

Effective mass density of liquid composites: Experiment and theory

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We present an effective medium theory based on the Maxwell-Garnett [J. C. Maxwell Garnett, *Philos. Trans. R. Soc. London, Ser. A* **203**, 385 (1904); **205**, 237 (1906)] and Bruggeman [D. A. G. Bruggeman, *Ann. Phys. (Leipzig)* **24**, 636 (1935)] approximations, to investigate the effective mass density of binary and ternary liquid composites. Excellent agreement between our experiment and theory is shown. The results are well interpreted in terms of intermolecular interactions, which affect the miscibility between liquid components. Thus, it becomes possible to theoretically predict the effective mass density of liquid composites. © 2007 American Institute of Physics. [DOI: [10.1063/1.2711406](https://doi.org/10.1063/1.2711406)]

I. INTRODUCTION

Predicting the effective physical properties, e.g., effective dielectric constants, effective thermal or electric conductivities, effective elastic constants, etc., of inhomogeneous composites has been a subject of scientific and engineering interest with a long history.¹⁻³ So far, many approaches and predictive schemes have been proposed.⁴⁻¹⁸ Among these approaches, bounding the possible range of the effective properties is of fundamental importance. Appropriate bounds can be used to assess a particular predictive scheme, and they can also constitute an accurate prediction of the effective properties when the bounding range is sufficiently narrow.^{19,20} One¹⁹ gave the lower and upper bounds on the effective conductivity (or dielectric constant) of a multiphase inhomogeneous composite (each phase of the inhomogeneous composite is homogeneous) by introducing a homogeneous comparison material. In other words, for achieving effective conductivities or dielectric constants, while one Maxwell-Garnett formula gives an upper bound, the other one offers a lower bound, and vice versa. But, the exact result must lie between the two bounds.¹⁹

As pointed out by Hashin and Shtrikman,¹⁹ the problems for predicting effective magnetic permeabilities, dielectric constants, electric conductivities, heat conductivities, and diffusivities of inhomogeneous composites are mathematically analogous. In this work, we shall use the effective medium concept, which works already for the above effective physical parameters, to treat effective mass densities of liquid composites of our interest.

The effective mass density of a liquid composite is one of the most basic quantities in material sciences and chemical engineering. As a basic quality, the effective mass density of a liquid composite has been widely considered. It is common sense that the effective mass density of a liquid composite should be their volume average. In detail, the common expression to describe it is volume average mass density (VAMD), which is written as $D_e = D_1 p_1 + D_2 p_2$,^{21,22} where D_1 and D_2 are the mass densities and p_1 and p_2 are the volume

fractions of the components. In the case of liquid composites, when two (or more) liquid components due to the effects of different types of intermolecular interactions between them dissolve into each other, the total volume does not equal the sum of the volume of the components. In this sense, the VAMD is no longer valid.

According to an effective medium concept, for binary composites, we shall present three formulas, namely two Maxwell-Garnett-type formulas (one of which gives an upper bound, and the other of which offers a lower bound. The exact result must lie between the two bounds.) and one Bruggeman-type formula (which predicts a result between the two bounds). It will be shown that the three formulas can predict almost the same accurate results, for which the bounding range is sufficiently narrow. To this end, excellent agreement will be shown between the three formulas and our experimental data. The investigation will be extended to ternary liquid composites. Good agreement between our theory and experiment will also be shown. Thus, it becomes possible to theoretically predict the effective mass density of liquid composites. Our results will be well interpreted in terms of intermolecular interactions, which affect the miscibility between liquid components.

The article is organized as follows. In Sec. II, we present our experiments on the measurement of the effective mass density of binary and ternary liquid composites. In Sec. III, we derive the original Maxwell-Garnett and Bruggeman formulas. In Sec. IV, based on an effective medium concept, the formalism is presented for the calculation of the effective mass density of the liquid composites of our interest. In Sec. V, both our experimental and theoretical results are displayed, with a focus on the comparison between them. Then, we interpret the results in Sec. VI. This is followed by a discussion and conclusion in Sec. VII.

II. EXPERIMENT

Ethanol (absolute alcohol), deionized water, and dimethyl sulphoxide (DMSO) were used to study the effective mass density of two different liquids with different mass ratio at room temperature (about 22 °C) and under about 1

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atmospheric pressure. A measuring cylinder was put on an electric scale and the liquids were added into it slowly. When the final amount of mass (e.g., 10 g) with different composite ratio was reached, the total volume was read. Then, the mass density of the homogeneous component or the mixed one (liquid composite) could be calculated accordingly. For ternary liquid composites of water/DMSO/ethanol, the mass fraction of one component was fixed at 20%, 40%, or 60%, and the other two liquids were adjusted accordingly with various mass fraction.

III. THE MAXWELL-GARNETT AND BRUGGEMAN APPROXIMATIONS

First, we briefly review the well-known Maxwell-Garnett and Bruggeman formulas, which were established for calculating effective dielectric constants of particulate composites.^{12–14} Composites often contain a macroscopic scale of inhomogeneity. In such a material, there are small, yet much larger than atomic, regions where macroscopic homogeneity prevails and where macroscopic parameters suffice to characterize the physics, but different regions may have quite different values for those parameters. If we are interested in the physical properties at scales that are much larger than those regions and at which the material appears to be homogeneous, then the macroscopic behavior can again be characterized by bulk effective values, e.g., effective dielectric constant ε_e . In what follows, by using different methods, we shall derive the two typical theories for calculating ε_e , namely, the Maxwell-Garnett approximation and the Bruggeman approximation.

A. The Maxwell-Garnett approximation

The Maxwell-Garnett approximation^{12,13} is also known as the Clausius-Mossotti approximation. Regarding how to derive the equation for the approximation, there are several approaches. Here, we start from the view of effective local electric fields.

Let us discuss a two-component composite where many particles of dielectric constant ε_1 and volume fraction p_1 are randomly embedded in a host medium of ε_h , in the presence of an external electric field E_0 along the z -axis. Then, denote the local electric field inside a particle by E_1 , and that inside the host medium by E_h . The solution of the Maxwell equations in electrodynamics yields

$$E_1 = \frac{3\varepsilon_h}{\varepsilon_1 + 2\varepsilon_h} E_h. \quad (1)$$

Then, the average electric field $\langle E \rangle$ inside the composite can be expressed as $\langle E \rangle \equiv p_1 \langle E_1 \rangle + (1 - p_1) \langle E_h \rangle$. Here $\langle \cdots \rangle$ denotes the volume average of \cdots . On the other hand, the effective dielectric constant ε_e is given by the ratio of the average displacement $\langle D \rangle$ to the average electric field $\langle E \rangle$ inside the composite, namely,

$$\varepsilon_e = \frac{\langle D \rangle}{\langle E \rangle}. \quad (2)$$

Hence, we obtain

$$\varepsilon_e = \frac{p_1 \varepsilon_1 \langle E_1 \rangle + (1 - p_1) \varepsilon_h \langle E_h \rangle}{p_1 \langle E_1 \rangle + (1 - p_1) \langle E_h \rangle}. \quad (3)$$

Taking into account Eq. (1), we obtain the expression for the Maxwell-Garnett approximation as

$$\varepsilon_e = \varepsilon_h \frac{\varepsilon_1(1 + 2p_1) + 2\varepsilon_h(1 - p_1)}{\varepsilon_1(1 - p_1) + \varepsilon_h(2 + p_1)}. \quad (4)$$

We re-express Eq. (4) in a commonly used form as

$$\frac{\varepsilon_e - \varepsilon_h}{\varepsilon_e + 2\varepsilon_h} = p_1 \frac{\varepsilon_1 - \varepsilon_h}{\varepsilon_1 + 2\varepsilon_h}. \quad (5)$$

The Maxwell-Garnett (MG) approximation is an asymmetrical theory, namely the physical property of the composite can be changed if one exchanges the notations 1 and h . The extension of this theory to multicomponent composites is straightforward as can be easily done on the same footing, and we obtain

$$\frac{\varepsilon_e - \varepsilon_h}{\varepsilon_e + 2\varepsilon_h} = \sum_{i=1}^n p_i \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + 2\varepsilon_h}, \quad (6)$$

where p_i and ε_i stand for the volume fraction and dielectric constant of the i th component in the $(n+1)$ -component composites.

Equation (6) holds for three-dimensional cases only. For general cases with arbitrary dimensions, it admits the following form:

$$\frac{\varepsilon_e - \varepsilon_h}{\varepsilon_e + (d^{\text{MG}} - 1)\varepsilon_h} = \sum_{i=1}^n p_i \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + (d^{\text{MG}} - 1)\varepsilon_h}, \quad (7)$$

where d^{MG} represents spatial dimensions, e.g., $d^{\text{MG}} = 2$ and 3 for two- and three-dimensional cases, respectively.

B. The Bruggeman approximation

Another approach to calculating ε_e for a multicomponent composite similar to the above was introduced by Bruggeman.¹⁴ This approach is called the Bruggeman approximation (or also the effective medium approximation). Its predictions are usually sensible and physically offer a means of quick insight into some problems that are difficult to attack by other approaches.

Also, we first discuss a two-component composite where many particles of one component with dielectric constant ε_1 and volume fraction p_1 are randomly embedded in the other component with ε_2 and p_2 , in the presence of an external electric field E_0 along the z -axis. Here, p_1 and p_2 satisfy the sum rule $p_1 + p_2 = 1$.

We shall derive the expression for the theory by considering the fact that the effective dipole factor $\langle b \rangle$ of the composite should be zero, namely

$$\langle b \rangle = 0. \quad (8)$$

On the other hand, we have

$$\langle b \rangle = p_1 b_1 + p_2 b_2, \quad (9)$$

where b_1 and b_2 are, respectively, the dipole factors of the particles of the two components in the effective medium, and they are, respectively, given by

$$b_1 = \frac{\varepsilon_1 - \varepsilon_e}{\varepsilon_1 + 2\varepsilon_e}, \quad (10)$$

$$b_2 = \frac{\varepsilon_2 - \varepsilon_e}{\varepsilon_2 + 2\varepsilon_e}. \quad (11)$$

It is apparent to see that the dipole factors b_1 and b_2 describe the polarization of the particles against the effective medium. Owing to Eqs. (8)–(11), we obtain the expression for the Bruggeman approximation,

$$p_1 \frac{\varepsilon_1 - \varepsilon_e}{\varepsilon_1 + 2\varepsilon_e} + p_2 \frac{\varepsilon_2 - \varepsilon_e}{\varepsilon_2 + 2\varepsilon_e} = 0. \quad (12)$$

The Bruggeman approximation is a symmetrical theory, namely the physical property of the composite can remain unchanged if one exchanges the notations 1 and 2. Its extension to multicomponent composite is also straightforward and can be readily done on the same footing as above, and we obtain

$$\sum_i^n p_i \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e} = 0, \quad (13)$$

where p_i and ε_i denote the volume fraction and dielectric constant of the i th component in the n -component composites.

Also, Eq. (13) holds only for three dimensions. For arbitrarily dimensional cases, it becomes

$$\sum_i^n p_i \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + (d^{\text{BT}} - 1)\varepsilon_e} = 0, \quad (14)$$

where d^{BT} is spatial dimensions, e.g., $d^{\text{BT}}=2$ or 3 for two or three dimensions.

IV. THEORY OF EFFECTIVE MASS DENSITIES

A. Binary liquid composites

To fit our experimental data of effective mass densities of binary liquid composites, there is commonly an expression for volume average mass density (VAMD),

$$D_e = D_1 p_1 + D_2 p_2, \quad (15)$$

where D_e represents the effective mass density of liquid composites, and p_1 (or p_2) denotes the volume fraction of liquid 1 (or 2) with mass density D_1 (or D_2). For Eq. (15), D_1 and D_2 can be determined from experiment, and p_1 can be calculated according to $p_1 = V_1 / (V_1 + V_2)$ with V_1 and V_2 being the volume of homogeneous liquid 1 and liquid 2, respectively. Similarly, $p_2 = V_2 / (V_1 + V_2)$.

Now, let us start from an effective medium concept. While we see liquid 1 embedded in liquid 2, in view of Eq. (7), we obtain one Maxwell-Garnett-type formula (MGF1) for the effective mass density $D_e = 1/\rho_e$ as

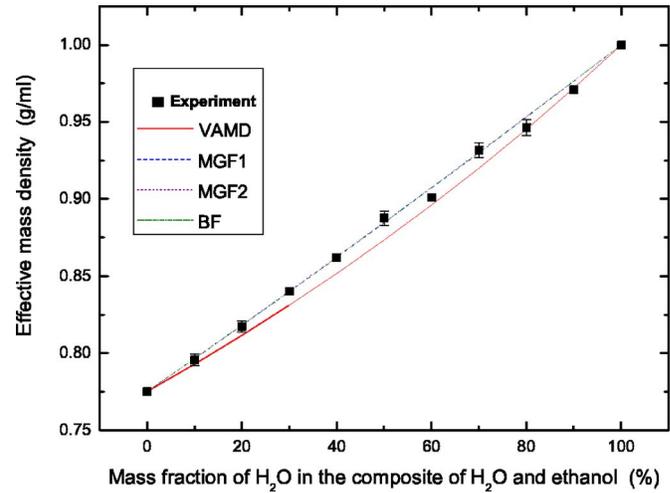


FIG. 1. (Color online) Fitting of the effective mass density of water/ethanol composites by using VAMD [Eq. (15)], MGF1 [Eq. (16)], MGF2 [Eq. (17)], and BF [Eq. (18)]. The points denote our experimental data. Note the curves predicted by the MGF1, MGF2, and BF are overlapped. For the curves predicted by the MGF1, MGF2, and BF, we adopt the same effective medium parameter $d=1.252$.

$$\frac{\rho_e - \rho_2}{\rho_e + (d-1)\rho_2} = f_1 \frac{\rho_1 - \rho_2}{\rho_1 + (d-1)\rho_2}. \quad (16)$$

If we see liquid 2 embedded in liquid 1, we achieve the other Maxwell-Garnett-type formula (MGF2) for the effective mass density $D_e = 1/\rho_e$ as

$$\frac{\rho_e - \rho_1}{\rho_e + (d-1)\rho_1} = f_2 \frac{\rho_2 - \rho_1}{\rho_2 + (d-1)\rho_1}. \quad (17)$$

In Eqs. (16) and (17), $\rho_1 = 1/D_1$, $\rho_2 = 1/D_2$, and f_1 (or f_2) the mass fraction of liquid 1 (or 2). On the other hand, if we see both liquids 1 and 2 embedded in an effective medium with (effective) mass density D_e , in view of Eq. (14), we obtain the Bruggeman-type formula (BF) as

$$f_1 \frac{\rho_1 - \rho_e}{\rho_1 + (d-1)\rho_e} + f_2 \frac{\rho_2 - \rho_e}{\rho_2 + (d-1)\rho_e} = 0. \quad (18)$$

When obtaining Eqs. (16)–(18) according to the well-known effective medium theories, namely, the Maxwell-Garnett approximation^{12,13} and the Bruggeman approximation,¹⁴ we have used the mathematical analog¹⁰ between the reciprocals of mass densities and dielectric constants. It is worth noting that in the above three effective medium formulas [Eqs. (16)–(18)], we have adopted mass fraction f rather than volume fraction p .

To fit the curve, the experimental data at $f=0.2$ was chosen to predict an effective medium parameter d (which is a phenomenological parameter and depends on the chemical nature of components and the operating temperature as well as the pressure of air) by using Eqs. (16)–(18). Then, by using the same d , all the other data were fitted very well; see Figs. 1–3.

B. Ternary liquid composites

For ternary liquid composites, the expression for VAMD becomes

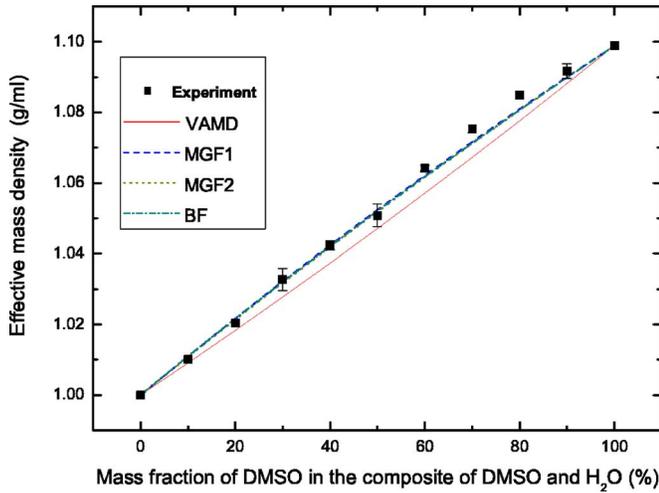


FIG. 2. (Color online) Fitting of the effective mass density of DMSO/water composites by using VAMD [Eq. (15)], MGF1 [Eq. (16)], MGF2 [Eq. (17)], and BF [Eq. (18)]. The points denote our experimental data. Note the curves predicted by the MGF1, MGF2, and BF are overlapped. For the curves predicted by the MGF1, MGF2, and BF, we adopt the same effective medium parameter $d=0.47057$.

$$D_e = D_1 p_1 + D_2 p_2 + D_3 p_3, \quad (19)$$

where D_e represents the effective mass density of the composites, and p_1 (p_2 , or p_3) denotes the volume fraction of liquid 1 (2, or 3) of mass density D_1 (D_2 , or D_3). For Eq. (19), D_1 , D_2 , and D_3 can be determined from experiment, and p_1 is calculated according to $p_1 = V_1 / (V_1 + V_2 + V_3)$, with V_1 , V_2 , and V_3 being the volume of homogeneous liquids 1, 2, and 3, respectively. Similarly, $p_2 = V_2 / (V_1 + V_2 + V_3)$ and $p_3 = V_3 / (V_1 + V_2 + V_3)$.

Now, let us also start from an effective medium concept. While we see liquids 2 and 3 embedded in liquid 1, considering Eq. (7), we obtain one Maxwell-Garnett-type formula (MGF1) for the effective mass density $D_e = 1/\rho_e$ as

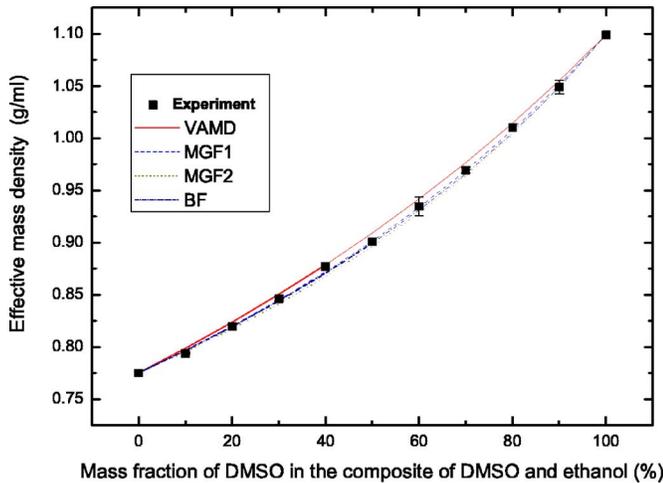


FIG. 3. (Color online) Fitting of the effective mass density of DMSO/ethanol composites by using VAMD [Eq. (15)], MGF1 [Eq. (16)], MGF2 [Eq. (17)], and BF [Eq. (18)]. The points denote our experimental data. Note the curves predicted by the MGF1, MGF2, and BF are overlapped. For the curves predicted by the MGF1, MGF2, and BF, we adopt the same effective medium parameter $d=-2.74778$.

$$\frac{\rho_e - \rho_1}{\rho_e + (d-1)\rho_1} = f_2 \frac{\rho_2 - \rho_1}{\rho_2 + (d-1)\rho_1} + f_3 \frac{\rho_3 - \rho_1}{\rho_3 + (d-1)\rho_1}. \quad (20)$$

If we see liquids 1 and 3 embedded in liquid 2 instead, we achieve another Maxwell-Garnett-type formula (MGF2) for the effective mass density $D_e = 1/\rho_e$ as

$$\frac{\rho_e - \rho_2}{\rho_e + (d-1)\rho_2} = f_1 \frac{\rho_1 - \rho_2}{\rho_1 + (d-1)\rho_2} + f_3 \frac{\rho_3 - \rho_2}{\rho_3 + (d-1)\rho_2}. \quad (21)$$

Also, if we see liquids 1 and 2 embedded in liquid 3, we get the third Maxwell-Garnett-type formula (MGF3) for the effective mass density $D_e = 1/\rho_e$ as

$$\frac{\rho_e - \rho_3}{\rho_e + (d-1)\rho_3} = f_1 \frac{\rho_1 - \rho_3}{\rho_1 + (d-1)\rho_3} + f_2 \frac{\rho_2 - \rho_3}{\rho_2 + (d-1)\rho_3}. \quad (22)$$

In Eqs. (20)–(22), $\rho_1 = 1/D_1$, $\rho_2 = 1/D_2$, and $\rho_3 = 1/D_3$, and f_1 , f_2 , and f_3 are the mass fraction of liquids 1, 2, and 3, respectively. On the other hand, if we see all three components (homogeneous liquid 1, 2, and 3) embedded in an effective medium with (effective) mass density D_e , owing to Eq. (14), we get the Bruggeman-type formula (BF) as

$$f_1 \frac{\rho_1 - \rho_e}{\rho_1 + (d-1)\rho_e} + f_2 \frac{\rho_2 - \rho_e}{\rho_2 + (d-1)\rho_e} + f_3 \frac{\rho_3 - \rho_e}{\rho_3 + (d-1)\rho_e} = 0. \quad (23)$$

To fit the curve, one experimental datum was chosen to extract an effective medium parameter d by using Eqs. (20)–(23). Then, by using the same d , all the other data were fitted very well; see Figs. 4–6.

V. COMPARISON BETWEEN EXPERIMENT AND THEORY

A. Binary liquid composites

The effective mass densities of each of two different liquids [ethanol (pure alcohol), deionized water, and DMSO] at different mass ratio were measured experimentally. According to the experimental data, the mass densities of homogeneous ethanol, water, and DMSO are, respectively, 0.775 19 g/ml, 1.0 g/ml (it is the same as the mass density of pure water at 4 °C and under 1 atmospheric pressure, which is probably due to the fact that the deionization did not yield very pure water) and 1.0989 g/ml. When the experimental data were fitted with the traditional VAMD, the comparison was not satisfactory, especially in the range of $f=0.4-0.6$. In comparison with the result of traditional VAMD, the results predicted by MGF1 [Eq. (16)], MGF2 [Eq. (17)], and BF [Eq. (18)] are in excellent agreement with the experimental data; see Figs. 1–3. For the theoretical calculations, f_1 and f_2 stand for the mass fraction of water and ethanol, respectively, for Fig. 1; of water and DMSO, respectively, for Fig. 2; and of ethanol and DMSO, respectively, for Fig. 3.

In the common expression of VAMD, there is a variable p (volume fraction), which is hard to determine in liquid-

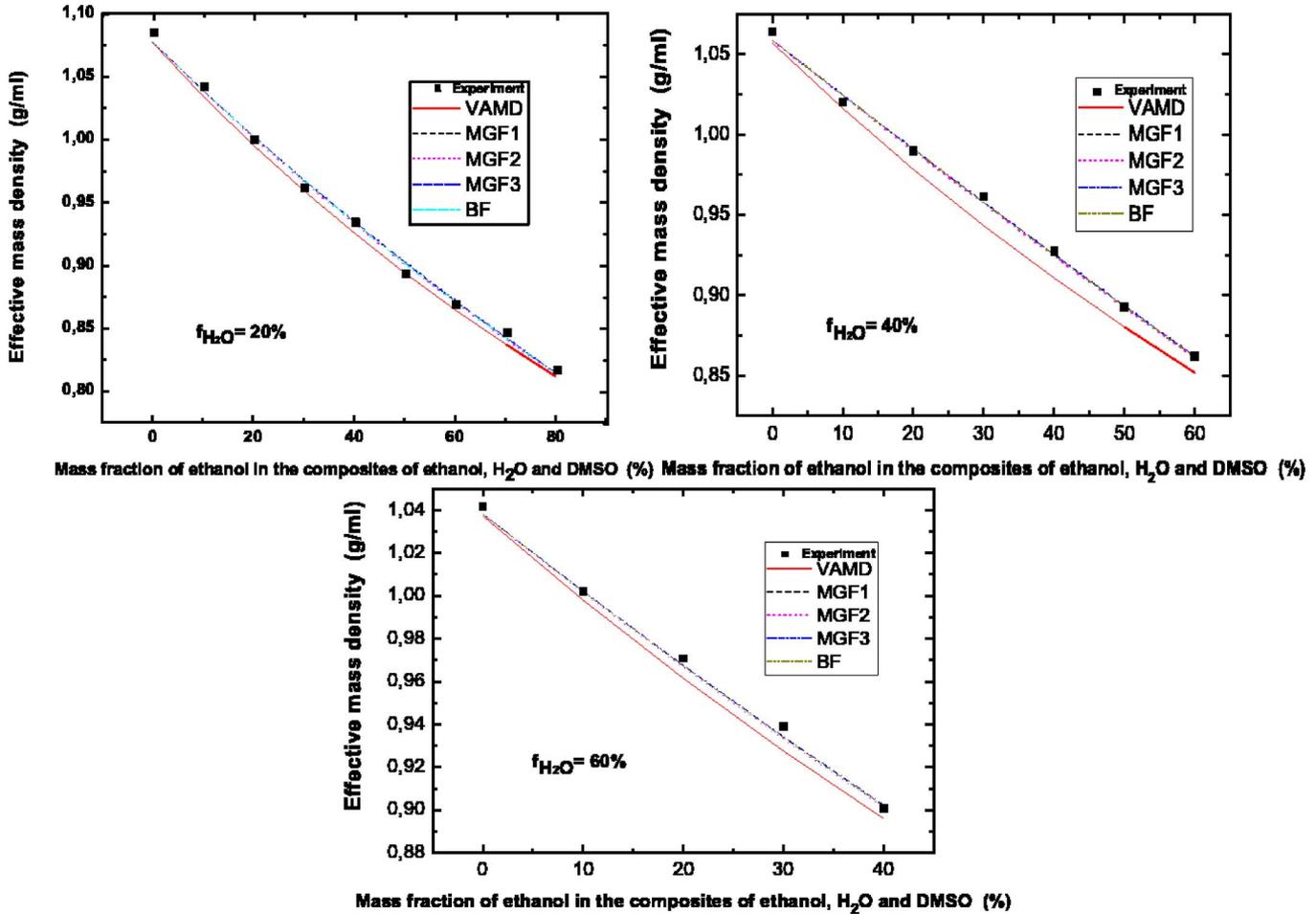


FIG. 4. (Color online) Fitting of the effective mass density of water/DMSO/ethanol composites (the mass fraction of water was fixed at 20%, 40%, and 60%, respectively), by using VAMD [Eq. (19)], MGF1 [Eq. (20)], MGF2 [Eq. (21)], MGF3 [Eq. (22)], and BF [Eq. (23)]. Note the curves predicted by MGF1, MGF2, MGF3, and BF are overlapped. For the panels of $f_{\text{H}_2\text{O}}=20\%$, $f_{\text{H}_2\text{O}}=40\%$, and $f_{\text{H}_2\text{O}}=60\%$, we adopt the effective medium parameter $d=2.914\ 48$, $d=1.346\ 52$, and $d=2.516\ 27$, respectively.

liquid composites because the total volume of the composite is not always equal to the sum of that of the components. In this sense, the effective mass density of the liquid-liquid composites might differ from that predicted by the VAMD naturally. Thus, it becomes more convenient to utilize the mass fraction f instead of the volume fraction p to fit the experimental data, as already used in Eqs. (16)–(18).

To achieve the effective mass densities of binary composites, while one Maxwell-Garnett formula gives an upper bound, the other one offers a lower bound, and vice versa. The result predicted by BF always lies between the two bounds. Apparently, the bounding range between MGF1 and MGF2 is so narrow that the three curves by MGF1, MGF2, and BF almost overlap.

To fit the curve of binary liquid composites, the experimental data at $f=0.2$ were chosen to extract an effective medium parameter d by using Eqs. (16)–(18). Then, by using the same d , all the other data were fitted very well. Actually, if we determine a d by considering the data at $f \neq 0.2$, almost the same d can be achieved. In this sense, the effective medium parameter d is universal for a specific binary liquid composite.

B. Ternary liquid composites

We have extended the investigation to ternary liquid composites; see Figs. 4–6. For the theoretical calculations, f_1 , f_2 , and f_3 represent the mass fraction of water, ethanol, and DMSO, respectively. It is clear that the result predicted by the VAMD deviates significantly from the experimental data. Interestingly, the corresponding Maxwell-Garnett-type formulas work very well. This further shows the validity of the developed formulas, which are based on an effective medium concept. In detail, for the ternary liquid composites, MGF3 offers an upper bound; MGF2 gives a lower bound. Both MGF1 and BF offer a result between the two bounds. In the meantime, the exact result should also be within the bounding region. Since the bounding region is very narrow, all four formulas thus predict a very good fit.

We discuss the case of the ternary liquid composites (Figs. 4–6), in which the mass density of one component is fixed while the other two components are varied accordingly. The experimental data at the mass fraction of one of the other two components $f=0.2$ were chosen to extract an effective medium parameter d by using Eqs. (20)–(23). Then, by using the same d , all the other data were fitted very well. Actually, if we determine a d by considering the data at f

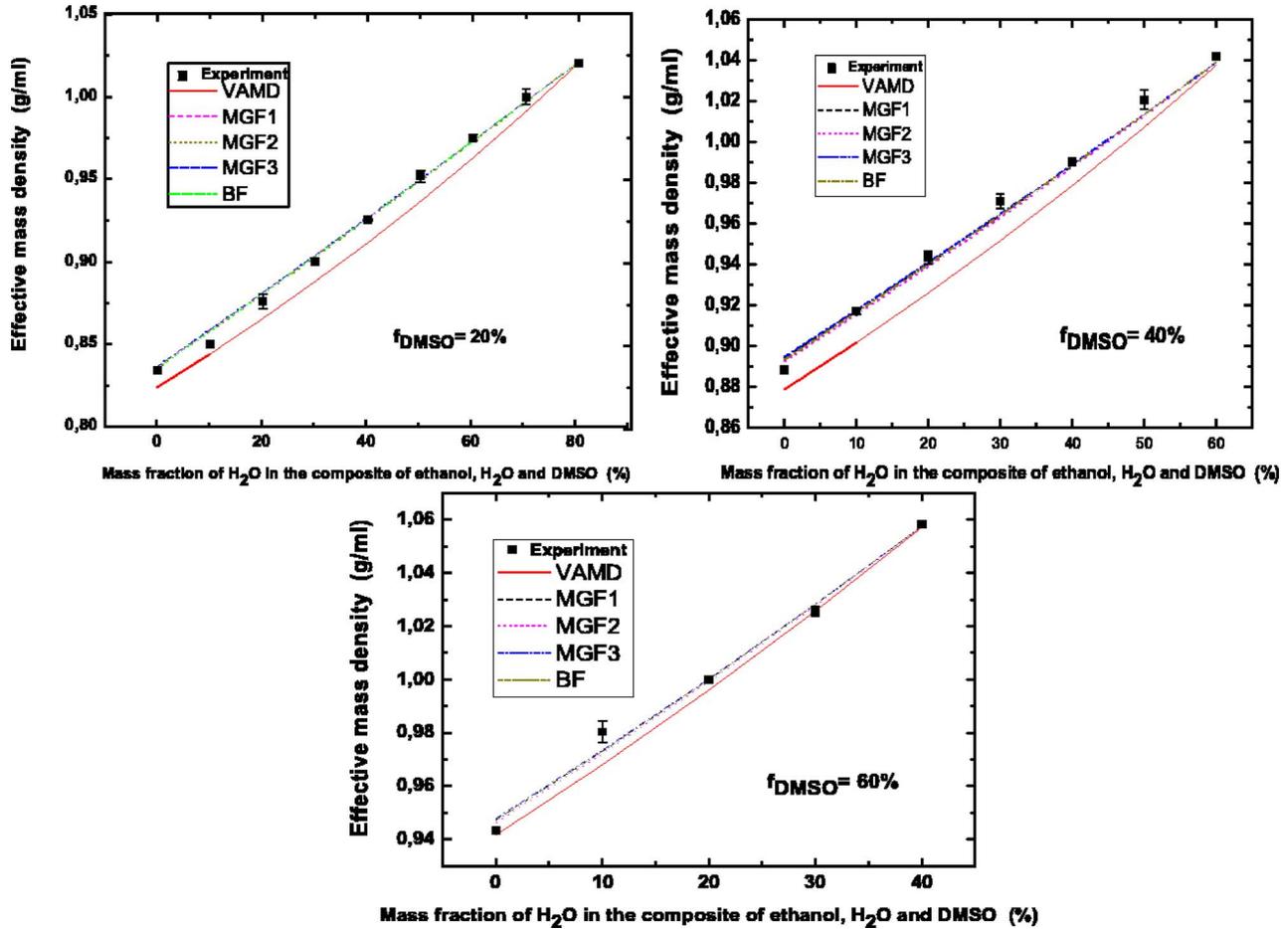


FIG. 5. (Color online) Fitting of the effective mass density of water/DMSO/ethanol composites (the mass fraction of DMSO was fixed at 20%, 40%, and 60%, respectively), by using VAMD [Eq. (19)], MGF1 [Eq. (20)], MGF2 [Eq. (21)], MGF3 [Eq. (22)], and BF [Eq. (23)]. Note the curves predicted by MGF1, MGF2, MGF3, and BF are almost overlapped. For the panels of $f_{\text{DMSO}}=20\%$, $f_{\text{DMSO}}=40\%$, and $f_{\text{DMSO}}=60\%$, we adopt the effective medium parameter $d = 1.28675$, $d = 1.70834$, and $d = 5.2177$, respectively.

$\neq 0.2$, almost the same d can be achieved. Thus, the effective medium parameter d is also universal for a specific ternary liquid composite in which the mass fraction of a certain component is fixed.

VI. INTERPRETATION OF THE RESULTS

Now, we are in a position to interpret the above comparison (Sec. V) in terms of intermolecular interactions, which affect the miscibility between components, and then, the deviation from the VAMD rule.

In Fig. 1, Eqs. (16)–(18) all fit well the experimental data of water/ethanol composites since this system is completely soluble due to its strong hydrogen bonding behavior. However, in the large water concentration range, the nonideality of the composite becomes more strong.

Figure 2 shows the results for DMSO and water. Since DMSO is a polar liquid but not a very strong hydrogen-bonding component as water, the DMSO/water composite should be completely soluble (or miscible) in the lower and higher concentration ranges, but become phase-separated in the middle range of concentration. In this case the gap between the upper and lower bounds is narrow, consequently Eqs. (16)–(18) all have well-correlated experimental data.

In Fig. 3, since ethanol is a much weaker hydrogen-bonding liquid than water, the DMSO/ethanol composite should have moderate intermolecular interactions, which ensure a good miscibility between DMSO and ethanol. Thus, the correlation using the above Eqs. (16)–(18) looks much better than for the other two systems as already displayed in Figs. 1 and 2.

In Figs. 4–6, Eqs. (20)–(23) all have fitted very well the experimental data of ternary composites. This may be attributed to the contributions of the ternary specific interactions, which make the ternary composites more miscible in the whole concentration range, leading to the success of the proposed equations. It is interesting to observe such a difference in the values of the effective medium parameter d when the panels of mass fraction f are varied between the three liquid components. This is mainly related to the difference in the ternary interactive contribution from each component.

VAMD sometimes underestimates, estimates reasonably well, or overestimates the effective mass density. Strictly speaking, from Figs. 1–3, VAMD either underestimates (see Figs. 1 and 2) or overestimates (see Fig. 3) the effective mass density, except at only two water mass fractions, 80% and 85% shown in Fig. 1. For the mass fraction 80% and 85%, VAMD estimates the effective mass density reasonably well.

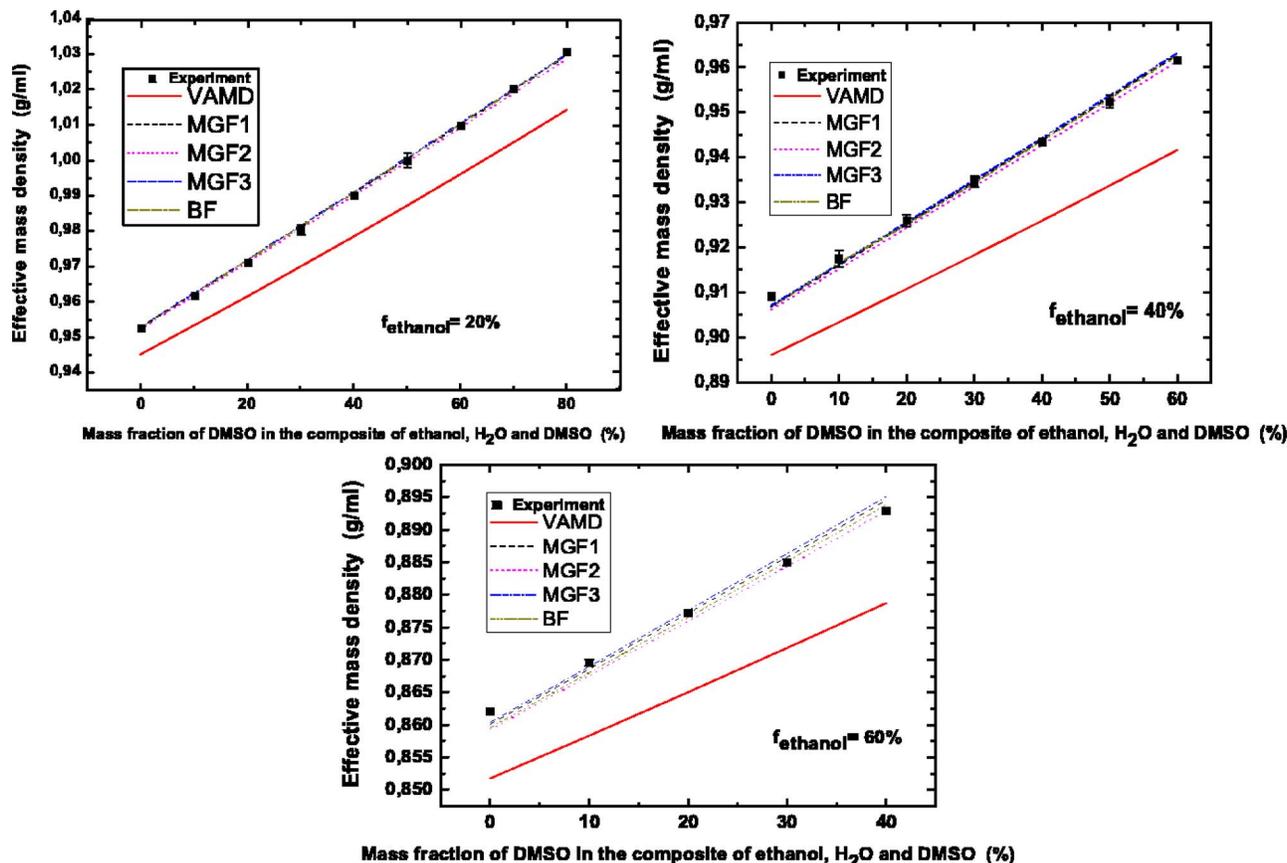


FIG. 6. (Color online) Fitting of the effective mass density of water/DMSO/ethanol composites (the mass fraction of ethanol was fixed at 20%, 40% and 60%, respectively), by using VAMD [Eq. (19)], MGF1 [Eq. (20)], MGF2 [Eq. (21)], MGF3 [Eq. (22)], and BF [Eq. (23)]. Note the curves predicted by MGF1, MGF2, MGF3, and BF are almost overlapped. For the panels of $f_{\text{ethanol}}=20\%$, $f_{\text{ethanol}}=40\%$, and $f_{\text{ethanol}}=60\%$, we adopt the effective medium parameter $d = 1.354\ 13$, $d = 1.348\ 92$, and $d = 1.662\ 57$, respectively.

It is known that the strength of intermolecular interaction (or hydrogen-bonding) between the molecule of the component satisfies water > DMSO > ethanol. Consequently, for water/ethanol and water/DMSO composites, the total volume of the liquid composites is smaller than the sum of the volumes of the corresponding pure components. However, for DMSO/ethanol composites, the total volume of the composite is a little larger than the sum of the volumes of the corresponding components. This is the reason why VAMD underestimates (see Figs. 1 and 2) or overestimates (see Fig. 3) the effective mass density. Regarding the cases of the 80% and 85% water mass fractions displayed in Fig. 1, the total volume is almost equal to the sum of the separate volumes of the components, and thus VAMD estimates the effective mass density reasonably well. Similarly, for ternary liquid composites investigated in Figs. 4–6, the total volume of the composites is generally smaller than the volumes of the components. Thus, VAMD predicts underestimated effective mass densities.

According to the results obtained in this work, for binary liquid composites the deviation between our theories and VAMD is generally small. For ternary composites, such deviation can be very big. So, while our theories present better predictions for both binary and ternary liquid composites, the VAMD is also a suitable method for binary liquid composites, within reasonable approximation.

VII. DISCUSSION AND CONCLUSION

Here, some comments are in order. From both experimental and theoretical sides, Figs. 1–6 have displayed the fact that the effective mass density of either binary or ternary liquid composites can be changed accordingly due to the change of the mass fraction of the corresponding component. For the above-mentioned fitting of the experimental data, the key point is to choose an appropriate effective medium parameter d , which is phenomenological and depends on the chemical nature of liquid components and operating temperatures as well as air pressures. The d can be seen as a characteristic parameter of a specific liquid composite. Once a d is determined according to a certain experimental datum, it can be used to fit all the other experimental data by using the present formulas [Eqs. (16)–(18) and (20)–(23)]. This shows the validity of the proposed method. The extension of our method to other kinds of liquid composites, or to composites with multicomponents, is straightforward, as long as the component liquids are dissolvable into each other. According to our results, more phases contained in liquid composites make the VAMD deviate more from the experimental data. Nevertheless, the corresponding formulas based on the effective medium concept work always very well due to the existence of very narrow bounding ranges.

The relative success of this work, with the use of only one effective medium parameter d , comes from the fact that

the three liquid components have some extent of chemical compatibility between them. This makes the whole binary or ternary system relatively miscible, leading to a narrow gap between the two bounds.

To sum up, according to an effective medium concept, we have proposed new theoretical methods to predict the effective mass density of liquid composites. The validity of the theoretical method has been shown by comparing with our experimental data very well. Thus, it becomes possible to theoretically predict the effective mass density of liquid composites.

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