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Electrical conductivity of dispersions: from dry foams to dilute suspensions

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Abstract

We present new data for the electrical conductivity of foams in which the liquid fraction ranges from two to seventy per cent. We compare with a comprehensive collection of prior data, and we model all results with simple empirical formulae. We achieve a unified description that applies equally to dry foams and emulsions, where the droplets are highly compressed, as well as to dilute suspensions of spherical particles, where the particle separation is large. In the former limit, Lemlich's result is recovered; in the latter limit, Maxwell's result is recovered.

1. Introduction

The electrical conductivity of dispersions is an age-old problem. One line of research concerns the 'very-wet' limit, where gas or liquid bubbles, or spherical solid particles, are widely separated in a large volume of liquid [1, 2]. Another line of research concerns the 'very-dry' or 'foam' limit, where bubbles are tightly compressed in a small volume of liquid [3–5]. In both, the goal is to understand the relative conductivity of the dispersion, $\sigma = \sigma_{\mathrm{sample}}/\sigma_{\mathrm{liquid}}$, in terms of the volume fraction of the continuous liquid phase, ε. Experimental measurement of σ could then be used to deduce the value of ε for an unknown sample. The well-accepted behaviour is as follows. In the very-wet limit of $\varepsilon \to 1$, Maxwell's result holds: $\sigma = 2\varepsilon/(3-\varepsilon) = 1 - (3/2)(1-\varepsilon) + (3/4)(1-\varepsilon)^2 + \mathrm{O}(1-\varepsilon)^3$ [1]. In the very-dry limit of $\varepsilon \to 0$, Lemlich's result holds: $\sigma = (1/3)\varepsilon$ [3]. The former follows from the form of the electric field in and around an isolated insulating sphere; the latter follows from the random orientation of Plateau borders, which are nearly straight channels of scalloped-triangular cross-section at which three soap films meet. Considerable effort is spent on deducing the next-order terms in both wet [6–10] and dry [11] limits. Considerable effort is also spent on developing experimental apparatus for both wet [12–14] and dry [11, 15, 16] extremes. Unfortunately, there is little understanding of the intermediate regime where both phases occupy significant volume. Also there are no data sets that span the entire range of liquid fraction. Furthermore, there appears to be little contact between researchers focusing separately on the very-wet and very-dry regimes. The two lines of research are essentially disjoint in terms of both theory and experiment.

In this paper we explore electrical conductivity in the intermediate regime. Our approach is twofold. First, we scour the literature for data sets obtained in both wet and dry limits. Second, we measure the relative conductivity for sequences of foams with known liquid fraction. We find that data in the wet and dry regimes match smoothly, and can be described by simple empirical formulae. This will facilitate experimental studies, and could guide future theoretical understanding.

2. Prior observations

In the very-dry 'foam' limit, we are aware of four widely cited data sets. The first was obtained by Clark for gas bubbles in five different aqueous solutions [17]. The second was obtained by Datye and Lemlich for gas bubbles of different size distributions in three different aqueous solutions [18]. The third was obtained by Peters for gas bubbles in aqueous solution [19, 11]. A fourth data set was obtained by Curtayne for two different size bubbles [20]; a polynomial fit to this data is shown in figure 9.2 of [4]. We extract conductivity data from figure 1 of [17] and from figure 5 of [11]; Datye kindly provided tables of his data; Hutzler kindly provided a table of Curtayne's data. In the very-wet limit, we are aware of three widely cited data sets. The first was obtained by Oker-Blom for spherical sand grains set in gelatin, with results tabulated by Fricke [21]. The second was obtained by Meredith and Tobias for oil-in-water emulsions [22]. The third was obtained by Turner for solid particles in aqueous solution [23]. We extract conductivity data from table 3 of [21], from figure 4 of [22], and from figure 3 of [23].

The range of data in the dry regime is primarily $\varepsilon < 0.3$, plus two lone points by Clark at $\varepsilon = \{0.4, 0.54\}$. The range of data in the wet regime is primarily $\varepsilon > 0.5$, plus one lone point at $\varepsilon = 0.4$ by both Oker-Blom and Turner. Thus the wet and dry data sets are nearly non-overlapping, and there is a dearth of data across the range $0.3 < \varepsilon < 0.5$.

3. New measurements

To bridge the gap between the data for very-dry and very-wet regimes, we perform two independent measurements of the relative conductivity of a sequence of foams. At Penn, the base aqueous solution is AOS (α-olefin sulfonate, Bio-Terge AS-40 CG-P, Stepan Company) plus NaCl with concentrations of 8% and 0.01% by weight respectively; the gas is nitrogen. At Orsay, the base solution is SDS (sodium dodecylsulfate) plus dodecanol; the gas is either pure C_2F_6 or else nitrogen plus trace amounts of C_6F_{14}. In most cases, the foams are produced by turbulent mixing with an apparatus similar to that of [24], giving polydisperse bubbles with an average diameter of 0.1 mm. For the driest foams at Orsay, bubbles are created by forcing gas through porous frits; by changing the porosity, the average bubble diameter can be varied from 1 to 4 mm.

At Penn, foam conductivity is measured as follows. The foam delivery hose is connected to an acrylic tube, 30 cm long and 1.27 cm inner diameter, that has brass hose fittings screwed on both ends. The hose fittings serve as electrodes, which are connected to an impedance meter (1715 LRC Digibridge, QuadTech). This meter is configured to measure the resistance of a parallel resistor–capacitor equivalent circuit, and to operate at a frequency of 1 kHz and voltage level of 1.00 V. At this frequency, the capacitive contribution is negligible. The resistivity of freshly produced foam is measured while it flows downwards through the vertically oriented tube. The results are normalized by the resistivity of the base aqueous surfactant solution, when it entirely fills the tube. The liquid fraction of the foam is measured by weighing a known volume of foam, collected from the output of the acrylic tube concurrently with the conductivity measurement. The flow speed of the foam is sufficiently great that no drainage or creaming is observed.

At Orsay, foam conductivity measurements are made in a Plexiglas column (height 50 cm, and cross-section 4 × 4 cm^2) in which 26 pairs of electrodes are embedded, facing each other along the height [25]. With this set of electrodes, we measure the foam conductance with an impedance meter (8284A, Hewlett-Packard). Frequency and voltage are the same as in the Penn experiment: 1 kHz and 1 V. For wet foams, $0.07 < \varepsilon < 0.50$, the cell is filled with a foam made out of the turbulent mixer apparatus. The foam conductivity is measured during the filling and immediately thereafter; absence of drainage is confirmed by the absence of vertical gradients in conductivity. For each run, after the cell is filled, a sample of foam is collected in a calibrated vessel and weighed to determine the liquid fraction. For dry foams, $0.02 < \varepsilon < 0.10$, a porous glass frit is mounted at one end of the conductivity cell, and the foam is made directly inside it by bubbling gas through the frit, which is immersed into the surfactant solution. The liquid fraction is varied by wetting the foam from above with the same surfactant solution, at a controlled injection rate Q. This method provides uniform foams with no vertical liquid fraction gradients [26]. The liquid fraction is determined by measuring the drainage front velocity, v, and using the conservation equation $\varepsilon = Q/(vA)$, where A is the foam cross section [4].

Altogether, we have measured relative conductivity over a liquid fraction range of $0.15 < \varepsilon < 0.80$ at Penn and $0.02 < \varepsilon < 0.50$ at Orsay.

4. Conductivity versus liquid fraction

The relative conductivity is plotted versus liquid volume fraction in figure 1 for all data sets, new and old. As expected, the Maxwell and Lemlich formulae appear to hold in their respective limits. For intermediate liquid fractions, prior very-wet and very-dry data sets are nearly disjoint but appear to extrapolate smoothly toward one another. Our new data fill in the gap and bear this out. This encourages us to seek simple empirical formulae that hold for *all* liquid fraction regimes. We are aware of three previous suggestions:

$$\varepsilon = 3\sigma - \tfrac{5}{2}\sigma^{4/3} + \tfrac{1}{2}\sigma^2, \tag{1}$$

$$\sigma = \tfrac{1}{3}\left(\varepsilon + \varepsilon^{3/2} + \varepsilon^2\right), \tag{2}$$

$$\sigma = \tfrac{1}{3}\varepsilon + \tfrac{5}{6}\varepsilon^2 - \tfrac{1}{6}\varepsilon^3. \tag{3}$$

The first is due to Lemlich [27], the second and third are due to Curtayne [20, 4]. These three formulae all obey the Maxwell and Lemlich limits but underestimate the conductivity data at intermediate liquid fractions. Curtayne's equation (2), plotted as a long-dashed curve in figure 1, comes closer to the data than the other two formulae.

Here we suggest modelling the data by rational functions formed by the ratio of second-order polynomials. From the point of view of a theorist wishing to predict conductivity in terms of a given liquid fraction, the appropriate form would be $\sigma = 2\varepsilon(1 + A\varepsilon)/[6 + (-7 + 3A)\varepsilon + (3 - A)\varepsilon^2]$. From the point of view of an experimentalist wishing to deduce liquid fraction in terms of the measured conductivity, the appropriate form would be $\varepsilon = 3\sigma(3 + B\sigma)/[3 + (9 + 2B)\sigma + (-3 + B)\sigma^2]$. All the numerical coefficients, except

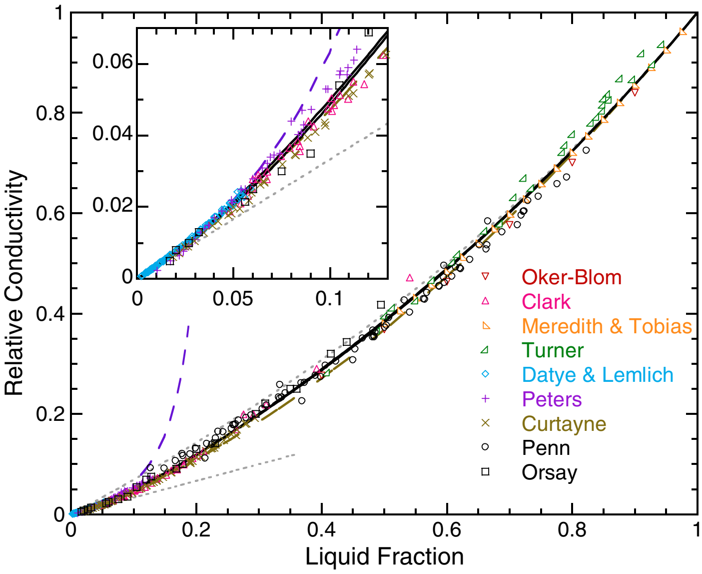

Figure 1. Relative conductivity $\sigma = \sigma_{\text{sample}}/\sigma_{\text{liquid}}$ versus liquid fraction ε for widely cited data sets, plus our two new data sets, as labelled. The dotted curves represent the Maxwell and Lemlich limits, $2\varepsilon/(3-\varepsilon)$ and $\varepsilon/3$, respectively; the long-dashed curve represent Curtayne's formula, equation (2); the short-dashed curve represents the non-analytic parametric formulation of [11]. The solid curves represent equations (4) and (5), which we construct to have the correct wet and dry limiting behaviours and to fit the data smoothly in between.

(This figure is in colour only in the electronic version)

for one, are fixed by requiring that the Maxwell and Lemlich limits be satisfied. Adjusting the free parameter to fit the entire collection of data, we find $A = 12 \pm 1$ and $B = 33 \pm 2$. The resulting empirical formulae,

$$\sigma = 2\varepsilon(1 + 12\varepsilon)/(6 + 29\varepsilon - 9\varepsilon^2), \tag{4}$$

$$\varepsilon = 3\sigma(1 + 11\sigma)/(1 + 25\sigma + 10\sigma^2), \tag{5}$$

give an excellent description of all data, as shown by the nearly identical solid curves in figure 1. These formulae can be used with some confidence owing both to their agreement with known limits and to the smooth way they interpolate between data sets in the wet and dry regimes.

Before closing, we compare higher-order behaviour with existing literature. On the wet side, the limiting expansions of equations (4) and (5) are respectively $\sigma = 1 - (3/2)(1-\varepsilon) + (0.65 \mp 0.01)(1-\varepsilon)^2 + O(1-\varepsilon)^3$. These compare well with [6, 7], which give the second-order term as $0.656(1-\varepsilon)^2$ and $0.588(1-\varepsilon)^2$ respectively. On the dry side, the limiting expansions of equations (4) and (5) are respectively $\sigma = \varepsilon/3 + (2.0 \pm 0.4)\varepsilon^2 + O(\varepsilon)^3$. These cannot be directly compared with [11], which proposes a non-analytic parametric formulation of liquid fraction and relative conductivity as $\varepsilon = 0.171a^2(1 + 1.5a)$ and $\sigma = 0.171a^2/(3 - 3.81a)$; eliminating the parameter a and expanding gives $\sigma = \varepsilon/3 - 0.185\varepsilon^{3/2} + 4.15\varepsilon^2 - 19.6\varepsilon^{5/2} + \cdots$. On this basis, we attempt to describe the data by $\sigma = [\varepsilon + (1+C)\varepsilon^{3/2}]/[3 - (1-2C)\varepsilon^{1/2} - C\varepsilon]$, which also obeys the Maxwell and Lemlich limits. The best fit, $C = 2.8 \pm 0.8$, has a χ^2 value that is about ten per cent worse than that for equation (4); it gives the leading correction to Lemlich as $+0.76\varepsilon^{3/2} - 0.85\varepsilon^2$. Due to scatter in the data (see inset of figure 1), we cannot rule out either of these contrasting non-analytic expansions.

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