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A Thermodynamic Model of the Adhesive Bond†

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An adhesive bond is considered as a thermodynamic system in which the properties of components are expressed in relevant thermodynamic terms. Two hypotheses are analysed, (i) that the maximum strength of the bond is achieved when the interfacial energy is a minimum, and (ii) that only those systems which exhibit a true zero-interfacial energy can be considered stable in terms of their durability.

Conditions are found expressed by the 'critical energy ratio', a^{CRIT} , under which the thermodynamic work of adhesion becomes negative and, accordingly, the strength of the adhesive bond is zero.

Thermodynamic Equilibrium Diagrams are constructed which allow analysis of bond performance in order to determine conditions for maximum strength, zero strength, and the 'no-bond' area, indicating zero-strength or spontaneous delamination tendency.

KEY WORDS Work of adhesion; Interfacial energy; Critical energy ratio; Thermodynamic equilibrium diagrams; Delamination; Adhesive bonds.

INTRODUCTION

In order to predict the performance of an adhesive bond under service conditions it is necessary to know (1) the conditions in terms of properties of bond components which promote the maximum strength, (2) the conditions under which a zero-strength or spontaneous delamination of the bond can be expected, (3) the strength

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deficiency of the bond (compared to the maximum achievable) outside the optimum point, and (4) the durability (stability under adverse environments) of the bond during its service.

Answers to the above are possible if an adhesive bond is considered as a thermodynamic system whose properties are described in terms of relevant thermodynamic parameters such as surface energies of components, and wettability characteristics.

BASIC TERMS AND ASSUMPTIONS

Conditions for the maximum strength

It has been claimed by numerous researchers that either the thermodynamic work of adhesion,^{1,2,3,4} critical surface tension for wetting,^{4,5,6} solubility parameter^{7,8} or interfacial energy^{4,5,9} are responsible for the strength of adhesive bonds. It can be shown, however, that all of these are interrelated with thermodynamic properties of bond components, as expressed by surface energies.

A knowledge of surface energies of substrate and adhesive, as well as a wettability characteristic, provides sufficient data for estimation of interfacial energies. Based on experimental evidence and analytical prediction we postulate, therefore, that (I) the minimum interfacial energy between bond components corresponds to maximum strength and durability of the adhesive bond, and (II) only those 'substrate/adhesive' systems that exhibit true zero interfacial energy under their conditions of service can be treated as stable in terms of their durability.

Conditions for zero-strength of adhesive bond

Adhesive bonding is governed by intermolecular forces exerted across the surface of contact between two phases. The force of attraction between two semi-infinite idealized bodies (*e.g.* substrate and cured adhesive) is described by a derivative of the energy of interaction which in a simplified example can be represented by the Lennard-Jones¹⁰ potential (see Appendix for terms used in equations), *i.e.*

$$F = \frac{d}{dr} \left[\frac{A}{r^6} + \frac{C}{r^{12}} \right]. \quad (1)$$

This function is illustrated in Figure 1.

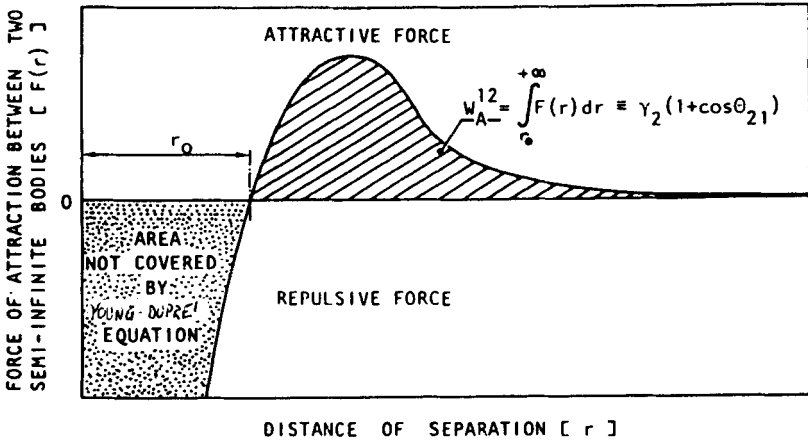


FIGURE 1 The area of relevance of the Young–Dupré equation for thermodynamic work of adhesion in respect to a character of the gross intermolecular force acting across a substrate–adhesive interface as determined from Lennard–Jones potential.

Conditions under which $W_A = 0$ are relevant where there is no net force across the interface phase 1/phase 2.

When $W_A < 0$ the existence of net repulsive forces cannot be excluded, *i.e.* conditions at the interface are such that the system may exhibit zero strength or may delaminate spontaneously.

Accordingly, we postulate that thermodynamic conditions at the interface under which $W_A = 0$ correspond to zero-strength of the adhesive bond.

Basic equations

We assume that the following equations for adhesion are valid:

(a) Dupré equation:

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} \tag{2}$$

(b) Young–Dupré equation:

$$W_A = \gamma_2(1 + \cos \theta_{21}) \tag{3}$$

where θ_{21} is an equilibrium in contact angle made by phase 2, whilst liquid, in contact with phase 1.

It is assumed for the simplicity that the equilibrium spreading pressure $\pi_e = 0$.

Wettability characteristic of the solid

The relationship between $\cos \theta_{21}$ and γ_2 is known as the wettability characteristic and was first described by Fox and Zisman,¹¹ *i.e.*

$$\cos \theta_{21} = 1 - b_0[\gamma_2 - \gamma_{C(1)}]. \quad (4)$$

There is some controversy as to the profile of the wettability characteristic.^{11,12,13,14} We assume, however, that it can be well approximated in a linear fashion, as Figure 2 illustrates.

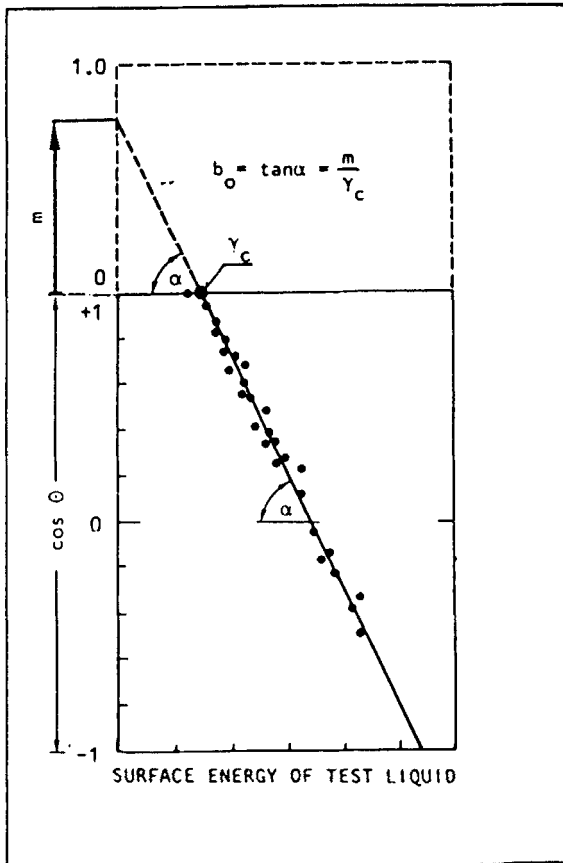


FIGURE 2 Graphical illustration of the wettability characteristic approximated in a rectilinear fashion, with the explanation of the sense of parameter 'm' as an intercept of axis parallel to $\cos \theta$.

Introducing the energy ratio 'a' of the substrate-adhesive system:

$$a = \gamma_1 / \gamma_2, \quad (5)$$

and a specific bonding efficiency factor Φ_0 , i.e.:

$$\Phi_{0(1)} = [\gamma_{C(1)} / \gamma_1]^{1/2} \quad (6)$$

we have:

$$\cos \theta_{21} = 1 - m_1 \left[\frac{1}{a \Phi_{0(1)}^2} - 1 \right]. \quad (7)$$

THERMODYNAMIC CONDITIONS FOR MAXIMUM STRENGTH OF ADHESIVE BOND

It has been postulated above that the maximum strength and durability of an adhesive bond are achieved under conditions where the interfacial energy is minimum under service conditions. The expression for the interfacial free energy of the system is obtained by rearrangement of Eqs. (2) and (3):

$$\gamma_{12} = \gamma_1 - \gamma_2 \cos \theta_{21}. \quad (8)$$

Further substitution of Eq. (7) in Eq. (8) and introduction of a physical limitation for complete wetting at $(\cos \theta_{21})^{\text{MAX}} = 1.0$, lead to either

$$\gamma_{12} = \gamma_1 - \gamma_2(1 + m_1) + m_1 \frac{\gamma_2^2}{\gamma_{C(1)}} \quad \text{for } \gamma_2 \geq \gamma_{C(1)} \quad (9)$$

or

$$\gamma_{12} = \gamma_1 - \gamma_2 \quad \text{for } \gamma_2 \leq \gamma_{C(1)}. \quad (10)$$

Conditions for the minimum interfacial energy are found from the first derivative of Eq. (9) with respect to γ_2 and they occur at the energy ratio:

$$a_{\text{MIN}} = \frac{2m_1}{(1 + m_1)\Phi_{0(1)}^2}. \quad (11)$$

The minimum interfacial energy is found by substituting Eq. (11) into Eq. (9)

$$\gamma_{12}^{\text{MIN}} = \gamma_1 - \frac{(1 + m_1)^2 \cdot \gamma_1 \Phi_{0(1)}^2}{4m_1}. \quad (12)$$

THERMODYNAMIC CONDITIONS FOR MAXIMUM BOND STABILITY (DURABILITY)

Conditions for the maximum bond stability are achieved when the 'substrate-adhesive' system exhibits a true zero-interfacial energy under service conditions. This is satisfied [see Eq. (9)] when the slope of the wettability characteristic yields the value of the parameter m

$$m_1^D = \frac{2}{\Phi_{0(1)}^2} [1 - (1 - \Phi_{0(1)}^2)^{1/2}] - 1. \quad (13)$$

THERMODYNAMIC CONDITIONS FOR ZERO-STRENGTH

As postulated earlier, conditions for zero-strength of an adhesive bond correspond to $W_A = 0$. It follows from Eqs. (3) and (7) that this occurs for any energy ratio:

$$a \leq a_1^{\text{CRIT}} = \frac{m_1}{(2 + m_1)\Phi_{0(1)}^2}. \quad (14)$$

The following can be determined from Eq. (14):

a) The surface energies of phase 1 and 2 at which adhesive bonding becomes impossible because the bond strength equals zero;

b) Those property values at which a change of thermodynamic properties of bond components at the interface (e.g. γ_1 , γ_2 , p_1 , d_1 , p_2 , d_2) produces the energy ratio $a \leq a^{\text{CRIT}}$. This phenomenon relates to the tendency to spontaneous interfacial delamination of the bond and failure of the structure. This may be brought about by environmental attack, e.g. absorption of water or fuel by adhesive, aging of the adhesive, oxidation or corrosion of the substrate's surface, etc.

Another condition for zero-strength of an adhesive bond is determined from the thermodynamic equation of state for adhesion proposed by the author,¹⁵ i.e.:

$$W_A = \gamma_1 + \gamma_2 - \gamma_{12} = \gamma_2(1 + \cos \theta_{21}) \\ = \gamma_1(1 + \cos \theta_{12}) = \text{CONSTANT} \quad (15)$$

The right-hand side of Eq. (15) defines another equilibrium contact angle, θ_{12} . It is explicitly exhibited by a liquid deposited on a cured adhesive, or appears in an implicit form when thermodynamic wetting takes place in the case of two solids in immediate contact. When a cured adhesive is regarded as a solid of surface energy γ_2 then, from Eq. (15):

$$\gamma_{12} = \gamma_2 - \gamma_1 \cos \theta_{12}. \quad (16)$$

The wettability characteristic of the cured adhesive is determined from reference to Figure 2:

$$\cos \theta_{12} = (1 + m_2) - \frac{m_2}{\Phi_{0(2)}^2} \frac{\gamma_1}{\gamma_2}, \quad (17)$$

where

$$\Phi_{0(2)} = [\gamma_{C(2)}/\gamma_2]^{1/2}. \quad (18)$$

Conditions for $W_A = 0$, pertaining to the wettability characteristic of cured adhesive, are found by rearranging Eqs. (17), (18) and the right part of Eq. (15). It follows that $W_A = 0$ for

$$a \geq a_2^{\text{CRIT}} = \frac{(2 + m_2)\Phi_{0(2)}^2}{m_2}. \quad (19)$$

It can be noted that a_2^{CRIT} , as expressed by Eq. (19), unexpectedly corresponds to the area of complete thermodynamic wetting of substrate by cured adhesive (*i.e.* $\theta_{21} = 0^\circ$) of constant surface energy γ_2 .

THERMODYNAMIC EQUILIBRIUM DIAGRAMS (TED) FOR DETERMINING BOND PERFORMANCE

From the above relations Thermodynamic Equilibrium Diagrams (TED) can be developed from which the performance of adhesive bonds can be determined in terms of (a) maximum strength, (b) zero-strength, (c) zero-contact angle, and (d) no-bond area.

Data necessary for the construction of TED are (i) surface energies of phase 1 and phase 2, *i.e.* γ_1 and γ_2 , and (ii) wettability characteristic of phase 1 or phase 2 to gain parameters: 'm' and γ_C .

TED may be in the coordinates:

a) γ_2 vs. $\gamma_{C(1)}$: for a procedure based on the wettability characteristic of substrate, or;

b) γ_1 vs. $\gamma_{C(2)}$: for a procedure based on the wettability characteristic of cured adhesive.

For convenience, a procedure based on the wettability characteristic of a cured adhesive is presented (see Figure 3).

Conditions for maximum strength in TED

Conditions for maximum strength are described by Eq. (11). The optimum surface energy of the substrate, γ_1^{OPT} , can be determined if

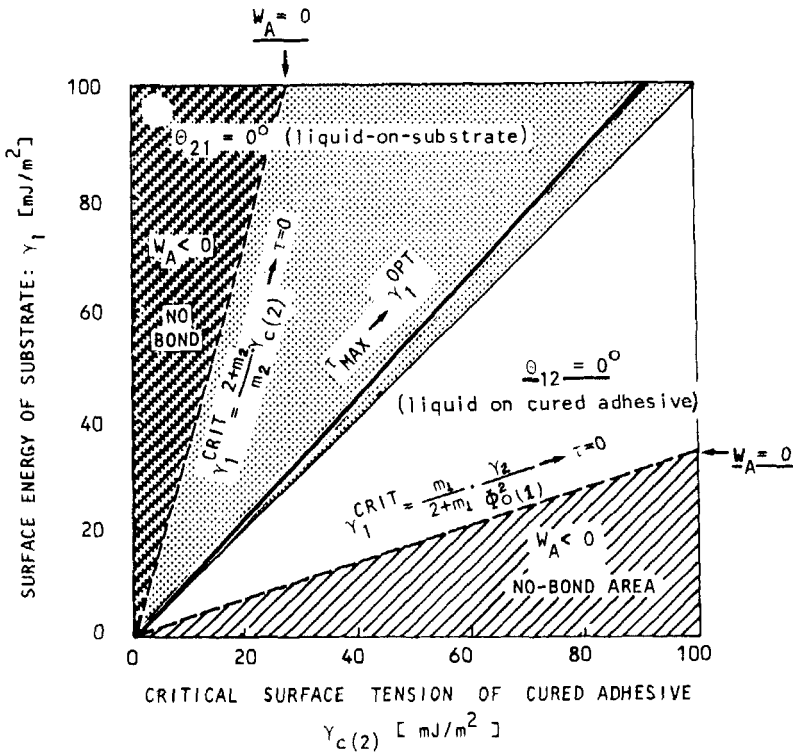


FIGURE 3 Thermodynamic Equilibrium Diagram (TED) based on the wettability characteristic of cured adhesive. (a) representation of conditions for the maximum strength [Eq. (20)] and zero-strength in TED [Eq. (22) and (23) for $m = 0.8$] with indicated areas of no-bond [as corresponding to $W_A \leq 0$]; and (b) the influence of value of parameter 'm' on location of γ_1^{CRIT} and γ_1^{OPT} .

Conditions for zero-contact angle θ_2 in TED

Conditions relevant to complete wetting of the cured adhesive are physically achieved when

$$\gamma_1 \leq \gamma_{C(2)} \quad (21)$$

which is represented in TED (Figure 3a) by a straight line with a constant slope of 1, *independent* of the parameter 'm'. Thus, the area below and including $\gamma_1 = \gamma_{C(2)}$ represents conditions which correspond to the thermodynamic wetting of the surface of the cured adhesive. The dotted area above $\gamma_1 = \gamma_{C(2)}$ relates to the complete wetting of substrates by a given adhesive of constant surface energy γ_2 , e.g. $\theta_{21} = 0^\circ$ in this zone.

Conditions for zero-strength and no-bond areas in TED

Conditions for zero strength of an adhesive bond are achieved when $W_A = 0$, as expressed by the right-hand side of equation of state (15). The first boundary value of surface energy of the substrate, γ_1^{CRIT} , at which $W_A = 0$ is determined from Eq. (19) i.e.:

$$\gamma_1^{\text{CRIT}} \geq \frac{2 + m_2}{m_2} \cdot \gamma_{C(2)}. \quad (22)$$

Physically, the line expressed by Eq. (22), as illustrated in Figure 3a by an upper broken line, constitutes a boundary for areas indicating conditions for existence and non-existence of adhesive bonds.

The hatched area between axis γ_1 and γ_1^{CRIT} relates to the conditions under which $W_A \leq 0$, as corresponding to no-bond in the system (e.g.: 'substrate-adhesive', etc.). The Young-Dupré equation, restricting W_A to positive values only, becomes irrelevant here as attractive forces across the interface do not exist (see Figure 2). The second boundary value where the surface energy of the substrate yields $W_A = 0$ with a given adhesive is found from Eq. (14), namely

$$\gamma_1^{\text{CRIT}} \leq \frac{m_1}{2 + m_1} \cdot \frac{\gamma_2}{\Phi_{0(1)}^2}. \quad (23)$$

Equation (23) is graphically represented by a lower broken line in Figure 3a located within the area of incomplete wetting of the

substrate by a given adhesive (*i.e.*, $\theta_{21} > 0^0$) [note that it corresponds to the complete thermodynamic wetting of the cured adhesive as indicated by θ_{12}]. Thus, any point located on or below the line equivalent to Eq. (23) falls into the zone where $W_A \leq 0$, *i.e.*, where zero-strength of an adhesive bond can be expected or spontaneous delamination occurs.

The above observations indicate that there are two different sets of conditions for $W_A \leq 0$ and therefore zero-strength of an adhesive bond. These are (I) as given by Eq. (22), relevant to complete wetting of the substrate by the adhesive and (II) as given by Eq. (23), which occurs within the area of no wetting.

The influence of wettability characteristic parameters on the value of demarcation points in TED.

Interesting observations may be made from the analysis of the influence of parameters related to the wettability characteristics of substrates and adhesives (*e.g.*: m , γ_C and Φ_0) on the values of γ_1^{OPT} and γ_1^{CRIT} described in the previous sections. For the maximum strength of the bond, the slope of the wettability characteristic of a cured adhesive has the following implications (see Figure 3b).

a) when $m < 1.0$, the maximum strength of the bond corresponds to thermodynamic conditions relevant to a zero contact angle θ_{21} at the 'substrate/adhesive' interface as exhibited by adhesive-on-substrate. [Note: this corresponds to a finite value of the imaginary contact angle: θ_{12}].

b) when $m = 1.0$, τ_{MAX} is achieved for thermodynamic conditions corresponding to a zero contact angle θ_{21} at the line $\gamma_1 = \gamma_{C(2)}$.

c) when $m > 1.0$ τ_{MAX} is achieved for condition corresponding to a finite angle θ_{21} , [Note: this relates to a zero—imaginary contact angle θ_{12}].

The above explains the long known but not explained dilemma: why in some cases the zero-contact angle of adhesive-on-substrate (*i.e.* θ_{21}) coincides with condition for the maximum strength whilst in others it does not.

Further analysis of Eqs. (20) and (22) indicates that decreasing the slope of the wettability characteristic (as relevant to decreasing

' m ') extends the area of positive adhesive bonding (*i.e.* when $\tau > 0$). This is illustrated by broken lines for γ_1^{CRIT} in Figure 3b which are relevant to the lower and higher limits for $\tau = 0$ respectively. In technical terms this means that the adhesive becomes more 'forgiving' (when ' m ' decreases) in respect to the successful bonding and, which applies to a larger difference between γ_2 and γ_1 .

An increase in the value of the parameter ' m ' has an adverse effect, indicated by the lines denoting γ_1^{CRIT} in Figure 3, and the area of positive bonding is narrowed.

Contact angle at the conditions for the maximum strength

It follows from the above argument that a finite contact angle *i.e.* $\theta_{21} > 0^\circ$, relates to the conditions for the maximum strength when the wettability characteristic of the substrate is such that $m_1 < 1.0$. Value of this contact angle, *i.e.* θ_{21}^{OPT} , is determined if Eq. (11) for the energy ratio a_{MIN} at γ_{12}^{MIN} (as corresponding to τ_{MAX}) is

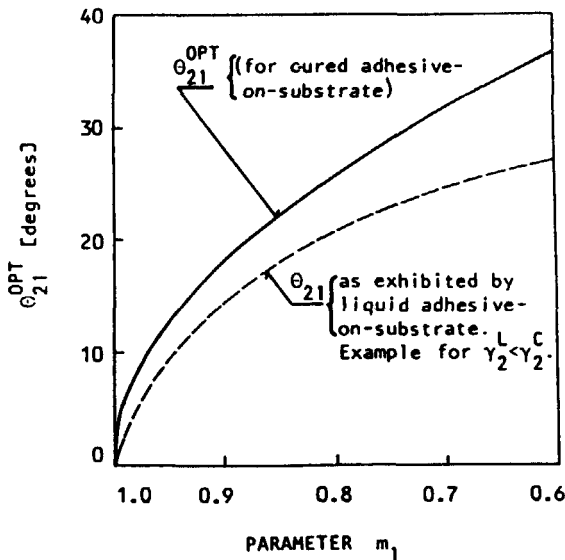


FIGURE 4 Contact angle θ_{21}^{OPT} corresponding to conditions for the maximum strength in relation to the slope of the wettability characteristic (as represented by ' m ').

substituted into Eq. (7), e.g.:

$$\theta_{21}^{\text{OPT}} = \cos^{-1} \frac{1 + m_1}{2}. \quad (26)$$

Equation (26), graphically presented in Figure 4, shows that only in the case where the slope of the wettability characteristic of the substrate yields $m = 1.0$, can the zero-contact angle, i.e. $\theta_{21} = 0$ indicate conditions for the maximum strength (when $\gamma_2 = \gamma_2^{\text{OPT}}$).

For any $m < 1.0$ (more shallow wettability characteristic), the value of θ_{21}^{OPT} is SIGNIFICANTLY higher than zero. When, for instance, $m = 0.99$, $\theta_{21}^{\text{OPT}} = 5.73^\circ$ whilst for $m = 0.8$ value of θ_{21}^{OPT} is as high as 25.84° .

The surface energy of the cured adhesive in most cases is higher than in its liquid state. Therefore, the value of θ_{21} [see Eq. (7)] as exhibited by a liquid adhesive on a substrate is lower than that corresponding to θ_{21}^{OPT} as calculated by Eq. (26) for a cured adhesive. This difference is clearly illustrated in Figure 4. The above indicates that in order to utilize θ_{21} (liquid adhesive on a substrate) as a technological indicator for optimum treatment of substrate, it is necessary to know the adhesive's surface energy in both the liquid and cured state.

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Appendix

NOMENCLATURE

γ_1, γ_2	total surface energy of phase 1 or 2
γ_C	critical surface tension for wetting
γ_{12}	interfacial energy
W_A	thermodynamic work of adhesion
θ	equilibrium contact angle
θ^{OPT}	θ , corresponding to the minimum interfacial energy
m	parameter dependent upon the slope of the wettability characteristic
m^D	' m ' for system durable under service conditions
Φ_0	specific bonding efficiency factor
$\gamma_{12}/\gamma_2,$ γ_{12}/γ_1	relative interfacial energy
$W_A/\gamma_2,$ W_A/γ_1	relative work of adhesion
$a = \gamma_1/\gamma_2$	energy ratio of the system
a^{CRIT}	critical energy ratio for $W_A = 0$, corresponding to zero-strength
a_{MIN}	optimum energy ratio for γ_{12}^{MIN} and $[\gamma_{12}/\gamma_1]_{\text{MIN}}$, corresponding to the maximum strength
γ_1^{CRIT}	γ_1 corresponding to the zero-bond strength (when phase 1 bonded with given phase 2)
γ_1^{OPT}	γ_1 corresponding to the maximum bond strength (when phase 1 bonded with given phase 2)
F	force of attraction
A	attractive constant
C	repulsive constant
r	distance of separation
τ	bond strength