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GENERALIZATION OF NEUMANN EQUATION FOR MULTIMEDIA SURFACE FREE ENERGY AND WETTABILITY ANALYSES VIA FUNCTIONAL COMPENSATION SCHEME

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Abstract
A functional compensation scheme required to generalize the popular Neumann equation of state for multimedia surface free energy (SFE) and wettability analyses is presented in this study. The compensation network was defined using relevant control theories and nonlinear regression methods. Reported apparent contact angle values of three popular test media including water, formamide and diiodomethane on a white marble sample measured at various nano roughness values were considered to demonstrate the application and performance of the proposed generalized Neumann equation. The effects of surface roughness on SFE value and wettability of the studied marble samples were verified using the mew method. The generalized Neumann equation was validated using the geometric mean approach suggested by Owens–Wendt.

1. Introduction

The tendency of a liquid droplet in contact with a solid surface to spread on the surface called wettability depends on the action of cohesion and adhesion forces which affect the equilibrium of the system. This important attribute of solid-liquid interaction systems is characterized by the contact (CA) which is the angle measured counter clockwise from the solid surface to the liquid-vapor interface. Reports have shown that solid surfaces are more hydrophobic or less wetted by a liquid that shows increased CA. Thus, the value of CA measured for a given liquid on a solid surface is basically considered as an indication of wetting property of the solid by the liquid involved which is essential in monitoring the quality of adhesion in commercial processes involving solid–liquid interaction such as surface coating. Other important applications of wettability can be found in the design of floating systems and considerations for effective cell–biomaterial interactions in living organisms. The latter is most fundamental to the growth of research in development of biomedical implants with improved osseointegration properties (Barbosa et al., 2017; Guastaldi et al., 2013).

The CA of a particular liquid on a given surface depends on both roughness and chemistry of the solid surface (Marmur, 2009). Although the measured CA of a liquid on a solid surface is an indication of the wetting property of the solid yet, it gives a value that depends on the test (or probe) liquid. This fact makes assessment of surface wettability based on CA measurements less reliable. To address this problem, the thermodynamic surface free energy (SFE) approach has been introduced. Thomas Young in his pioneering work (Young, 1805) suggests that the equilibrium of a system of liquid droplet on a flat, smooth ideal surface which is chemically homogeneous and inert is controlled by three interfacial forces including; the liquid surface tension, γ_l acting along the liquid-vapor interface, the solid SFE, γ_s acting parallel to the surface and the solid-liquid interfacial force, γ_{sl} which acts in opposite direction to γ_s as illustrated in Figure 1.

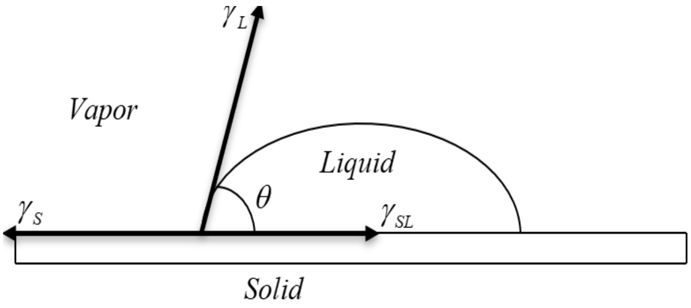

Figure 1. Schematic Diagram of the Contact Angle and Interfacial Tensions of at the Three-Phase Boundary

Young further described the contact angle θ using the force balance in the equilibrium condition according to equation 1.

$$cos\theta = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \tag{1}$$

In a real system, solid surfaces show certain degree of roughness/chemical heterogeneity. Also solid surfaces can assume complex geometry and may absorb a liquid in contact with it over time. Thus, the measured CA (called apparent contact angle), θ_A usually gives a valued that is considerably different from the ideal value. Thus, further formulation of the relationship between, γ_s, γ_l, γ_{sl} and θ is required in order to extend the Young's theory to more realistic solid-liquid interaction systems. In this line Wenzel (Wenzel, 1936) and Cassie-Baxter (Cassie, Cassie, & Baxter, 1944), developed appropriate relationships between θ_A and θ, for a homogeneous drop and a composite drop containing both liquid and air gap respectively. The Wenzel theory relies on application of a roughness factor to correlate θ and θ_A, while the Cassie-Baxter approach utilizes the interface ratios such as liquid-air and solid-liquid interface ratios for the same purpose.

The term γ_{sl} contained in the Young equation cannot be measured using an instrument as in γ_l and contact angle, thus achieving the solution for γ_s through direct application of Young equation is deemed impossible. As a result, a lot of research works have been directed towards further development of the Young's SFE approach. The idea of partitioning the surface free energy (SFE) into singular components was introduced in literature. Fowkes in his pioneering work (Fowkes, 1963) proposed that each surface tension (γ_s or γ_l) can be considered the sum of a number of components representing different intermolecular forces as illustrated in equation (2).

$$\gamma_l = \gamma_l^{LW} + \gamma_l^{AB} = \gamma_l^d + \gamma_l^p + \gamma_l^h + \gamma_l^i + \gamma_l^{AB} + \gamma_l^0 \tag{2}$$

where d, p, h, i, LW and AB respectively represent the dispersion, polar, hydrogen-bonding, induction, Lifshitz/Van der Waals interactions and acid-base interactions. The γ^0 represents additional interactions. Wu later suggested that the surface free energy, γ itself can be considered as a sum of the dispersion component γ^d and the polar component γ^p (Wu, 1971). This theory led to the development of the geometric mean approach which changed Fowkes idea. A popular method in this class is the Owen-Wendt (Owens & Wendt, 1969) described in equation (3).

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p}\right) \tag{3}$$

Similar partitioning hypotheses were developed by other researchers including; Chaudhury - Good and Van Oss (Van Oss, Chaudhury, and Good, 1988). Identification of interfacial energy components gives additional information on the cohesion and adhesion forces or dipole moments controlling the equilibrium of the system. However, this development apparently led to further complication of the mathematical problem by introducing more unknown terms in the describing equation. To address this problem, the idea of using coupled models to reduce the number unknowns to be determined in the solution steps has been developed. A typical example in literature is the modified Owen – Wendt equation presented in equation (4).

$$(1+cos\theta)\gamma_l = 2\sqrt{\gamma_s^p\gamma_l^p} + 2\sqrt{\gamma_s^d\gamma_l^d} \tag{4}$$

This kind of modification definitely leads to a major simplification of the mathematical problem and is highly popularized in literature. Calculation of SFE through the modified Owen–Wendt approach simply requires that the contact angles obtained for at least two different probe liquids of known polar and dispersive energy components are utilized to solve simultaneously for the two basic unknown parameters including γ_s^p and γ_s^d. The results are then combined according to Wu's theory to obtain the total SFE of the solid.

In some closely related studies, Neumann and his research group developed some equations of state for solid–liquid interaction which contain an adjustable parameter β. The most popular version is recalled from (Neumann et al. 1974) as equation (5).

$$\gamma_s - \gamma_{sl} = -\gamma_l + 2\sqrt{\gamma_s\gamma_l}e^{-\beta(\gamma_l-\gamma_s)^2} \tag{5}$$

The authors used relevant experimental studies and iterative procedure to obtain a useful value of $\beta[= 0.0001247(m^2mJ^{-1})^2]$ that validates the method. As in the alternative approaches, the Neumann equation of state (EOS) also contains two unknown variables, γ_s and γ_{sl} which are often required to characterize solid–liquid interaction system. Since none of the two terms can be quantified by instrumental measurements, application of equation (5) definitely requires either prior calculation of one of the unknown terms through the alternative methods or appropriate substitution could be made (similar to the one leading to equation 4) to further reduce the number of unknown terms in equation (5). A common practice in literature involves replacing the term $(\gamma_s - \gamma_{sl})$ in equation (5) with its equivalent derived from the Young equation as expressed in equation (6).

$$(1+cos\theta)\gamma_l = 2\sqrt{\gamma_s\gamma_l}e^{-\beta(\gamma_l-\gamma_s)^2} \tag{6}$$

Equation (6) preferably called the extended Neumann (EN) equation defines γ_s as an implicit function of γ_l and θ, which allows the SFE of solids, γ_s to be calculated using the ideal contact angle, θ of a single probe liquid whose surface tension, γ_l is already known. Except for the Neumann EOS approach through the EN equation (6), all alternative methods require at least two probe liquids for calculating the SFE of solids. Thus, the development of the Neumann approach is considerably a major breakthrough in addressing problems involving SFE evaluation which is capable of facilitating the process. However, many authors have argued that the EOS approach proposed by Neumann et al. is impractical because of its absolute dependence on the probe liquid (Calvimontes 2017). Other controversies arise with the question of whether the value obtained for β is a universal constant for a specific material or just a quantity obtained as a result of the iterative procedures applied in the original study. Many reports in literature have emphasized that SFE values determined via Neumann EOS approach using different probe liquids show significant disparities. Thus, the present study attempts to complete a detailed quantitative study that would highlight the performance of the distinguished Neumann approach with some popular probe liquids to; clarify the arguments on its practicability, illustrate its limitations and explore avenues for possible improvement of the approach.

This study is also motivated by some independent observations made from comprehensive review of relevant publications. Proliferation of research in this area reveals that the results of SFE calculation methods that are based on contact angle measurements are generally affected by the choices of the probe liquid and the mathematical method. Currently, there is no standard procedure for selection of probe liquid. However, some useful suggestions have been provided by researchers in literature to avoid obtaining invalid results. For example, recent works whose objectives were tailored towards the development and application of the conventional multiple probe liquid (MPL) approaches suggest a combination of polar liquids and at least one nonpolar liquid to ensure improved result accuracy. Evidently, achieving good result accuracy through the conventional MPL approaches essentially depends on proper combination of the probe liquid. There are also minor concerns on increased measurement efforts and possible multiplication of measurement errors in practical cases involving MPL methods. Thus, the current effort to reappraise the Neumann EOS approach and further develop a framework to generalize the approach for multi-media SFE/wettability analysis of solids is quite justifiable.

2. Method

2.1. Analysis of the Extended Neumann (EN) equation

The EN equation can be written as equation (7a)

$$(1+cos\theta)/2 = \sqrt{\gamma_s/\gamma_l}\,e^{-\beta\left[\gamma_l\left(1-\frac{\gamma_s}{\gamma_l}\right)\right]^2} \tag{7a}$$

and more compact as equation (7b)

$$\phi(\theta) = \chi e^{-\beta\gamma_l^2(\chi^4-2\chi^2+1)} \tag{7b}$$

Where

$$\phi(\theta) = (1+cos\theta)/2 \tag{8}$$

$$\chi = \sqrt{\gamma_s/\gamma_l} \tag{9}$$

From which

$$\gamma_s = \chi^2\gamma_l \tag{10}$$

The results obtained for γ_s through equation (10) for a specific solid sample using different test liquids are theoretically expected to be of the same value. However, this is scarcely the case in reality. To explain the possible cause of the observable discrepancies in the results from different test liquids, we may recall that contact angle measurements are usually carried out at metastable equilibrium conditions. Thus, image analysis of liquid droplets through which contact angle values are usually determined is inherently prone to instrumentation errors. Such errors which are considerably small at face value can be multiplied by the nature of the mathematical equations solved to obtain the solution. In this regard, nonpolar liquids such as an organic solvent are intuitively expected to show less precision in results of contact angle measurements owing to their high dispersive/unstable nature. This conforms with previous research findings that led to suggestions of useful of droplets' volume and measurement durations (which are typically short) to minimize influence of unaccounted processes (such as evaporation and adsorption) on the equilibrium of the system. Contact angle dynamics depends on both thermodynamic/ thermophysical properties of test media and the experimental condition. Thus, possible generalization through contact angle dynamics requires wider investigation of these variables. A feasible but pure mechanistic approach to generalize the Neumann EOS called the surface free energy (SFE) compensation technique is proposed in the present study. In the proposed method, a SFE compensation term Γ_l (whose value vanishes with increasing performance of the probe liquid) is determined using nonlinear parameter estimation method. The result of Γ_l is then added to the solution provided by the standard Neumann EOS according to equation (11). The best value of Γ_l that ensures adequate compensation is obtained when equation (11) is fitted to the available data on γ_s resulting from equation (10) and the target considered as $\gamma_{s,c}$.

$$\gamma_{s,c} = \gamma_s + \Gamma_l(\gamma_l^d - \gamma_l^p)cos\theta_A \quad (11)$$

A sufficiently small value of Γ_l is an indication that relying on data from the associated test liquid could provide accurate results with the extended Neumann equation without compensation, otherwise, possible result compensation could be implemented by making necessary substitution for Γ_l in equation (11) to obtain more accurate results as $\gamma_{s,c}$.

2.2. Analysis of the Modified Owen–Wendt

Further analysis required to compute the dispersive, γ_s^d and the polar, γ_s^p solid SFE components following the generalized Neumann EOS approach is presented in this section. The popular modified Owen–Wendt equation is re-expressed in more compact notations as equation (12).

$$\gamma_s^d = \left(X_l - \psi\sqrt{\gamma_s^p}\right)^2 \quad (12)$$

Where

$$X_l = \frac{(1+cos\theta)\gamma_l}{2\sqrt{\gamma_l^d}} \text{ and } \psi = \sqrt{\gamma_l^p/\gamma_l^d} \quad (13)$$

According to Wu (1971) γ_s is equivalent to the sum of the polar and dispersive surface free energy components i.e.

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (14)$$

Combining equation (12) and equation (14) we have equation (15)

$$\gamma_s = \gamma_s^p + \left(X_l - \psi\sqrt{\gamma_s^p}\right)^2 \quad (15)$$

Expansion of equation (15) gives equation (16) which could be expressed succinctly as equation (17).

$$\gamma_s - X_l^2 = (1+\psi^2)\gamma_s^p - 2\psi X_l\sqrt{\gamma_s^p} \quad (16)$$

$$A = B\gamma_s^p - \sqrt{\gamma_s^p} \quad (17)$$

Where

$$A = \frac{\gamma_s - X_l^2}{2\psi X_l} = \frac{1}{\sqrt{\gamma_l^p}}\left[\frac{\gamma_s \gamma_l^d}{(1+cos\theta)\gamma_l} - \frac{(1+cos\theta)\gamma_l}{4}\right] \tag{18}$$

$$B = \frac{1+\psi^2}{2\psi X_l} = \frac{1}{\sqrt{\gamma_l^p}}\left(\frac{1}{1+cos\theta}\right) \tag{19}$$

In a typical problem the quantities γ_l^d, γ_l^p and γ_l are basically known for a regular probe liquid. The value of θ can be evaluated from the measured apparent contact angle, θ_A via Wenzel theory or equivalent theory. The intermediate variables designated A and B are quantified by equation (18) and equation (19) respectively. Thus the SFE components γ_s^d and γ_s^p can then be estimated from equation (14) and equation (17) respectively.

2.3. Wenzel/Cassie-Baxter Theories

Wenzel in his work (Wenzel, 1936) described the relationship between the apparent contact angle, θ_A of a liquid droplet on a presumed rough surface and the ideal contact angle, θ suggested by the Young's equation as stated in equation (20).

$$cos\theta_A - R_f cos\theta = 0 \tag{20}$$

Where R_f is a roughness factor which is defined as the ratio of the total surface area measured over the surface asperities under the liquid drop to the projected area. Cassie-Baxter theory considered possible air gaps between surface topographic projections and modified Wenzel equation using liquid–air interface ratio, f_{LA} as stated in equation (21).

$$cos\theta_A + f_{LA} = (1 - f_{LA})R_f cos\theta \tag{21}$$

2.4. Solution approach

The apparent contact angles of three popular probe liquids including; water, Formamide and Diiodomethane on a Mugla white marble sample measured at five different surface roughness values were utilized in the present study. We recall that water is a common polar liquid, while Formamide and Diiodomethane represent a bipolar and a nonpolar liquid respectively. The surface tension of these popular test liquids are presented in Table 1. The marble samples (made of pure calcite crystals) were processed to show five different levels of surface roughness (labeled 1M–5M) using standard abrasive polishing method. A roughness parameter, S_{dr} defined as the ratio of the area increase due to surface roughness to the projected area of the solid surface covered by the liquid drop was utilized to quantify the roughness characteristics of the samples. The results of both the contact angle measurements and the surface topography characterization achieved using appropriate image analyses were combined with acid-base approach of Van Oss, Chaudhury, and Good (1988) to complete a previous study on determination of mineral surface energy using impact of rough topography (Can & Çiftçi, 2019). A relevant section of the results to the present study was lifted from this reviewed article as presented in Table 2. The details to the experimental procedure and the results of the acid-base approach to SFE evaluation of the marble sample are contained in the previous report by Can and Çiftçi.

Table 1. Standard Surface Tension and Surface Tension Components of Water, Formamide and Diiodomethane

Liquid	$\gamma_l\ (nJ/cm^2)$	$\gamma_l^{\mathrm{P}}(nJ/cm^2)$	$\gamma_l^{d}(nJ/cm^2)$
Water	72.8	51.0	21.8
Formamide	58.2	18.7	39.5
Diiodomethane	50.8	2.3	48.5

Table 2. Measured Contact Angle of Some Popular Test Liquids on Mugla White Marble at Various Nano Surface Roughness Values

Sample	Water $\theta_A(Deg.$	Formamide $\theta_A\ (Deg.)$	Diiodo-Methane $\theta_A(Deg)$	Nano roughness parameter $S_{dr}(\%)$
1M	30.5	17.4	34.7	5.19
2M	36.9	23.4	30.0	14.7
3M	40.4	19.2	30.3	16
4M	44.9	32.2	40.2	18.5
5M	34.4	15.2	37.0	6.85

In the present study, we are concerned with taking these results a little further to validate the Neumann EOS approach and its proposed generalization for multi-media SFE analysis considering its suitability to demonstrate the new concept. In the solution steps, nonlinear parameter estimation method was applied, first to solve equation (7b) for χ considering only one probe liquid at a time. The results were then substituted in equation (10) to obtain the values of γ_s, with respect to the various probe liquids. The results obtained at this stage were used to validate the extended Neumann equation by comparing with results obtained via modified Owens–Wendt equation. At the next step, the SFE compensation term, Γ_l was calculated for the various probe liquids by performing nonlinear fit of equation (11) to the validating data set. The value of Γ_l obtained for the various test liquids was then used to compute $\gamma_{s,c}$ based on equation (11). The results obtained for $\gamma_{s,c}$ which stand for the corrected results of the Neumann EOS approach were equally compared with the validating data set to confirm the performance of the proposed SFE compensation scheme in the generalized Neumann equation.

3. Results and Discussion

3.1. Evaluation of Roughness Factor, R_f and Ideal Contact Angle, θ

The report of nano roughness parameter value, S_{dr} of the marble sample after each stage of the 5-stage surface polishing process conducted was considered as presented in Table 2. From the definition of S_{dr}, the relationship between R_f and S_{dr} can be expressed mathematically as $R_f = 1 + (S_{dr}/100)$. The result of R_f computed from this expression at any step was combined with the apparent contact angle, θ_A using Wenzel equation (19) to obtain the corresponding values of θ. From the results, consistent increase in nano roughness value was recorded as the polishing process progresses from 1M up to 4M. Similar trend was also seen in the results of contact angle of water, suggesting that wettability of the sample is opposed by increasing nano roughness value. The other examined probe liquids show some levels of uncertainties in the results of surface polishing on nano roughness value of the samples. Considering the method adopted for the surface polishing process, increased nano roughness values was achieved through improved polishing with abrasives of reduced grain sizes, which does not allow for removal of large particle from the surface but further exposes new surfaces in nano dimension. In other words, an increase in nano roughness value is literally equivalent to a decrease in micro (or macro) roughness. Thus, the results obtained for contact angle measurements also suggest that wettability of the solid sample is favored by increase in micro/macro roughness. This observation agrees with literature reports in which moderate macro surface roughness values was identified to guarantee improved wettability.

3.2. Validation of the Extended Neumann Equation for Solid SFE Calculation

The performance of the extended Neumann equation in calculating SFE in the exemplified case of Mugla white marble over the observed range of nano-roughness values is presented in Figure 2. The results show that as the mesh size of the abrasive was increased from 1M to 5M, there were reduced attrition and an increased tendency to create new surfaces in nano dimension. This results in an increased nano roughness value and reduced SFE of the marble leading to decreased wettability. However, the discrepancies recorded when the results from the three probe liquids were compared on the same scale with that of the validating data set provided by the geometric mean approach as presented in Figure 2 remains a major concern. The results gathered using water as a probe liquid show notable agreement with the validating data. This suggests that the choice of water (a polar liquid) as the test medium allowed accurate calculation of the SFE of the studied samples while formamide (a bipolar liquid) and diiodomethane (a nonpolar liquid) could be considered as inappropriate test media for application of the standard Neumann equation. The excellent performance of the extended Neumann equation with selection of water as the preferred test liquid could be explained by the observed precision in contact angle measurements. From the available data on contact measurements, there are indications of irregularities possibly caused by increased instrumentation/measurement errors as nonpolar liquids were considered.

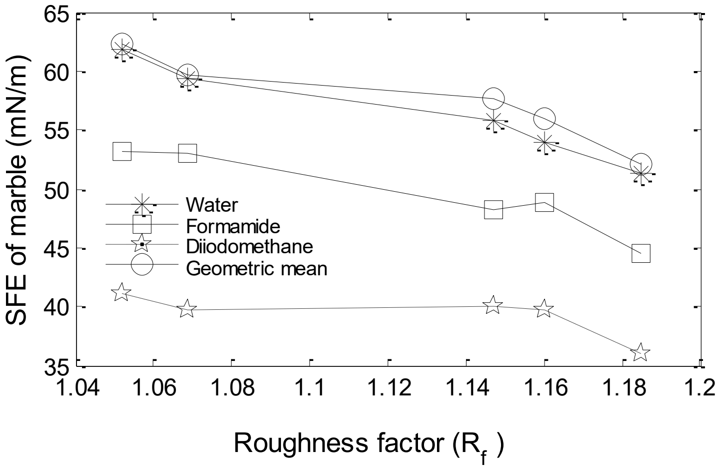

Figure 2. Comparison Between the Performances of the Standard Neumann EOS Approach and the Modified Owens–Wendt Equation in Calculating the SFE of the Marble Sample Gathered at Various Nano Roughness Values

3.3. Validation of the Proposed Generalized Neumann Equation for SFE Calculation

Following the solution approach for the proposed generalized Neumann presented in section 2.4, the value obtained for the compensation term, Γ_l with respect to the various test media are: $\Gamma_W = -0.0482$, $\Gamma_F = 0.4153$, and $\Gamma_D = 0.4780$. The result $\Gamma_W \approx 0$ is an indication that no compensation is required to achieve accurate result with the standard Neumann EOS approach when water is applied as a test medium. Attempts to choose formamide and diiodomethane as the preferred test media resulted in significant differences in the energy range of 10–30mN/m occurring between the results of the extended Neumann equation and the geometric mean approach suggested by Owens–Wendt. The extent to which the proposed compensation scheme could correct this anomaly and guarantee harmonized results for the three conventional test media was examined and the results are compared with that of a standard geometric mean approach in Figure 3.

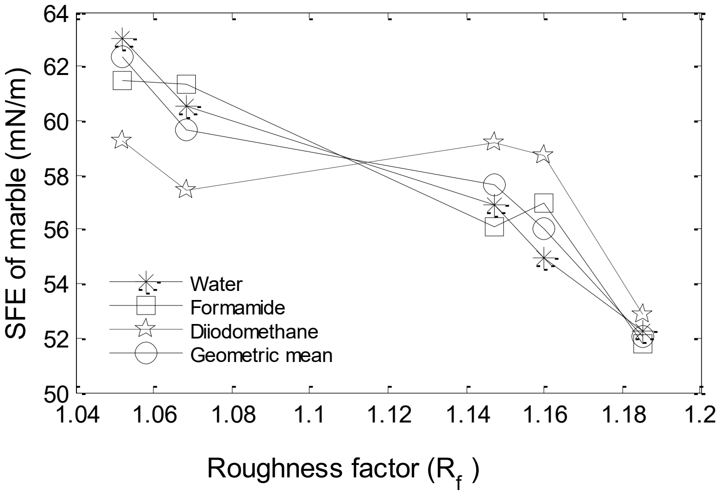

Figure 3. Comparison Between the Performances of the Proposed Generalized Neumann Equation and the Modified Owens–Wendt Equation in Calculating the SFE of the Marble Sample Gathered at Various Nano Roughness Values

The best performance of the proposed generalized Neumann equation presented in Figure 3 was obtained when the product of the slack energy term (measured in terms of the difference between the value of dispersive SFE component and the polar component of the probe liquid) and the cosine function of the apparent contact angle were used to formulate the compensator network as illustrated in equation (11). Evidently, the generalized Neumann equation achieved with the proposed compensation scheme adequately resolved the discrepancies in the results of SFE calculations achieved with the three popular probe liquids. The persistent separation of the results of SFE with Diiodomethane as the probe liquid to the tune of 2mN/m could be associated to increased loss of precision in reading of contact angle values which could be minimized with strict adherence to the experimental procedures.

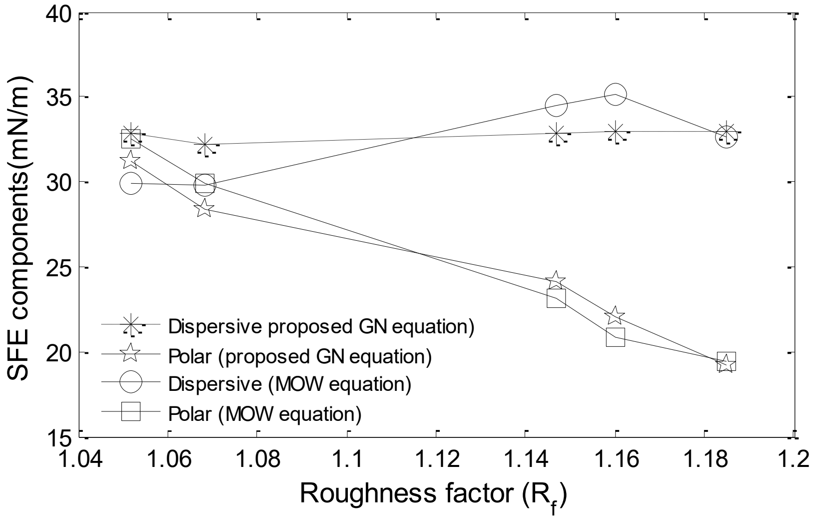

Figure 4. Comparison Between the Performances of the Proposed Generalized Neumann (GN) Equation and the Modified Owens–Wendt (MOW) Equation in Calculating the SFE of the Marble Sample Gathered at Various Nano Roughness Values

Further validation of the proposed generalized Neumann (GN) equation was implemented using the calculated SFE components. The results obtained using water as a single probe liquid with the GN equation were compared with those obtained via modified Owens–Wendt equation utilizing both water and diiodomethane in the multiple probe liquid approach as presented in Figure 4. Again reasonable quantitative agreements were recorded between the two approaches. The results on SFE components suggest that increasing nano surface roughness value of the studied marble sample through higher order polishing has notable effects of reducing the polar SFE component while increasing the dispersive energy component at a much lower rate leading to a significant decrease in total SFE and reduced wettability.

4. Conclusion

The results of this study suggest that the extended Neumann equation of state approach to SFE analysis which requires data of contact angle measurements from a single probe liquid does not guaranty result accuracy with every probe liquid, thus proper assessment of its performance with a preferred probe liquid is necessary to ensure result accuracy. The generalized Neumann equation developed in this study via functional compensation scheme allows the surface free energy and wettability of surfaces to be evaluated more accurately using different probe liquids.

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