Solid–liquid interfacial free energies of benzene

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Abstract

In this work we determine for the range of melting temperatures $284.6 \leq T \leq 306.7$ K, corresponding to equilibrium pressures $20.6 \leq P \leq 102.9$ MPa, the benzene solid–liquid interfacial free energy by a cognitive approach including theoretical and experimental physics, mathematics, computer algebra (MATLAB), and some results from molecular dynamics computer simulations. From a theoretical and mathematical points of view, we deal with the elaboration of an analytical expression for the internal energy derived from a unified solid–liquid–vapor equation of state and with the elaboration of an existing statistical model for the entropy drop of the melt near the solid–liquid interface. From an experimental point of view, we will use our results obtained in collaboration with colleagues concerning the supercooled liquid benzene. Of particular interest for this work is the existing center-of-mass radial distribution function of benzene at 298 K obtained by computer simulation. Crystal-orientation-independent and minimum interfacial free energies are calculated and shown to increase slightly with the above temperatures. Both crystal-orientation-independent and minimum free energies agree with existing calculations and with rare existing experimental data. Taking into account the fact that the extent of supercooling is generally admitted as a constant, we determine the limits of supercooling by which we explore the behavior of the critical nucleus radius which is shown to decrease in terms of the above temperatures. The radius of the, and the number of molecules per, critical nucleus are shown to assume the average values of 20.2 Å and 175 with standard deviations of 0.16 Å and 4.5, respectively.

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1. Introduction

In both the classical nucleation theory (CNT) [1] and an existing generalized nucleation theory (GNT) [2,3] the experimental determination of the solid–liquid interfacial free energy, $\sigma_{dl}$, has not gained much impact since the earlier determinations prior to 1974 [4], which were performed under the hypothesis of homogenous nucleation. The difficulties in measuring directly or indirectly $\sigma_{dl}$ are mainly three: (1) The solid–liquid interface is not easily identified experimentally for it has a transient thickness. (2) Values of $\sigma_{dl}$ for most solid–liquid interfaces examined so far are on the order of 480 mJ m$^{-2}$ and lower (477 mJ m$^{-2}$ for Si and 335 mJ m$^{-2}$ for Ta [5]), being extremely small to be retrieved experimentally. (3) In some experimental tests, however, while it is possible to evaluate $\sigma_{dl}$ from the equation $\sigma_{dl} = \sigma_{sv} - \sigma_{lv} \cos \theta$ [6], where $\sigma_{sv}$ and $\sigma_{lv}$ are the interfacial solid–vapor and liquid–vapor free energies, respectively, and $\theta$ is a contact angle, deeper investigations have shown that some inconsistencies in the values of $\theta$ measured by conventional goniometer techniques arise leading consequently to similar inconsistencies in the values of $\sigma_{dl}$ [7]. When all those difficulties are removed still there is a question of reliability on how to conduct a homogenous nucleation experiment.

In order to complete the task concerning the determination of $\sigma_{dl}$, a number of theoretical and (semi)-empirical equations expressing $\sigma_{dl}$ either in terms of measurable thermodynamic quantities [9,10] including sometimes the radial distribution function (RDF) [11,12] or as an extra function of ($\sigma_{sv}$, $\sigma_{lv}$) [7,8] have been put forward. In the
former cases [9,10,12,13], values of $\sigma_{sl}$ for metals and some organic substances were evaluated and tabulated together with existing experimental data. It is worth mentioning that the equation derived in Refs. [11,12], which writes
\[
\sigma_{sl} = \left( \frac{1}{4} \right) \left( \frac{d_s \Delta H_m}{V_s} \right) + \left( \frac{N_A k_B T_m}{V_1} \right) \int_0^D g(r) \ln g(r) \, dr,
\]

is in good agreement with most of the experimental data examined in Ref. [9]; disagreements have been observed in three cases out of 23 applications to metals and semi-metals exclusively. In Eq. (1), $d_s$ is the (total) length of nearest neighbor broken bonds in the solid—a length that extends from the solid–liquid interface until the last broken bond in the solid, $\Delta H_m$ is the molar enthalpy change between the solid and liquid phases at the melting temperature $T_m$, $g(r)$ is the liquid RDF, $D$ is the cutoff distance defined such that $g(r) \approx 1$ for $r > D$, and $V_s$ and $V_1$ are the molar volumes for bulk solid and liquid phases at $T_m$, respectively. $R = N_A \times k_B$ are three known universal constants. In Eq. (1), the second term has been derived in Ref. [11] by a statistical approach and the first term is an established generalization [12] of the corresponding term in Ref. [11], a correction by which the formula (1) becomes applicable to any crystal [12]. Since its derivation, Eq. (1) has not been applied to molecular substances. One of the purposes of this paper is to add corrections to both terms of Eq. (1) which take into account their temperature dependence then apply it to the benzene solid–liquid interface to derive its free energy for the range of melting temperatures $284.6 \leq T \leq 306.7 \text{ K}$, corresponding to equilibrium pressures $20.6 \leq P \leq 102.9 \text{ MPa}$. In an intermediate step, the RDF will too be determined as a function of $T$ and plotted for a set of $T$-values.

From a computational point of view, computer simulation has gained some impact in determining the solid–liquid interface [14–17]. One of the improved techniques in molecular dynamics (MD) [14] is the circuitvention of the well-known time-barrier limitation which arises when the nucleation rate is lower than $10^{20} \sim 10^{25} \text{ cm}^{-3} \text{ s}^{-1}$. Concerning the liquid benzene, its center-of-mass (CM) and total RDF’s have been determined by MD simulation using a molecular-mechanics potential [18,19]. In this paper we will rely partly on the results derived in Refs. [18,19], particularly, on the CM RDF of liquid benzene, $g(r)$, at 298 K shown in Fig. 1. The latter has been re-derived later by Monte Carlo simulations [20].

Knowing the nucleation temperatures of supercooled liquid benzene [21] for the range of melting temperatures $284.6 \leq T \leq 306.7 \text{ K}$, we will be interested in determining too the corresponding interfacial energies and radii of critical nuclei. Some parts of this work are theoretic while other parts have been made possible using a Computer Algebra System. The MATLAB M-file script is provided in the Appendix and some extracts are shown in the text to clarify the analysis. The M-file is a set of line codes and comments numbered from 1 to 110.

![Fig. 1. Center-of-mass radial distribution function (CMRDF) at 298 K.](image-url)
planes with broken bonds all of them parallel to the interface [12]. The first of these planes is in contact with the melt and the next planes have gradually decreasing numbers of broken bonds. If $d_{hk1}$ is the interplanar spacing corresponding to the orientation $(hk1)$ then $d_s$ is on the order of $d_{hk1}$ times the number of crystallographic planes $(hk1)$ with broken bonds. In a random situation, such as that arising in the formation of an embryo of nucleation, there is no preferable orientation and $d_s$ assumes an average effective value. In this case, the volume of the unit cell may well provide an average value for $d_s^3$.

The structure of solid benzene has been determined at 4.2 and 270.15 K to be orthorhombic in the space group Pbc a with $Z = 4$ molecules per unit cell [23,24]. In Refs. [23,24] the parameters of the unit cell are provided for 4.2 and 270.15 K, respectively; furthermore in Ref. [23] an illustration of the unit cell showing the relative disposition and orientation of the molecules is depicted, which has been used very recently [25]. Moreover, MD simulation [18] has proven that under constant atmospheric pressure the structure of solid benzene is stable up to 290 K—well above the melting temperature (278.5 K). We will assume that this conclusion extends to higher pressures including the range 20 MPa to 290 K—well above the melting temperature (278.5 K).

The second term in (1) has been identified as the interfacial free energy is due to a decrease in the entropy of the melt such that

$$d = \frac{Z_cRT_c}{P_c}d_s,$$

where $b$ is the compressibility factor at the critical point, the new constants $c_r$ and $d_r$ and the eight following constants $a_0$, $a_1$, $a_2$, $n$, $b_0$, $b_1$, $b_2$ and $m$ are substance dependent,

$$a_1(T_r) = a_0 + a_1 T_r \exp(-a_2 T_r^m),$$

$$b_1(T_r) = b_0 + b_1 \exp(-b_2 T_r^m),$$

where $T_r = T/T_c$ is a reduced temperature. The corresponding numerical constants for benzene are as follows [26]

$$P_c = 4.894 \text{MPa}, \quad T_c = 562.05 \text{K}, \quad Z_c = 0.3750290, \quad c_r = 0.3397686, \quad d_t = 0.3345894.$$  

$$a_0 = 0.31125, \quad a_1 = 1.5930, \quad b_0 = 0.3280, \quad b_2 = 26.6678, \quad n = 1.51, \quad b_1 = -9.64236 \times 10^{-2}, \quad b_2 = 26.6650, \quad m = 4.0.$$  

Upon integrating ($\partial F/\partial V)_T = -P$, where $P$ is given by the r.h.s. of Eq. (5), we obtain the molar free energy $F$ (compare with Ref. [21, Eq. (7)])

$$F = -RT \left( \frac{d - b}{c - b} \ln |V - b| + \frac{c - d}{c - b} \ln |V - c| + \ln f(T) \right) - \frac{a}{V},$$

where $f(T)$ is a constant of (the partial) integration with respect to $V$—arbitrary function of $T$. Upon further use of the equation $U = F + TS = U - T(\partial F/\partial T)_V = -T^2(\partial^2 F/\partial T^2)_V$, we obtain the molar internal energy which we rewrite as

$$U = RT \left[ T' + \frac{(d - c)T}{f} \ln |V - b| + \frac{c - d}{c - b} \ln |V - c| - \frac{d - b}{c - b} \frac{bT}{V - b} + \frac{dT - a}{RTV} \right],$$

where the prime (’) denotes the total derivatives with respect to $T$. At low pressures ($P \to 0$) and densities ($\rho \to 0$; $V \to \infty$), the r.h.s. of Eq. (12) approaches $K(T) \equiv RT^2 f'/f$. Since at these limits ($P \to 0$ and $\rho \to 0$) the substance behaves as an ideal gas, hence the term $K$ is a pure kinetic contribution to the internal energy. At the same time, this fixes the origin of $U$. Introducing the dimensionless excess internal energy by $E \equiv (U - K)/RT$, Eq. (12) writes

$$E = \frac{(d - c)T}{f} \ln |V - b| + \frac{d - b}{c - b} \frac{bT}{V - b} + \frac{dT - a}{RTV}.$$  

The second term in (1) has been identified as the contribution of the melt to the interfacial free energy [11]. Let the interface lies in the $xy$-plane with total area $A_1$ and the melt extends in the positive $y$-direction from $0$ to $D$. Consider the volume $A_1D$ of the melt such that $g(y) \simeq 1$ and $g(y) \ln g(y) \simeq 0$ for $r > D$. The contribution of the melt to the interfacial free energy is due to a decrease in the entropy of the melt near the interface, more precisely inside the volume $A_1D$, whose value per molecule is given by Ref. [11]

$$s = -\frac{k_B}{D} \int_0^D g(y, Y) \ln g(y, Y) \, dy.$$  

Here $g(y, Y)$ is defined by Ref. [11]

$$g(y, T) = \frac{D \exp[-\beta u(y)]}{I_s(T)} = \frac{D \exp[-\beta u(y)]}{\int_0^D \exp[-\beta u(y)] \, dy},$$
where \(1/\beta = k_B T\) and \(I_A(T)\) is a function of \(T\) defined by the integral in the last equation and in Eq. (17). \(u(y)\) is the potential function of the melt in the direction of \(y\). Many works have identified \(g(y, T)\) with the RDF \( [9, 11, 12] \), we too will identify, however for a while, \(g(y, T)\) with the CMRDF of benzene and replace the variable of integration \(y\) by \(r\) and name the space region extending over the interface for \(0 \leq r \leq D\) by the “Region of Ordered Melt” (ROM).

In the next section we will employ the statistical analysis outlined in Ref. [11] to develop an expression for the dimensionless excess internal energy of the melt \(E\) in terms of \(g(r, T)\) and \(I_A(T)\), which upon evaluating at 298 K and using Eqs. (21), (22) we will be able to extract \(u(r)\) and \(g(r, T)\) shown in Figs. 2 and 3, respectively.

3. Statistical and numerical analyses

In the statistical model developed in Ref. [11], the integral of \(g(r)\) over the ROM should satisfy, as seen from Eq. (15), the condition

\[
\int_0^D g(r, T) \, dr = D. \tag{16}
\]

If we restrict ourselves to particles inside the volume \(A_1 D\), as was assumed earlier in Eqs. (14), (15), the partition function of a particle is

\[
Z_1 = A_1 I_A(T) = A_1 \int_0^D \exp[-\beta u(r)] \, dr \tag{17}
\]

Fig. 2. The one-dimensional potential function of liquid benzene in contact with its crystal as described by the model developed in Ref. [11]. The potential has the shape of a shifted 12-6 potential of the form 
\[4 \varepsilon [(\sigma/r)^{12} - (\sigma/r)^6] - \varepsilon\] with \(\varepsilon = 3.5847\) kJ mol\(^{-1}\), \(\sigma = 33.336\) kJ mol\(^{-1}\) and \(\sigma = 4.8263\) Å.

Fig. 3. Modified center-of-mass radial distribution functions \(g_{cm}(r, T)\) at 285, 295, and 305 K.
and the number density of the melt writes [11]

\[ \eta(r, T) = \frac{N_A}{V_1(T)} g(r, T). \]  

(18)

The total number of molecules per unit area of the interface is

\[ N_1 = \frac{1}{A_1} \int_0^D \eta(r, T) A_1 dr = \frac{N_A}{V_1} \int_0^D g(r, T) dr = \frac{DN_A}{V_1}, \]

(19)

where we have used Eq. (16). \( N_1 \) includes only molecules that extend over the ROM and whose contribution to the entropy drop is non-zero. From the general formula \( F = U - TS \) and using Eqs. (14), (19), we derive the melt contribution to the interfacial free energy by

\[ -T N_1 \delta s = \left( \frac{N_A k_B T}{V_1} \right) \int_0^D g(r, T) \ln g(r, T) dr, \]

(20)

which is the second term shown in Eq. (1). This derivation is similar to that performed in Ref. [11] with the exception that in Ref. [11] \( N_1 \) was quoted but not derived as we have done in Eq. (19). In Eq. (20) \( T \) does not refer necessarily to the melting temperature; here \( T \) refers to the temperature of the melt that is exposed to its crystal, hence \( T < T_m \) if the melt is supercooled (metastable equilibrium), \( T > T_m \) if the melt is superheated (another metastable equilibrium), or \( T = T_m \) in the melt-crystal stable equilibrium.

Since Eq. (16) has been employed in Eqs. (19), (20) it is then a necessary condition as to the application of this simplified model. However, the numerical analysis implemented in the MATLAB M-file (Appendix) allows one to check that the area in Fig. 1 below the graph of \( g(r, T = 298) \) from 0 to \( D = 17 \) Å, which is represented by the number \( \Gamma \) in line 56 of the M-file, is lower than 17 violating thus Eq. (16). In fact, we can show from Fig. 1 that \( \int_0^r g(r') dr' < r, \forall r \).

The use of \( g(r) \) shown in Fig. 1 leads to further contradictions. This is due to conflicts between the two models, the one described in Ref. [11] and here and the other described in Refs. [18,19]. In the first model [11], the drop in the entropy of the melt, Eq. (14), is due to the fact that the particles of the melt near the interface are more ordered than those far away from the interface; this means that the first pick of the RDF, localized near the interface, would be higher than if the particles were uniformly ordered as in the model described in Refs. [18,19]. Hence, the RDF derived in Refs. [18,19] is not suitable, without appropriate modification, for the description of liquids in contact with solids. In order to obtain consistent results with both models, we need to raise the height of the first pick of \( g(r, 298) \), which appears at \( r = 5.4344 \) Å, until condition (16) is fulfilled. The line 57 of the M-file shows how to modify \( g(r, 298) \) until condition (16) is fulfilled. The modified CMRDF \( g_m(r, 298) \) and the original one \( g(r, 298) \) are depicted in Fig. 1. The former describes a melt in contact with its crystal while the latter describes a melt at points in space sufficiently far away from any interface. In the M-file, \( g(r, 298) \) and \( g_m(r, 298) \) are represented by the splines \( sp \) and \( spm \) (lines 56 and 57), respectively [27].

Upon executing the program, the plots Figs. 1–4 are depicted as shown in this paper. The plot of Fig. 1 is depicted upon running the lines from 59 to 63. The area below the graph of \( g_m(r, 298) \) from 0 to 17 is represented by \( Im \) (line 58). After running the program one may get the value of this area by typing \( Im \) in the Command Window then pressing \( Enter \) to get 16.9993.

From now on, we will replace in all our formulas \( g(r, T) \) by \( g_m(r, T) \), particularly, Eq. (15) reads

\[ g_m(r, T) = \frac{D \exp[-\beta u(r)]}{I_A(T)}. \]

(21)

With this new notation, the code \( \text{Im} g_m(r, 298) \) (line 64) provides the value of the integral of \( g_m(r, 298) \ln g_m(r, 298) \) by

\[ \int_0^{17} g_m(r, 298) \ln g_m(r, 298) dr = 7.5955 \text{ Å}. \]

(22)

The partition function of \( N \) particles of the melt inside the volume \( A_1 D \) is \( Z_N = Z_N^m N! = I_N^m I_A(T)/N! \), with \( I_A(T) \) defined in Eqs. (15), (17). The internal energy is defined by

\[ U = K - \frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta}, \]

(23)

where the first term is the kinetic contribution. Employing Eqs. (17), (21), we obtain

\[ \frac{\partial Z_N}{\partial \beta} = - \frac{N Z_N}{I_A(T)} \int_0^D u \exp(-\beta u) dr = - \frac{N Z_N}{D} \int_0^D u g_m(r, T) dr. \]

Hence, Eq. (23) writes for \( N = N_A \)

\[ U - K = \frac{N_A}{D} \int_0^D u g_m(r, T) dr. \]

(24)

Now reversing Eq. (21) by

\[ u(r) = k_B T \ln(D/I_A(T)) - \ln g_m(r, T), \]

(25)
then inserting this last equation into Eq. (24), we obtain \( E \) in terms of \( g_m(r, T) \) and \( I_A(T) \)
\[
E = \ln \left( \frac{D}{I_A(T)} \right) - \frac{1}{D} \int_0^D g_m(r, T) \ln g_m(r, T) \, dr.
\]
(26)

Here \( E \) is the excess internal energy of the melt contributed exclusively by those particles evolving inside the ROM. If we suppose that reordering molecules near the interface does not change their internal energy, then Eqs. (13) and (26) are similar.

Next, we evaluate \( E \) in both Eqs. (13) and (26) at 298 K. In Eq. (13) we have to replace \( V \) by \( V_I(T) \) using the second line in Eq. (2) then evaluate at 298 K to get \( E = -13.88187 \) and in Eq. (26) we make use of Eq. (22). The calculations are performed in line 66 of the M-file leading to
\[
I_A(298) = 1.1621 \times 10^7 \text{ Å.}
\]
(27)

Now, with the value of \( I_A(298) \) known one may determine \( u(r) \) from (25) upon inserting \( I_A(298) = 17 \text{ Å} \), and replacing \( g_m(r, 298) \) by its spline \( spm \) provided by the line 57 of the M-file. The resulting potential function \( u(r) \) is represented by the spline \( spm \). In the M-file, the evaluation of \( u(r) \), of its spline \( spm \) and the sketching of its graph, shown in Fig. 2, are performed in lines from 68 to 72.

Now, the evaluation of \( g_m(r, T) \) from (21) is straightforward as shown in the lines from 79 to 96 of the M-file. The numerical set of temperatures is the MATLAB vector \( Tn \) (line 39) including values from 284 to 306 incremented each degree and totaling 23 components \((m:1-->23)\). The numerical set of radial distances is the vector \( r \) (line 39) including values from 0.0001 to 17.0001 incremented each two thousandths and totaling 85001 components \((n:1-->85001)\). In line 89 the vector \( Izt(m) \), which represents \( I_A(T) \), is evaluated. For instance, to find out what is \( I_A(305) \), with \( T = 305 \text{ K} \) solve for \( m = 22 = (305 - 284) + 1 \), type \( Izt(22) \) in the Command Window then press Enter. Typing \( Izt \) then pressing Enter gives all the 23 values of \( I_A(T) \) corresponding to \( Tn \). In the same line 89 the nth row \( gt(m, :) \) (of the matrix \( gt(m, n) \)), which represents the CMRDF \( g_m(r, T) \) at \( T = 283 + m \), is evaluated. For instance, a plot of \( g_m(r, T = 285) \), with \( m = 2 \), is sketched upon executing the codes \( plot(rn, gt(2, :) \)) as shown in line 97 of the M-file. Finally, the vectors \( Iglgt(m) \) & \( Ssl1(m) \) in lines 90 and 91 represent \( \int_0^D g_m(r, T) \ln g_m(r, T) \, dr \) and \( \sigma_{sl}(T) \) at \( T = 283 + m \), respectively. In Fig. 3, three plots of \( \eta_m(r, T) \) at 285, 295, and 305 K are depicted from the left to the right, respectively.

The lines from 97 to 106 elaborate on the sketching of Fig. 3 while Fig. 4 showing the dependence of \( \sigma_{sl} \) on \( T \) has been obtained upon executing the codes in lines from 107 to 110.

4. Interfacial free energy of benzene

The solid–liquid interfacial free energy shown in Fig. 4 and in column 3 of Table 1 has been evaluated at the melting temperature \( T_m \) (column 1); in column 3 of Table 1 we have replaced the subscript “sl” by “m”. According to our remark given in the paragraph following Eq. (20), this latter equation and Eq. (1) are applicable to the case where the liquid is supercooled below its melting temperature. If the temperature of nucleation \( T_n < T_m \) is known, one may calculate the interfacial free energy at \( T_n \), denoted by \( \sigma_n \), from Eq. (1) as follows.

Starting from a stable solid–liquid equilibrium at \( T_m \) and cooling further the liquid by dropping the temperature from \( T_m \) to \( T_n \) at a predefined rate [21], one may assume that the drop in the entropy \( s \) given by Eq. (14), with \( g(y) \) replaced by \( g_m(r, T) \), is insensitive to the supercooling of the liquid. With this assumption one may use interchangeably \( s \) to evaluate both \( \sigma_m \) and \( \sigma_n \). Column 2 of Table 1 shows the values of \( s \) in terms of \( T_m \). In the M-file, \( D = 17 \),

<table>
<thead>
<tr>
<th>( T_m ) (K)</th>
<th>( -s/k_B )</th>
<th>( \sigma_m ) TW</th>
<th>( \sigma_{m(min)} ) TW</th>
<th>( T_{superf} ) (K) TW</th>
<th>( r^* ) (Å)</th>
<th>( \sigma_{(max)} ) [10]</th>
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</table>

Columns 1 and 5 are the melting and limits of supercooling temperatures (29), respectively. Column 2 shows with the opposite sign the entropy drop in units of \( k_B \). Columns 3 and 4 are the crystal-orientation-independent and minimum interfacial free energies, respectively. Column 7 shows the maximum free energies obtained from Eq. (35) of this paper (derived in Ref. [10]) upon using our Eqs. (2), (3). Nomenclature: “TW” for “This Work”.

The graphical procedure does not define criteria by which the properties of the liquid are extended to the solid region. It will be shown below that the nucleation temperatures provided by Eq. (30) are not the limits of supercooling since the size of the critical nucleus determined from Eq. (31) setting \( T_n = T_n(\text{theor}) \) overestimates what is existing in the literature [5]. The lowest nucleation temperatures or “predicted” limits of supercooling \( T_n(\text{pred}) \) for benzene, derived in Eq. (32), are well below \( T_n(\text{theor}) \) and provide consistent values for the size of the critical nucleus as shown in column 6 of Table 1.

Since we are evaluating average values for \( \sigma_m \) and \( \sigma_n \) over all possible orientations (hkl), it is then a good approximation to employ Eqs. (28), (30) to estimate the value of the critical nucleus radius derived in CNT by [28]

\[
r^* = \frac{2\sigma_n T_m V_s}{(T_m - T_n)\Delta H}.
\]

Upon substituting Eqs. (28), (30) into Eq. (31), however using \( \sigma_{m(\text{min})} \) instead of \( \sigma_m \) in Eq. (28), we have determined \( r^* \) as a function of \( T_m \) with an average value of \( \langle r^* \rangle = 49.9 \text{ Å} \). While benzene is a polyatomic substance, one may allow for a comparison of this average value with that of the critical nucleus radii of monatomic substances ranging from about 10 Å (Ni), 12 Å (Cu) and 14 Å (Ta) to about 15.2 Å (Ti) and 16.5 Å (Zr) [5]: It seems that \( \langle r^* \rangle = 49.9 \text{ Å} \) overestimates the critical nucleus radius one would obtain from a maximum undercooling of benzene. Another way to check the consistency of the latter conclusion is that it is generally noticed that the extent of supercooling \( \theta_{\text{sc}} = T_n/T_m \) is a constant [5,29]. In Ref. [30, Table 3.4] lists measured values of the extent of supercooling under normal pressure for 48 substances among which one finds metals, miscellaneous inorganic and organic compounds, and alkali halides. If we exclude bismuth, gallium, mercury, and tin from the list [30], the values of \( \theta_{\text{sc}} \) for the remaining 44 substances range from 0.673 for tellurium through 0.748 for benzene to 0.878 for cyclopropane. If we suppose that for benzene the value of \( \theta_{\text{sc}} = 0.748 \), which has been determined under normal pressure [31,32], remains valid for the range of melting temperatures and pressures we are considering, then the limits of supercooling write

\[
T_n(\text{pred}) = 0.748 T_m
\]

and are shown in column 5 of Table 1. Now, upon substituting Eqs. (28), (32) into Eq. (31), however using \( \sigma_{m(\text{min})} \) instead of \( \sigma_m \) in Eq. (28), we determine \( r^* \) as a concave up (convex) decreasing function of \( T_m \) with an average value of \( \langle r^* \rangle = 20.2 \text{ Å} \) and a standard deviation of 0.16 Å. The values of \( r^*(T_m) \) are listed in column 6 of Table 1, shown in Fig. 5 versus \( T_m \) and evaluated in line 94 of the M-file (vector \( x_{c(M)} \)). We have also evaluated the number of molecules per critical nucleus, \( (4/3)\pi r^3 N_A/V_s \), which too behaves as a concave up decreasing function of \( T_m \) with an average value of 175 molecules and a standard deviation of 4.5.
Fig. 5. Critical nucleus radius of supercooled benzene for $284 \leq T \leq 306$ K.

Finally, the crystal-orientation-independent (column 3) and minimum (column 4) interfacial energies are well represented by quadratic functions given respectively by ($T$ in K)

$$\sigma_m (\text{mJ m}^{-2}) = -0.0011987T^2 + 0.78089T - 91.297,$$

(33)

$$\sigma_{m(mn)} (\text{mJ m}^{-2}) = -0.00063129T^2 + 0.41727T - 42.331.$$  

(34)

5. Conclusion

The first term in Eq. (1), which is the contribution to the interfacial free energy due to broken bonds in the bulk phases and formed bonds in the interface [12], is assumed to be equal to the number of broken bonds in the solid times the change of enthalpy per molecule [12]. The second term in Eq. (1) is a cumulated energy due to entropy drop. As one moves in the melt from "infinity" towards the interface, one observes a drop in the entropy due to the ordering of the molecules as we approach the interface, whose value in absolute value times the temperature of the melt cumulates as a surface energy. In this work, we have applied Eq. (1) to benzene for the first time since it has been derived and employed combined approaches, including theory, computer algebra, and results from previous experiments and simulations, to evaluate both terms as functions of the temperature thus introducing corrections to count for the temperature dependence. We have shown that the surface energy increases slightly with the temperature for the range $284.6 \leq T \leq 306.7$ K we have considered. This conclusion has been confirmed by other works [14] and references therein. We have also shown that the critical nucleus radius decreases with the temperature.

Another fact derived in this work is the new value of the height of the first pick of $g_m(r, T)$, which is a measure of the probability of finding molecules from the melt near the interface. At 298 K, this value has passed from 2.014 for $g(r, 298)$ to 4.322 for $g_m(r, 298)$. As we mentioned earlier the use of $g(r, 298)$, instead of $g_m(r, 298)$, would lead to contradictions such as some CMRDF's $g(r, T)$ for $T \neq 298$ never approached unity.

Another fact, however less important than the previous one, is that the one-dimensional potential function of the melt $u(r)$ can well be represented by a shifted 12-6 potential of the form $4\delta[(\sigma/r)^{12} - (\sigma/r)^6] - e$ with $\varepsilon = 3.5847 \text{ kJ mol}^{-1}$, $e = 33.336 \text{ kJ mol}^{-1}$ and $\sigma = 4.8263 \text{ Å}$.

Other equations have been applied to benzene but just at the normal melting temperature [10,13]. From a theoretical point of view, it is worth mentioning the equation derived in Ref. [10] upon employing the concept of interplanar adhesion function [33]. The equation evaluates the solid–liquid interfacial free energy by

$$\sigma_m = \left(\frac{3}{2}\right) \frac{k_B T_m}{\Omega_s^{2/3}} \delta^2 \exp \left(\frac{\Delta H_m}{3N_A k_B T_m}\right),$$

(35)

where $\Omega_s = V_s/N_A$ is the atomic volume of the solid and $\delta$ assumes values from 0.5 to 0.7 [10]. Letting $\delta = \delta_{\text{max}} = 0.7$, column 7 of Table 1 shows the results obtained from (35) upon using Eqs. (2), (3), providing thus maximum values for $\sigma_m$ which are in good agreement with those values obtained in this work and shown in column 3. Line 97 of the M-file shows how to evaluate column 7 where the vector $\text{SD(m)}$ represents $\sigma_m(\text{max})$. With $\delta = \delta_{\text{min}} = 0.5$, the values of $\sigma_m$ obtained from (35) are still comparable to those values obtained in this work and shown in column 4 of Table 1.

From an experimental point of view, there are no available experimental data for $\sigma_m$ in the ranges of pressure and temperature we are considering. At atmospheric pressure, Ref. [4] provides $22 \pm 2$ & $44 \pm 10 \text{ mJ m}^{-2}$ while in Ref. [34] one reads $21.7 \text{ mJ m}^{-2}$ for $\sigma_m(\text{exp})$, depending apparently on the orientation ($hkl$) of the sample and/or on the experiment. In Ref. [34] it is not mentioned whether the value of $21.7 \text{ mJ m}^{-2}$ has been obtained merely experimentally or by cognitive analysis. In spite of that, both results in columns 3 and 4 are in agreement with these experimental data.

Appendix

To make this paper self-contained this section has been appended as a part of the numerical method. The following MATLAB M-file script may be copied and saved under any name. Running this script program will open four windows showing the first four figures (Figs. 1 → 4) of this paper as depicted here and evaluate some key functions used in this paper and some others. To get the result of numerical calculations one has to return to the Command Window and type in the code of the corresponding entity as has been explained in the text of this paper (Sections 3 and 4). The lines from 1 to 19 are useful
The vector \( g \) with 50 components versus the vector \( r \) is the original CMRDF \( g(r) \) at 298 K extracted from Refs. [18,19]. Those data sites (components of \( g \) & \( r \)) in lines from 26 to 38 have been obtained upon using the MATLAB functions (not shown in the M-file): imread, imshow, & ginput applied to Ref. [19, Fig. 1].

001 \% V: molar volume in (m3), T: temperature in (K).
002 \% r: radial distance in (A = 10e-10m)
003 \% Functions of T:
004 \% vsol & vliq: molar volumes of the solid & liquid at melt (m3).
005 \% DH: molar change in the enthalpy in (mJ.mol-1)
006 \% dsn: average length of broken bonds in (m)
007 \% Ssl: interfacial free energy in (mJ.m-2)
008 \% a in (Pa.m6), b in (m3): Functions of Tr (reduced T)
009 \% ap & bp: derivatives of a & b / T
010 \% ar, br: Dimensionless functions of Tr
011 \% Functions of (T, V):
012 \% E = (U - K)/RT, dimensionless excess internal energy
013 \% The constants:
014 \% Tc(K), Pc(Pa): critical temperature, critical pressure
015 \% Zc: critical compressibility factor
016 \% vc: critical volume (Not needed)
017 \% R(J.K-1.mol-1): the universal gas constant
018 \% c(m3), d(m3), vliq0(m3), dsmint(m), Other constants: dimensionless.
019 \% Application: Solid-Liquid Benzene Interface.

clear all
020 cr = 0.3397686; dr = 0.3345894; Zc = 0.3750290; Tc = 562.05; Pc = 4.894e+6; a0 = 0.31125; a1 = 1.5930; a2 = 2.6678; n = 1.51; b0 = 0.3280; b1 = -9.64236e-2; b2 = 26.6560; m = 4.0; R = 8.314510; c = cr*(Zc*R*Tc/Pc); d = dr*(Zc*R*Tc/Pc);
023 vsoln = double(subs(vsol,T,Tn)); dsn = (4*vsoln/NA).^(1/3); On = vsoln/NA;
025 syms V T;
026 a = ((R*Tc)^(1/2))/Tc; b = (Zc*R*Tc/Pc)*a;
027 ar = a0 + a1*(Tr*exp(-a2*Tr^n)); bp = (Zc*R*Tc/Pc)*b;
028 dp = diff(b,T); ap = diff(a,T);
052 \text{Ap} = \text{diff}(\text{Ar},T); \text{Ap} = (d-c) \cdot \text{bp}/(c-b)^2; \text{Ap}: \text{derivative of Ar}
053 \text{E} = (\text{Ap} \cdot \text{T} \cdot \log(\text{abs}((V-b)/(V-c)))) - \text{bp} \cdot \text{T} \cdot \text{Ar}/(V-b) + (\text{ap} \cdot \text{T} - a)/(\text{R} \cdot \text{V} \cdot \text{T});
054 \text{En} = \text{double}([\text{E},\text{T},\text{V}],[298,\text{vliq}0]);
055 \% \text{At T} = 298: \text{Modifying g(r) & Finding the potential u(r)}:
056 \text{sp} = \text{spline}(\text{r}, \text{g}, \text{rn}); \text{Im} = 0.0002 \cdot \text{sum}(\text{sp});
057 \text{gm} = 1.0732 \cdot (\exp(-(\text{r}-5.4344)^2)+1); \text{g}; \text{spm} = \text{spline}(\text{r}, \text{gm}, \text{rn});
058 \text{Im} = 0.0002 \cdot \text{sum}(\text{spm});
059 \text{plot}(\text{rn}, \text{sp}, '--k', \text{rn}, \text{spm}, 'b', 'LineWidth', 1.5);
060 \text{xlabel}('fn fit r g(\text{Å})', 'FontSize', 13);
061 \text{title}('Radial Distribution Function at fn T g = 298 K', 'FontSize', 14);
062 \text{text}(\text{rn}(41251), \text{sp}(41251), 'n \leftarrow fn fit g g(\text{fn fit g})', 'FontSize', 12);
063 \text{text}(\text{rn}(30001), \text{spm}(30001), 'n \leftarrow fn fit g g_{fn rm m g(\text{fn fit g})}', 'FontSize', 12);
064 \text{glgm} = \text{spline}(\text{r}, \text{gm} \cdot \log(\text{gm}), \text{rn}); \text{Iglgm} = 0.0002 \cdot \text{sum}(\text{glgm});
065 \% \text{Iglgm} = 7.5955 \text{ is the integral of gm*log(gm) over r from 0 to 17;}
066 \text{lnL} = \text{En} + \text{Iglgm}/17; \text{Iz} = 17 \cdot \exp(-\lnL);
067 \% \text{We set L = 17/Iz}
068 \% \text{Finding the potential u(r)}:
069 \text{u} = k \cdot 298 \cdot (\text{lnL} - \log(\text{gm})); \text{um} = \text{u}; \text{rm} = \text{r}; \text{um}(1:2) = []; \text{rm}(1:2) = [];
070 \text{spum} = \text{spline}(\text{rm}, \text{um}, \text{rn}); \text{figure}, \text{plot}(\text{rn}, \text{spum}, 'k', 'LineWidth', 1.4);
071 \text{axis}([2 17 -7e-20 3e-20]); \text{xlabel}('fn fit r g(\text{Å})', 'FontSize', 13);
072 \text{ylabel}('fn fit u g(\text{fn fit r g})(J)', 'FontSize', 13);
073 \text{title}('Potential Function of the Melt', 'FontSize', 14);
074 \% \text{Verification}:
075 \text{q} = \exp(-\text{spum}/(k \cdot 298)); 0.0002 \cdot \text{sum}(\text{q});
076 \% 0.0002*sum(q) = 1.1640e+007 \text{ compare with Iz} = 1.1621e+007
077 \% Evaluating gm as function of (r,T): matrix gt
078 \% Evaluating the integral of gm*(ln gm) as function of T: vector Iglgt
079 \% Evaluating the interfacial free energy as function of T: vector Ssl
080 \% Preallocate vectors & matrices:
081 \text{qt} = \text{zeros(length(Tn),length(rn))}; \text{Izt} = \text{zeros}(1,length(Tn)); \text{gt} = \text{zeros}(length(Tn),length(rn));
082 \text{Iglgt} = \text{zeros}(1,length(Tn)); \text{Ssl} = \text{zeros}(1,length(Tn)); \text{Smin} = \text{zeros}(1,length(Tn)); \text{Snu} = \text{zeros}(1,length(Tn));
083 \text{rc} = \text{zeros}(1,length(Tn)); \text{SD} = \text{zeros}(1,length(Tn));
084 \text{for m = 1:length(Tn)}
085 \text{for n = 1:length(rn)}
086 \text{qt}(m,n) = \exp(-\text{spum}(n)/(k \cdot \text{Tn}(m)));
087 \text{Izt}(m) = 0.0002*\text{sum}(\text{qt}(m,:))/\text{Izt}(m);
088 \text{Iglgt}(m) = 0.0002*\text{sum}(\text{gt}(m,:).*((\text{log}(\text{gt}(m,:))+\text{eps})));
089 \text{Ssl}(m) = \text{dsn}(m) \cdot \text{DHn}(m)/(4 \cdot \text{vsoln}(m) + ((10^(-7)) \cdot \text{R} \cdot \text{Tn}(m) \cdot \text{Iglgt}(m))/\text{vliqn}(m);
090 \text{Smin}(m) = \text{dsmin} \cdot \text{DHn}(m)/(4 \cdot \text{vsoln}(m) + ((10^(-7)) \cdot \text{R} \cdot \text{Tn}(m) \cdot \text{Iglgt}(m))/\text{vliqn}(m);
091 \text{Snu}(m) = \text{dsmin} \cdot \text{DHn}(m)/(4 \cdot \text{vsoln}(m) + ((10^(-7)) \cdot \text{R} \cdot \text{Tnu}(m) \cdot \text{Iglgt}(m))/\text{vliqn}(m);
092 \text{rc}(m) = (10^(-110)) \cdot (2 \cdot \text{Snu}(m) \cdot \text{Tn}(m) \cdot \text{vsoln}(m))/((\text{Tn}(m) - \text{Tnu}(m)) \cdot \text{DHn}(m));
093 \text{SD}(m) = \text{Dc} \cdot (3000 \cdot k/8) \cdot (\text{Tn}(m)/\text{On}(m)^{(2/3)}) \cdot \exp(\text{DHn}(m)/(3000 \cdot \text{NA} \cdot \text{k} \cdot \text{Tn}(m)));\text{end}
094 \text{figure}, \text{subplot}(1,3,1); \text{plot}(\text{rn}, \text{gt}(2,:), 'r', 'LineWidth', 1.3);
095 \text{axis}([0 18 0.46]); \text{set(gca, 'xtick', [0 10 17]);}
096 \text{ylabel}('\{\text{it r}\} (\text{Å})', 'FontSize', 13);
097 \text{text}(6,4,'\{\text{it T}\}=285 K', 'FontSize', 12);
098 \text{subplot}(1,3,2); \text{plot}(\text{rn}, \text{gt}(11,:), 'k', 'LineWidth', 1.3); \text{axis}([0 18 0.46]);
099 \text{set(gca, 'xtick', [0 10 17]); \text{xlabel}('\{\text{it r}\} (\text{Å})', 'FontSize', 13);
100 \text{text}(6,4,'\{\text{it T}\}=295 K', 'FontSize', 12);
101 \text{title}('Radial Distribution Function in Terms of \{\{\text{it r}, \text{T}\}\}', 'FontSize', 14);
102 \text{subplot}(1,3,3); \text{plot}(\text{rn}, \text{gt}(21,:), 'b', 'LineWidth', 1.3); \text{axis}([0 18 0.46]);
103 \text{set(gca, 'xtick', [0 10 17]); \text{text}(6,4,'\{\text{it T}\}=305 K', 'FontSize', 12);
104 \text{figure}, \text{plot}(\text{Tn}, \text{Ssl}, 'k', \text{Smin}, 'b', 'LineWidth', 1.5);
108 xlabel('\(\text{\textit{fn iT T}}\) (K)', 'FontSize', 13);
109 ylabel('\(\text{\textit{fn iT n sigma}}_g\text{\textit{fn rm sl}}\) (mJ\(\text{\textit{\textbullet cm^2}}/C0\text{\textit{\textbullet g}}\))', 'FontSize', 13);
110 title('Interfacial Free Energy of Benzene', 'FontSize', 14);

References

[28] In Eq. (31) the change in the chemical potential \(\Delta \mu\) has been approximated by \((T_m - T_0)\Delta H/(T_m V_s)\). A direct derivation of \(\Delta \mu\) is possible from the EOS however unnecessary.