8		31.2[37]	18.6	21.9	33.0	1.711	20.4
p-Dichlorobenzene	26.4		39.7[38]	27.8	32.6	30.0	1.525	9.42
p-Formyldimethylaniline	21.0		36[39]	27.0	31.7		0.855	5.60
Diphenyl	17.8	24.0[2]	20.8[37]	22.9	26.8	34.5	0.846	7.07
Durene	20.5		30.7[40,41]	27.2	31.9		0.889	6.14
Ethylene dibromide	21.7	35 ± 7[2], 19.5[4]		19.9	23.3	38.4	1.368	10.8
Heptane	13.7	17.1[4]		17.8	20.9	20.1	0.608	6.39
Lauric acid	22.5	71 ± 15[24]		34.7	40.7	28.5	0.964	6.05
Myristic acid	23.7	81[23]		38.5	45.2	28.6	1.025	6.10
Naphthalene	24.4	27.2[2]		29.4	34.5	28.8	1.057	6.13
α-Naphthol	26.2		44.8[33]	32.2	37.7		1.228	6.89
Neopentyl alcohol	5.8		5.0[42]	7.0	8.2		0.248	6.04
m-Nitroaniline	36.9		38.1[43]	41.1	48.1	50.3	1.579	6.03
m-Nitrobenzoic acid	27.8		40.6[44]	32.9	38.5		1.259	6.55
p-Nitrophenol	26.3		41.9[45]	28.4	33.3	33.9	1.280	7.30
Pentachloropyridine	25.5		52.2[46]	26.1	30.6		2.518	21.1
Phenanthrene	16.4		22.1[37]	21.7	25.5		0.776	7.00
Pivalic acid	2.9	2.7 ± 0.2[25]		3.4	4.1		0.133	6.59
Pyrene	15.4		26.8[47]	21.0	24.6		0.668	6.12
Pyrogallol	38.2		64.1[41]	43.3	50.8		1.593	5.79
Resorcinol	34.9		50.1[40]	38.7	45.3		1.521	6.19
Stearic acid	25.7	106–151[23]		45.2	52.9	28.9	1.093	5.97
Succinonitrile	7.1	7.9 ± 0.8[26]	9.0[42]	7.0	8.2	47	0.370	8.08
s-Tetrachlorobenzene	37.4		46.3[48]	39.3	46.1		2.195	9.68
Trans-decalin	12.8	18.4[4]		17.5	20.5	29.9	0.516	5.54
Urea	45.3		54.7[33]	41.7	48.9		1.849	5.60

γ_2 and γ_3 are calculated in terms of Eqn (1) with $\tau = 0.30$ and 0.35 while the units of ΔH_m and V_g are $kJ\,mol^{-1}$ and $cm^3\,mol^{-1}$ rather than $J\,(g\text{-atom})^{-1}$ and $cm^3\,(g\text{-atom})^{-1}$, respectively, listed in this table.
[a] From Refs. 27–30.

Eqn (11). In terms of the above discussions, the predictions of γ_0 are at least qualitatively correct in size range; namely, Eqn (11) can be extended to organic crystals.

CONCLUSION

In summary, a simple thermodynamic model, originally established for metals in terms of the Gibbs–Thomson equation and discussions for homogeneous nucleation, has been extended to predict the solid–liquid interface energy of organic crystals. The model predictions are generally in agreement with available experimental and other theoretical results for 17 elemental crystals and 38 organic crystals.

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