# Determination of the Dielectric Constant of Nanoparticles. 1. Dielectric Measurements of Buckminsterfullerene Solutions

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The static dielectric constant $\epsilon$ of buckminsterfullerene ($C_{60}$) particles is determined in *cis*-decalin, toluene, and 1,2-dichlorobenzene using continuum models for spherical and spherical shell inclusions. The value for $\epsilon$ for isolated $C_{60}$ in *cis*-decalin and toluene agrees well with molecular beam measurements using a spherical shell model, but the $\epsilon$ estimate in the highly polar solvent 1,2-dichlorobenzene deviated from these other measurements. Complications of measurements in highly polar solvents are summarized. We conclude that virial measurements have a great potential for determining the effective properties of nanoparticles from the properties of nanofilled materials over a range of dilute filler concentrations.

## 1. Introduction

Particle dispersions have been of interest in materials development since the dawn of history. In pre-scientific times there was much interest in perfumes, inks, and balms that improved the quality of life and in recent times this interest in particle dispersions remains strong. Heterogeneous media have the advantage that they retain many of the properties of their components, so that adjustment of the composition often allows material properties to be tailored for specific applications without the synthesis of new materials. Properties of interest fall into the general areas of mechanical (e.g., flexural modulus and fracture toughness), viscoelastic (e.g., viscosity and dynamic modulus), and electromagnetic (e.g., conductivity, dielectric constant and refractive index). A myriad of models have arisen for the purpose of predicting these specific properties. In this paper, we will be concerned with models that predict electromagnetic properties, or more specifically the dielectric properties of heterogeneous media.

Predictive models for the dielectric properties of composite materials have existed since the 1800's, going back to classic works by Maxwell,[1] Rayleigh,[2] and many others. These models attempted to account for the bulk electrical properties of spherical inclusions embedded in a continuous matrix. Despite the importance of calculating the properties of particle dispersions there has been very little work addressing itself to the influence of particle shape, apart from phenomenological treatments incorporating empirical "shape factors". Most theoretical treatments focus on generalizing the problem of spherical dispersed particles to finite concentrations. The methods include rigorous and heuristic bounds on the "effective" properties of the mixtures and many effective medium type models have been proposed (e.g., Bruggeman,[3] Böttcher,[4] Hsu,[5] and Landau and Lifshitz[6]) to estimate mixture properties. Brown[7] and Landau and Lifshitz[6] have shown how to develop a systematic expansion of dispersion properties for the dielectric constant of a particle dispersion when the mismatch between the dielectric constant of the medium and the particles is small. Until recently,

ellipsoids were the only family of particle shapes that could be rigorously and accurately estimated using continuum modeling, even in the limit of vanishing particle concentration where a virial expansion is applicable. Douglas and Garboczi[8,9] recently made an important advance in treating more complicated shaped objects by recognizing that the virial coefficient of the dielectric constant (and other electromagnetic properties) could be expressed in terms of electric and magnetic polarizability tensors or related functionals of particle shape (e.g., hydrodynamic virtual mass tensor, logarithmic capacity). These quantities have been under investigation in the mathematical and engineering communities for a very long time,[10] and the results of Douglas and Garboczi[8] can be immediately applied to calculating the leading virial coefficient of the dielectric constant for a wide range of shapes (ellipsoids, anchor rings, spindles, two spheres, and lenses). These results have restricted applicability, however, because they are limited to filler particles that have a much higher or lower dielectric constant than the medium to which they are added. More recent work utilizing a path-integral calculation of the polarizability coefficients[11] has allowed for the accurate calculation of the electrical polarizability tensor for essentially arbitrarily shaped objects, but this advance still does not allow for the calculation of virial coefficients of particles that have a general dielectric mismatch with the suspending medium. Garboczi and Douglas[9] introduced an effective approximate method for calculating the leading dielectric virial coefficient for particles of arbitrary shape and general particle-medium dielectric mismatch by combining a perturbative expansion[6,12] about the small property mismatch limit with information for the polarizability (electric and magnetic) tensors of the particles. The completion of this program to treat just the leading virial coefficient of an arbitrary shaped particle dispersion with arbitrary property mismatch still requires an accurate means for calculating the magnetic polarizability tensor for conductive particles of general shape (or equivalently the hydrodynamic "virtual mass" tensor), but good approximate values for this quantity can be obtained by finite element calculations.[8,9] At any rate, we now have a much enlarged class of particles for which accurate estimates of the leading dielectric virial coefficient exist.

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Continuum models of the properties of particle dispersions are normally found to be accurate for particles on the order of a $\mu$m or larger. When the length scale is decreased further to molecular dimensions, e.g., chlorobenzene in hexane, these continuum models have been observed to break down due to what is commonly termed a "solvent effect". The "solvent effect" makes the value of the polarization obtained by extrapolation to infinite dilution not equal to estimates obtained by measurements of isolated molecules in the gas phase. Several theoretical models have been put forth to explain the effect by "self-consistent" modifications of mean-field theory[13] and by accounting for the solvent geometry.[14,15] Experimental procedures have been developed to minimize the errors due to the solvent effect.[16-25] This situation then brings us to an important question. Are nanoparticles large enough to be reasonably described by continuum theory or do these materials lead to the same problems as found for molecular dispersions?

Many of the existing models for heterogeneous materials assume that a continuum description is applicable and that the properties of the dispersed particles are the same as in the bulk. Recent measurements have indicated that the properties of very small particles can deviate substantially from their bulk values. Some examples in which nanometer-scale materials embedded in a matrix behave differently from those in a "bulk" sample include, but are not limited to, (1) the change in the glass transition temperature (dielectric loss peak temperature) of polymers confined in nanoporous glass as a function of pore size,[26,27] (2) the shift in the nematic/isotropic transition temperature for liquid crystals confined in nanoporous glass,[28] (3) superheating of nanometer size spheres of solid argon by 480 K due to confinement in aluminum pores,[29] (4) melting point depression of approximately 600 K for gold nanoparticles,[30] and (5) the difference in the dielectric constant of buckyballs in solid films versus isolated $C_{60}$ molecules.[31,32] These observations raise the additional problem of how to determine $\epsilon$ and other properties of nanoparticles that are required to utilize continuum models of nanoparticle dispersions. Thus, the theoretical description of nanoparticle dispersions is complicated by finite particle size effects, even if continuum theory is applicable to such small particle dispersions. There is no simple means to determine the properties of nanoparticles and part of the motivation of the present work is to develop such a method. We report measurements of the dielectric properties of $C_{60}$ particle dispersions and interpret the data in terms of the continuum models. The validity of these models can then be determined by comparing the results to those obtained by independent molecular beam measurements[32] of $\epsilon$ for $C_{60}$.

In the present work, we employ part of the method of Halverstadt and Kumler[18] to determine the dielectric constant of isolated $C_{60}$ molecules. This method, for concentrations with a mass fraction of solute of less than 0.01, is based on two linear fits. The first is the measured static dielectric constant $\epsilon_{12}$ as a function of mass fraction of solute $w_2$,

$$\epsilon_{12} = \epsilon_1 + \beta w_2 \tag{1}$$

and the specific volume (1/density) $v_{12}$ as a function of mass fraction of solute

$$v_{12} = v_1 + \gamma w_2 \tag{2}$$

Halverstadt and Kumler also perform the extrapolations using mole fractions with $\beta$ and $\gamma$ being replaced by $\beta'$ and $\gamma'$, respectively. By using these extrapolations to determine the static dielectric constant $\epsilon_1$ and specific volume $v_1$ of the solvent,

their claim is that several problems can be circumvented. First, they state that under ordinary handling conditions, the solutions are exposed to air longer than the solvent, which can result in a higher moisture uptake by the solutions. Second, because $\epsilon_1$ and $v_1$ are key parameters in the determination of the polarization of the solute and are measured only once, their values are weighted in the calculations far more heavily than any single measurement of $\epsilon_{12}$ or $v_{12}$, respectively. Additionally, the effects of solvent polarization are eliminated by determining the static dielectric constant of the solvent by extrapolation to $w_2 = 0$. Finally, linearity in a plot of $v_{12}$ vs $w_2$ suggests a lack of specific interactions.

From the extrapolations cited above, Halverstadt and Kumler then used the slopes and intercepts to calculate the molar solute polarization at infinite dilution. In the present paper, we are interested in examining the continuum model approach for estimating the dielectric constant of buckyballs as a model nanoparticle. Buckyballs are truncated regular icosahedrons,[33] but they can be reasonably described as nearly spherical (see below). We shall examine the predictions of two simple, effective medium theories (EMT) based on spherical particle shape: the Maxwell model for a dilute dispersion of uniform spherical particles and a model for a dilute dispersion of spherical shell-like particles. The equations can be expressed in terms of a reduced dielectric constant $\epsilon_{12}(\phi_2)/\epsilon_1$, where $\epsilon_{12}(\phi_2)$ is the static dielectric constant of the mixture at a given volume fraction $\phi_2$ of particles and $\epsilon_1$ is the static dielectric constant of the matrix (obtainable by the method of Halverstadt and Kumler and by dielectric measurements of the pure solvent). The Maxwell equation for $\epsilon_{12}(\phi_2)/\epsilon_1$ in the case of spherical particles equals[1,6]

$$\epsilon_{12}(\phi_2)/\epsilon_1 \equiv 1 + [\epsilon]\phi_2 + O(\phi_2^2) = 1 + \frac{3(z_\epsilon - 1)}{(z_\epsilon + 2)}\phi_2 + O(\phi_2^2) \tag{3}$$

where $[\epsilon]$ is the leading dielectric constant virial coefficient ("intrinsic dielectric constant"), $z_\epsilon$ is the relative dielectric constant (dielectric mismatch) of the particle ($z_\epsilon = \epsilon_2/\epsilon_1$), and $O(\phi_2^2)$ indicates terms on the order of $(\phi_2)^2$ which are negligible for small $\phi_2$. [A probabilistic computation[11] for the virial coefficient in the highly conducting limit ($z_\epsilon \rightarrow \infty$) for a truncated icosahedron gives 3.0409(8) rather than the value of 3 which follows from eq 3 for the case of a sphere. The virial coefficient for insulating particles ($z_\epsilon \rightarrow 0$) is approximately $-3/2$ for nearly spherical particles. Equation 3 is accurate for arbitrary shapes for $z_\epsilon \simeq 1$.] The virial coefficient in eq 3 evidently becomes insensitive to the dielectric constant of the particle $\epsilon_2$ when $z_\epsilon$ is too large so that the use of eq 3 to determine $\epsilon_2$ is limited to suspending media in which $z_\epsilon$ is on the order of $z \sim O(0.1-10)$. This effect can readily be seen in Figure 1. Extension of eq 3 to complex particle shapes is described by Garboczi and Douglas.[9]

More generally, the virial expansion for a dilute dispersion of spherical shell-like particles with a core dielectric constant $\epsilon_c$ equals[34,35]

$$\epsilon_{12}(\phi_2)/\epsilon_1 =$$
$$1 + \phi_2\left\{\frac{3[(\epsilon_c - \epsilon_2)(2\epsilon_2 + \epsilon_1) + \gamma(\epsilon_c + 2\epsilon_2)(\epsilon_2 - \epsilon_1)]}{2(\epsilon_c - \epsilon_2)(\epsilon_2 - \epsilon_1) + \gamma(\epsilon_c + 2\epsilon_2)(\epsilon_2 + 2\epsilon_1)}\right\} + O(\phi_2^2) \tag{4}$$

where $\epsilon_c$ is set equal to unity for vacuum in this paper. $\gamma$ is a dimensionless parameter describing the ratio of the outer to core
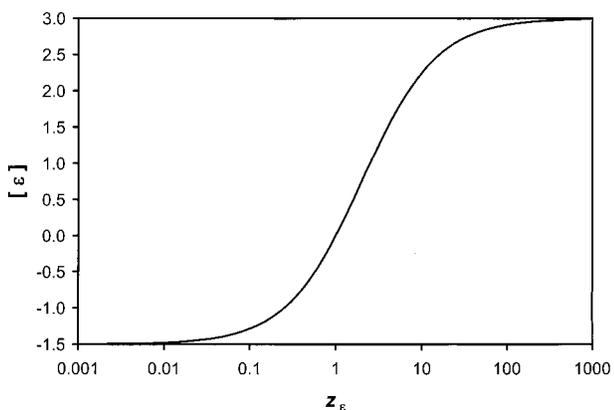
**Figure 1.** "Intrinsic dielectric constant" $[\epsilon(z_\epsilon)]$ as a function of the dielectric mismatch. The range over which the virial coefficient saturates depends on the particle shape.[9]

sphere volumes,

$$\gamma = \frac{(b+h)^3}{b^3} \tag{5}$$

where $h$ is the shell thickness and $b$ is the radius of the spherical core. (Note that eq 4 reduces to eq 3 when $\epsilon_c = \epsilon_2$ and $h = 0$.) For our calculations, we will use the core and shell values from the polarization wave model of $C_{60}$ introduced by Lambin and co-workers[36] ($h = 1.8$ Å, $b = 2.6$ Å). Equations 1 and 2 will be used to verify the values for the dielectric constant and specific volume obtained from measurements on the pure fluids.

To evaluate the results from the solution measurements on the $C_{60}$ molecule, we can compare these estimates of $\epsilon_2$ to those obtained for isolated molecules. Conveniently, a molecular beam method has been used to determine that the electric polarizability $\alpha$ of isolated $C_{60}$ molecules is 76.5 Å$^3$ $\pm$ 8.0 Å$^3$ (converting their value to SI units yields $\alpha_{SI} = 8.50 \times 10^{-39} \pm 8.9 \times 10^{-40}$ C$^2$ m$^2$ J$^{-1}$).[32] From the mean-field Clausius−Mosotti relationship for spherical particles (which is nearly the case for Buckminsterfullerene), we have (in SI units)[37,3]

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\left(\frac{M}{\rho}\right) = \frac{N_A}{3\kappa_0}\alpha_{SI} \tag{6}$$

in the absence of a permanent dipole moment. The static dielectric constant (the zero frequency limiting dielectric constant) $\epsilon_0$ of isolated $C_{60}$ molecules can then be obtained, where $N_A$ is Avogadro's constant, $M$ is the relative molecular mass, $\kappa_0$ is the permittivity of vacuum (8.854 pF/m), and $\rho$ is the density. Using the value for $\alpha$ cited above, we find a value of $\epsilon_0 = 3.6 \pm 0.4$ for an isolated $C_{60}$ nanoparticle. (It should be noted that the experimental value cited for the polarizability of isolated $C_{60}$ molecules is in good agreement with the results of many theoretical polarizability models.[39]).

## 2. Experimental Section

**2.1. Materials.** Buckminsterfullerene (98% purity), *cis*-decahydronaphthalene (*cis*-decalin, 99% purity), anhydrous toluene (99.8% purity), and 1,2-dichlorobenzene (99% purity) were obtained from Aldrich Chemical Co. and used as received.[40]

**2.2. Sample Preparation.** All samples used in this study were prepared in the same way. Using the solubility data of Ruoff and co-workers,[41] a solution with the maximum concentration of $C_{60}$ in the respective solvents was prepared. This "master"

batch was placed in a sonicator for 7 h. Ordinarily, there was some precipitate left in this master solution (probably containing the 2% impurities), so the solution was decanted off. Fifteen mL samples of the decanted solution were placed into glass vials which had been thoroughly cleaned and dried under vacuum. The mass of the vial prior to and after the addition of the 15 mL was recorded, with the final mass being buoyancy corrected against the displaced volume of 15 mL of air. This value was used to determine the ambient density of the "master" batch. The solvent was slowly evaporated off and after no solvent was visible, the vial was heated above the boiling point of the solvent and was cooled under vacuum. The mass of the vial was then determined to obtain the concentration of master solution. Aliquots of the master solution were then transferred to clean dry vials and were diluted with pure solvent to prepare solutions with modified concentrations. After combining the master batch and the pure solvent, the vials were sonicated for 6 h each. A minimum of three samples of each concentration was prepared. Each set of three was prepared prior to the day in which the measurements were to be performed. The vials were equilibrated overnight in the high precision temperature bath described below. (*N.B.* For the 1,2-dichlorobenzene, all samples were prepared under dry nitrogen conditions.)

**2.3. Dielectric Measurements.** All dielectric measurements were performed in a constant-temperature bath, which had a manufacturer's stated temperature stability of $\pm 0.001$ °C. The temperature of the dielectric cell was determined with a NIST calibrated standard reference thermometer to be 20.188 °C $\pm$ 0.001 °C (an expanded standard uncertainty with a 95% confidence level for the temperature of interest was reported in the calibration certificate to be $\pm 0.001$ °C).

Dielectric measurements were performed for each sample on a Hewlett-Packard 4284A LCR meter over a frequency range ($f$) of 100 Hz to 1 MHz and on an Andeen-Hagerling 2500A 1 kHz Ultra-Precision Capacitance Bridge, the latter of which had been recently calibrated to a relative capacitance value of $40 \times 10^{-6}$ against a NIST calibrated General Radio model 1404-CSI Reference Standard Capacitor. The 4284A measurements were performed at 1 V and the 2500A measurements were performed at 1.5 V. (These measurements were compared to measurements performed on the 4284A at 0.1 V and were within the experimental uncertainty, suggesting that Ohmic heating was not a problem. Therefore, the higher voltage was utilized to decrease the experimental uncertainty. Furthermore, measurements on the most concentrated solution in *cis*-decahydronaphthalene of the conductivity $G_s$ as a function of frequency (from 100 Hz to 1 MHz) was no greater than that of the empty dielectric test cell, which was on the order of $1 \times 10^{-10}$ S.) The cell constant (or geometric capacitance) $C_g$,

$$C_g = \frac{C_{meas}}{\epsilon_{air}} \tag{7}$$

was determined from the measured capacitance by calculating the dielectric constant of the air $\epsilon_{air}$ in the cell using the data reduction techniques described by one of us in an earlier paper and measurements of ambient temperature, barometric pressure, and relative humidity.[42] The cell constant (capacitance in a vacuum) was determined, prior to measurement of the solutions, on each day after the cell had been cleaned, dried, and reequilibrated in the temperature bath. The average value determined for $C_g$ was 11.521 pF $\pm$ 0.002 pF.[43] The variation in $C_g$ was on a day to day basis (after cleaning and drying) which indicates that the mechanical stability of the dielectric

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cell was such that the relative reproducibility of capacitance measurements was on the order of $2 \times 10^{-4}$. This was substantiated by further measurements on the solvents used in these studies.

The liquid dielectric test cell was a small-volume (10 mL) three-terminal, guarded concentric cylinder fixture with gold-plated electrodes based on the small-capacity cell for referee tests and research investigations described in American Society for the Testing of Materials (ASTM) Test Method D 924-92.

**2.4. Density Measurements.** The density measurements were performed by measuring the period of oscillation of a vibrating sample cell with a sample volume of 0.7 mL. The sample density $\rho$ is related to the period $t$ by the following relation

$$t^2 = A\rho + B \qquad (8)$$

where $A$ and $B$ are contain the spring constants of the oscillator, the empty oscillator's mass, and the volume of the sample that undergoes oscillation. Calibration of the density meter can be performed by measurement of the period of two substances of known density and the density difference $\rho_1 - \rho_2$ equal to

$$\rho_1 - \rho_2 = \frac{1}{A}(t_1^2 - t_2^2) \qquad (9)$$

Calibration of the density meter was performed using air and ultrapure water. The density of dry air as a function of temperature $T$ and pressure $P$ is given by

$$\rho_{air}(T,P) = \frac{(1.7238 \times 10^{-1} \text{ g cm}^{-3} \text{ Pa}^{-1})P}{[1 + (3.67 \times 10^{-3} \text{ °C})T]} \qquad (10)$$

The density of water as a function of temperature was obtained by a fourth-order polynomial fit to the 400 data points (between 0 and 40 °C) provided in the manual. The fitted quadratic equals

$$\rho_{H_2O} = A_1T^4 + A_2T^3 + A_3T^2 + A_4T + A_5 \qquad (11)$$

This expression has a maximum relative residual of $3 \times 10^{-6}$ ($A_1 = -4.67337 \times 10^{-10}$ g cm$^{-3}$ °C$^{-4}$, $A_2 = 7.70894 \times 10^{-8}$ g cm$^{-3}$ °C$^{-3}$, $A_3 = -8.75500 \times 10^{-6}$ g cm$^{-3}$ °C$^{-2}$, $A_4 = 6.59869 \times 10^{-5}$ g cm$^{-3}$ °C$^{-1}$, $A_5 = 0.99842$ g cm$^{-3}$).[44] The manufacturer's specified accuracy for the system is $\pm 1.5 \times 10^{-6}$ g/cm$^3$.

## 3. Results and Discussion

**3.1. Static Dielectric Constant Determination.** The static dielectric constant $\epsilon_0$ is determined by extrapolation of the frequency dependent dielectric constant $\epsilon^*(\omega)$ to zero angular frequency ($\omega = 0$, where $\omega = 2\pi f$). For ordinary low viscosity liquids, $\epsilon^*(\omega)$ measured at frequencies as high as 1 MHz is commonly referred to as the static dielectric constant.[37] However, the addition of the C$_{60}$ molecule makes it desirable to further demonstrate that the measured dielectric constant is equal to the static dielectric constant.

The frequency dependent dielectric constant can be obtained by a bridge type capacitance measurement which can be used to determine the complex frequency dependent dielectric constant $\epsilon^*$ defined as

$$\epsilon^* = \epsilon' - i\epsilon'' \qquad (12)$$

where $\epsilon'$ is the real component, $\epsilon''$ is the imaginary (loss) component, and $i = \sqrt{-1}$. If no time dependent changes are
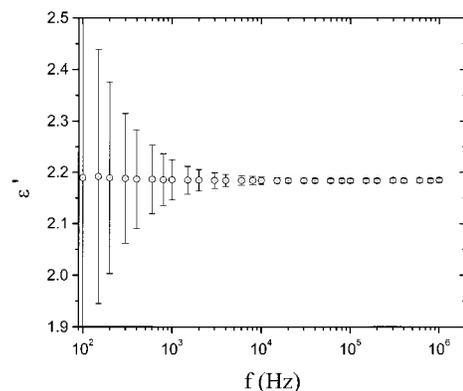


**Figure 2.** $\epsilon'$ as a function of measurement frequency $f$ for C$_{60}$ in *cis*-decahydronaphthalene at 20.118 °C. The error bars were obtained from the manufacturer's specifications.[45]



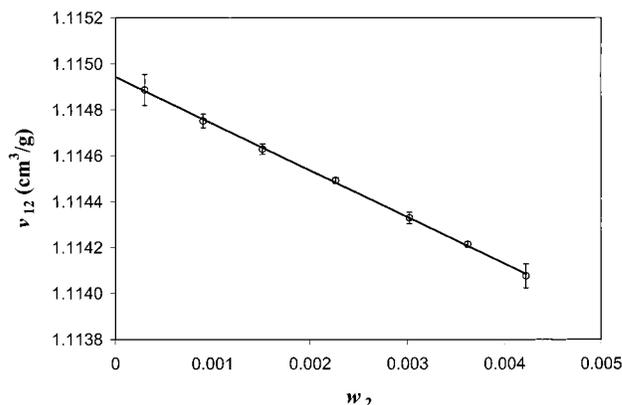**Figure 3.** Specific volume $v_{12}$ versus mass fraction $w_{12}$ for C$_{60}$ in *cis*-decahydronaphthalene at 20.1 °C.

occurring over a time scale comparable to $\omega$ (such as a relaxation process) and no conductivity is present, then $\epsilon''$ is zero and $\epsilon'$ can be extrapolated to low frequencies. However, if a loss is present ($\epsilon'' \neq 0$) then the extrapolation is less trivial.

A sample plots of $\epsilon'$ versus $f$ is shown in Figure 2 for the most concentrated *cis*-decahydronaphthalene solution. The error bars, obtained from the manufacturer's specifications, are a function of impedance, loss, cable length, instrument temperature, integration time, and frequency. Similar behavior was observed for toluene and 1,2-dichlorobenzene solutions. Because $\epsilon'$ is frequency independent over the entire range of measured frequencies, a single measurement of $\epsilon'$ by the higher accuracy 2500A bridge at 1 kHz will be used to determine $\epsilon_0$ in the following analyses.

**3.2. Dielectric Constant and Specific Volume of the Pure Liquids.** To verify the values for the specific volume $v_1$ and static dielectric constant of the pure solvent $\epsilon_1$, the method of Halverstadt and Kumler described previously, was used for comparison with values obtained by measurements on the pure liquids. In Figures 3−5 we have plotted the specific volume fraction of the mixture ($v_{12}$) as a function of weight fraction of C$_{60}$ ($w_2$). Because of the variability in the literature regarding the definitions of mass fraction and volume fraction, we wish to explicitly define our use of these terms. Mass fraction $w_2$ is defined as

$$w_2 = \frac{m_2}{m_1 + m_2} \qquad (13)$$

where $m_1$ and $m_2$ are the masses of components 1 and 2, respectively. Similarly, the volume fraction of the second
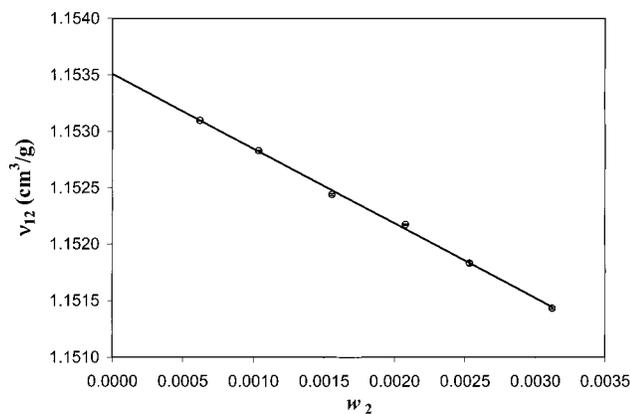
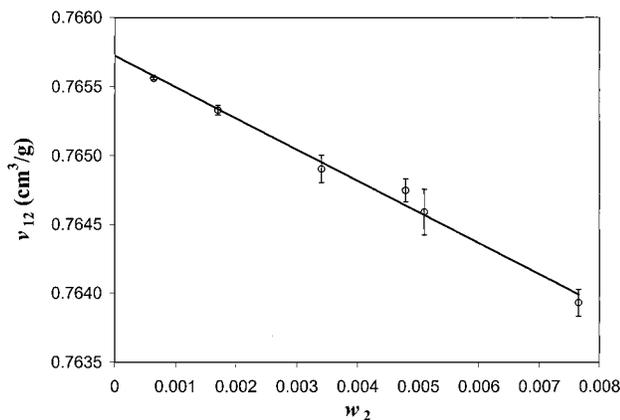**Figure 4.** Specific volume $v_{12}$ versus mass fraction $w_{12}$ for $C_{60}$ in toluene at 20.1 °C.



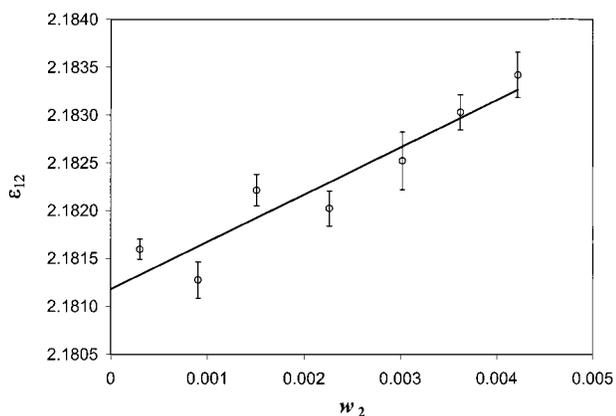**Figure 5.** Specific volume $v_{12}$ versus mass fraction $w_{12}$ for $C_{60}$ in 1,2-dichlorobenzene at 20.1 °C.



**Figure 6.** Static dielectric constant $\epsilon_{12}$ versus mass fraction $w_{12}$ for $C_{60}$ in *cis*-decahydronaphthalene at 20.118 °C.

component $\phi_2$ is defined as

$$\phi_2 = \frac{m_2 v_2}{m_1 v_1 + m_2 v_2} = \frac{V_2}{V_1 + V_2} \qquad (14)$$

where $V_1$ and $V_2$ are the volumes of components 1 and 2, respectively. Figures 6−8 are the corresponding plots of static dielectric constant $\epsilon_{12}$ versus mass fraction $w_2$. The results of the analyses of Figures 3−8 are shown in Table 1.

It should be apparent that all of the extrapolated values for $v_1$ and $\epsilon_1$ are in excellent agreement with the measured values, with the exception of the dielectric constant of toluene. However, in both cases (i.e., measured and extrapolated values for $\epsilon_1$),
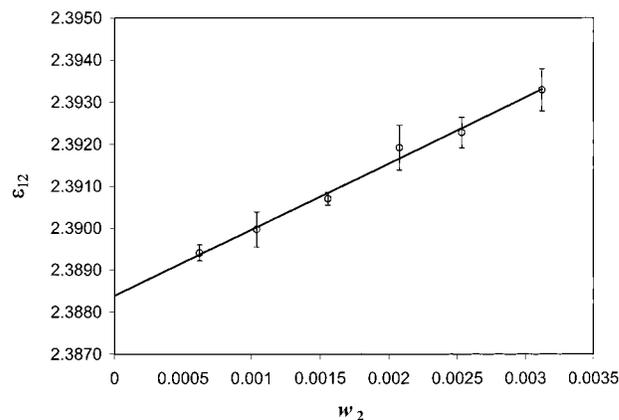


**Figure 7.** Static dielectric constant $\epsilon_{12}$ versus mass fraction $w_{12}$ for $C_{60}$ in toluene at 20.118 °C.
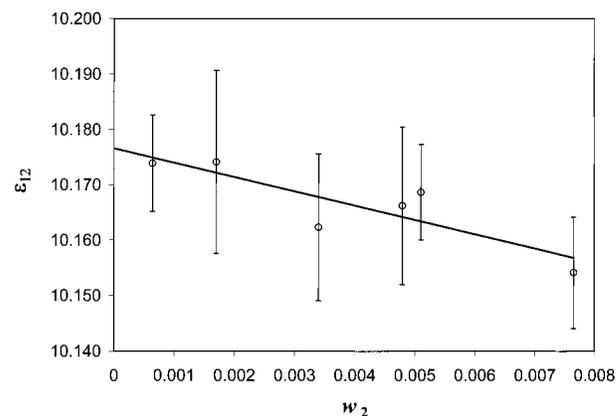


**Figure 8.** Static dielectric constant $\epsilon_{12}$ versus mass fraction $w_{12}$ for $C_{60}$ in 1,2-dichlorobenzene at 20.118 °C.

the relative difference between the measured and extrapolated values is less than $5 \times 10^{-4}$. In anticipation of our final results, we shall assume that a difference of this magnitude can be neglected. It is notable that because the value for $\epsilon_1$ obtained by extrapolation is greater than the measured value for toluene, it is possible that some moisture uptake has occurred. As stated previously, the amount appears to be very small. With the exception of the specific volume of ODCB, the literature values listed in Table 1 lie within the experimental uncertainty of all values for $v_1$ and $\epsilon_1$.

**3.3. Dielectric Constant of Isolated $C_{60}$ Molecules.** Figures 9−11 are plots of the reduced dielectric constant $[\epsilon_{12}(\phi)/\epsilon_1]$ as a function of volume fraction of $C_{60}$ ($\phi_2$). (In calculating the reduced dielectric constant, we used the value for $\epsilon_1$ obtained by eq 1.) The slope of the plots were analyzed according to eqs 3 and 4. The results of these analyses are given in Table 2. In examining the effectiveness of our solution measurements in obtaining the correct value for the dielectric constant of the isolated $C_{60}$ particle, we will split the results into each of the model predictions. In the spherical particle model (Maxwell model) the results in *cis*-decahydronaphthalene agree within the experimental uncertainty with the value obtained from molecular beam measurements, but disturbingly, the values for toluene and ODCB do not. This might lead one to the conclusion that an induced dipole moment is present in systems where there is a polar solvent, since toluene and ODCB have a permanent dipole moment with toluene having a dipole moment of $1.2 \times 10^{-30}$ C m (0.36 D) and 1,2-dichlorobenzene having a dipole moment of $8.3 \times 10^{-30}$ C m (2.50 D). *cis*-Decahydronaphthalene has a very small dipole moment, and this solvent is "nonpolar".[46] Rough estimates of the apparent dipole moment $\mu$ can be

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**TABLE 1: Density and Specific Volume of the Solvents**

| | *cis*-decalin | toluene | 1,2-dichlorobenzene |
|---|---|---|---|
| $v_1$ measured (cm³/g) | 1.11489 ± 0.00003 | 1.15350 ± 0.00003 | 0.76567 ± 0.00002 |
| $v_1$ extrapolated (cm³/g) | 1.11494 ± 0.00002 | 1.15351 ± 0.00003 | 0.76563 ± 0.00002 |
| $v_1$ lit. value[a] (cm³/g) | 1.115 | 1.154 | 0.76640 |
| $\epsilon_1$ measured | 2.1818 ± 0.0004 | 2.3873 ± 0.0005 | 10.177 ±0.002 |
| $\epsilon_1$ extrapolated | 2.1812 ± 0.0004 | 2.3883 ± 0.0003 | 10.177 ± 0.005 |
| $\epsilon_1$ lit. value | 2.176[b] ±0.006 | 2.391[c] ± 0.004 | 10.3 ± 0.3[d] |

[a] The specific volumes listed are for 20.0 °C and were obtained from the density data in the *CRC Handbook*.[51]  [b] The dielectric constant for *cis*-decahydronaphthalene at 20.0 °C ± 0.1 °C and 505 kHz was obtained from the work of Bird and Daly.[52]  [c] The dielectric constant of toluene was determined at 20.1 °C by linear extrapolation of data at 10 kHz obtained at several temperatures from the work of Mopsik.[43,47]  [d] The dielectric constant of 1,2-dichlorobenzene was determined at 20.1 °C by linear extrapolation of data obtained at several temperatures for two sets of dielectric data, one by Curry and Gilkerson at 10 kHz and one by Flaherty and Stern at an unspecified frequency.[43,53,54]
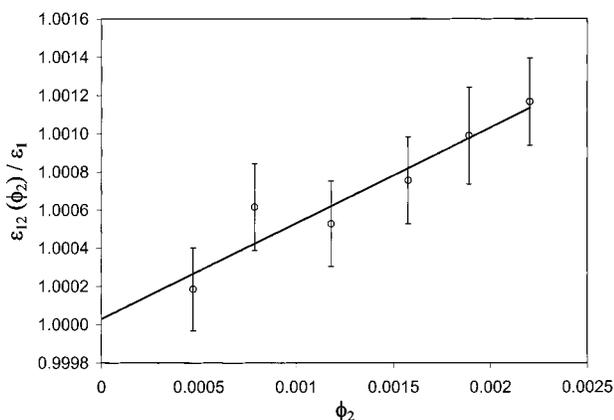


**Figure 9.** Reduced dielectric constant $\epsilon_{12}(\phi_2)/\epsilon_1$ as a function of volume fraction of Buckminsterfullerene for $C_{60}$ in *cis*-decahydronaphthalene at 20.118 °C.
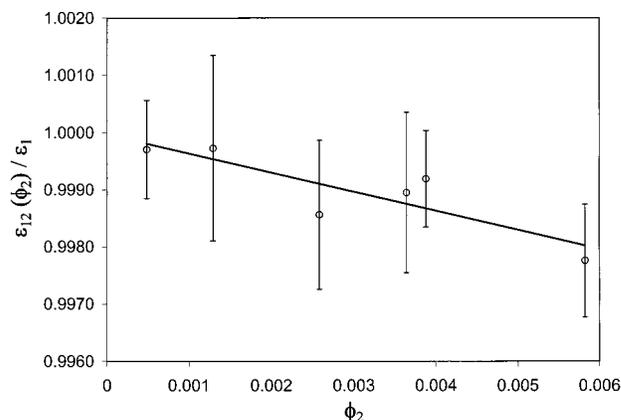


**Figure 11.** Reduced dielectric constant $\epsilon_{12}(\phi_2)/\epsilon_1$ as a function of volume fraction of Buckminsterfullerene for $C_{60}$ in 1,2-dichlorobenzene at 20.118 °C.
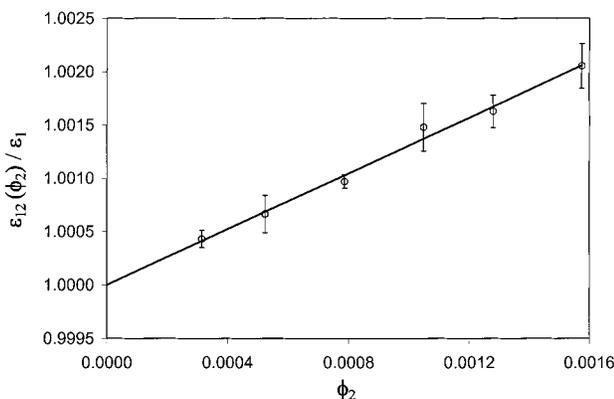


**Figure 10.** Reduced dielectric constant $\epsilon_{12}(\phi_2)/\epsilon_1$ as a function of volume fraction of Buckminsterfullerene for $C_{60}$ in toluene at 20.118 °C.

obtained using the Debye−Langevin equation (in SI units)

$$P = \frac{\epsilon - 1}{\epsilon + 2}\left(\frac{M}{\rho}\right) = \frac{N_A}{3\kappa_0}\left(\alpha_{SI} + \frac{\mu^2}{3k_BT}\right) \qquad (15)$$

where $k_B$ is Boltzmann's constant. The value for $\alpha_{SI}$ used in the above equation was that obtained from the dielectric constant of $C_{60}$ which, in turn, was determined from measurements in cis-decahydronaphthalene and eq 6. The apparent dipole moments calculated using eq 15 were $7 \times 10^{-30} \pm 1 \times 10^{-30}$ C m (2.2 ± 0.3 D) for $C_{60}$ in toluene and $7 \times 10^{-30} \pm 2 \times 10^{-30}$ Cm (2.0 ± 0.6 D) for $C_{60}$ in 1,2-dichlorobenzene. Within the expanded standard uncertainty of the measurements, there is no statistical difference between these two dipole moments. The concept of an induced dipole moment in the case of toluene is easily disproved, since measurements similar to those presented

**TABLE 2: Static Dielectric Constant of the Isolated $C_{60}$ Molecule**

| solvent | $\epsilon_2$ (eq 3) | $\epsilon_2$ (eq 4) |
|---|---|---|
| molecular beam[32] | 3.6 ± 0.4 | |
| *cis*-decahydronaphthalene | 3.6 ± 0.8 | 2.9 ± 0.7 |
| toluene | 7.9 ± 0.8 | 3.8 ± 0.4 |
| 1,2-dichlorobenzene | 7 ± 2 | 13 ± 4 |

in this paper were performed for toluene at 15 °C and 30 °C. The result was that there was no temperature dependence which could be attributed to a dipole moment. This finding indicates that we should model the geometry of the buckyballs more realistically, before rejecting the validity of the continuum model description of the dielectric constant of these dispersions. We then model the buckyballs as hollow spherical particles and assume that the core has a dielectric constant equal to that of vacuum. Notably $\epsilon$ of dry air differs from that of vacuum by approximately 0.05% ($\epsilon_{air} \simeq 1.0005$ at 20 °C).

Using the spherical shell model, the static dielectric constant of isolated $C_{60}$ molecules measured in *cis*-decahydronaphthalene and toluene agree within the experimental uncertainty with those measured by the molecular beam technique. There still is a large discrepancy between the molecular beam estimate of the dielectric constant for $C_{60}$ and the virial estimate for the highly polar solvent, 1,2-dichlorobenzene, however. (Toluene is only slightly polar, so that induced polarization effects should be weak.[47]) It is noted that the ODCB data set exhibits a much higher degree of scatter than the other measurements which leads to the possibility that other effects may complicate these measurements. For example, clustering has been reported for $C_{60}$ in other solvents[48−50] and we strongly suspect that this might be occurring in the ODCB solution. Light scattering measurements as in previous studies[48,49] on benzene solutions of $C_{60}$ could help to resolve this possibility. The ODCB solutions

are also potentially sensitive to moisture contamination, even though we endeavored to maintain dry conditions. It is then premature to ascribe a precise cause to the deviant estimate for $\epsilon$ in this solvent. Further studies of our method of estimated $\epsilon$ of nanoparticles, especially in the case of polar solvents, seems to be warranted. A greater understanding of the origin of the nanoparticle clustering phenomena in various solvents is also evidently needed.

There are several implications of these measurements as they pertain to nanoparticle suspensions. We have demonstrated (at least for the case of the two solvents with a relatively small dielectric mismatch between solvent and nonpolar particle) that the dielectric constant of the isolated nanoparticle can apparently be determined using a continuum model and the results compare favorably with independent molecular beam measurements. There is no appreciable "solvent effect" under these conditions. We do find complications in the case of the highly polar solvent ODCB. This finding indicates that we must examine the applicability of continuum models to estimate the properties of nanoparticles in greater detail, especially in the case of polar solvents or suspending media. There are several complications found in these polar solvents (water uptake, "solvent effect", etc.) that need to be examined further before our methodology can be applied to estimating the dielectric constant of nanoparticles reliably. In the future, we plan to perform measurements on buckytubes in *cis*-decahydronaphthalene and toluene to examine the effect of particle asymmetry on the virial coefficient for buckytubes in solution and to systematically explore the impact of particle clustering on the solution dielectric properties of solutions of nanoparticles such as $C_{60}$.

## 4. Conclusions

We have presented the results of our measurements on the specific volume and static dielectric constants of Buckminster-fullerene ($C_{60}$) solutions. It has been demonstrated that continuum model predictions are successful in predicting the dielectric properties of nonpolar nanoparticles in a matrix with a low dielectric mismatch.

We have shown that solution measurements minimize the normal problems inherent in determining the dielectric properties of $C_{60}$ films, such as dissolved oxygen, interfacial impurities, etc.[31] Preliminary measurements have indicated large deviations of molecular beam and solution measurements of the dielectric constant of $C_{60}$ in the case of a highly polar solvent, ODCB. These solutions are subject to a number of complications and it is not yet clear where fundamental modifications of the continuum model are necessary. It is clear that the polar solvents must be made very pure and the complication of water contamination is a general concern when highly polar solvents are utilized in this type of study.

A great deal of further experimentation will be necessary to determine whether continuum models can successfully predict bulk material properties of nanoparticle filled materials based upon the appropriate parameters for the matrix and the inclusions. However, we feel that this work does suggest that careful choice of a matrix will allow for determination of the dielectric properties of nanometer-scale objects. It should also be possible to extend this approach to many other properties of interest[9] (shear modulus, refractive index, magnetic permeability, etc.) so this simple method promises to have wide applicability.

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