Plasma-Like Negative Capacitance in Nano-Colloids

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A negative capacitance has been observed in a nano-colloid between 0.1 and $10^{-5}$ Hz. The response is linear over a broad range of conditions. The low-$\omega$ dispersions of both the resistance and capacitance are consistent with the free-carrier plasma model, while the transient behavior demonstrates an unusual energy storage mechanism. A collective excitation, therefore, is suggested.

The origin of the negative capacitance (NC) observed in many systems with mesostructures has been debated since 1988. Experimentally, this reactive response is probed by the phase shift between the applied ac voltage, $V_{ac}$, and the resulting current, $I_{ac}$, at a frequency $\omega$. A negative phase-angle between $I_{ac}$ and $V_{ac}$, therefore, represents a NC. Jonscher, Penin et al., and others, however, repeatedly emphasize that the clue to these unusual observations lies in the equivalent negative transient current $\Delta I(t > 0) = [I(t) - I(\infty)]$ after a positive voltage jump $\Delta V = V(0^+) - V(0^-)$ at $t = 0$. Such a retarded current response, consequentially, is attributed to the inertia of the associated process. Penin\textsuperscript{2} refers to such a process, which is characterized by the equation $dI/dt + I/\tau = bV$ with parameters $\tau$ and $b$, as a $\tau$ system. The equation, it should be pointed out, is actually that of a free-carrier plasma with the solution of $I_{ac}/V_{ac} = 1/R - i\omega C = b/(i\omega + 1/\tau) = b \cdot (1/\tau - i\omega)/(\omega^2 + 1/\tau^2)$, where $R$ is the resistance, $C$ is the capacitance, and $1/\tau$ represents the plasma damping. It is therefore interesting to note that the proper mesostructures may theoretically lead to a negative dielectric response and any negative static $\epsilon'$ (which leads to NC at $\omega = 0$) can be described as ghost-plasmons.\textsuperscript{2}

A true plasma-like response, however, should also have a linear $I - V$ characteristic as well as follow the causality correlation between $R$ and $C$. The observed $\Delta I(0^+)/\Delta V$, for example, should include a component of $\Delta I_1 = 1/R_{ac=\infty} - 1/R_{ac=0} = -b\tau$ from the $R$-dispersion in addition to the term of $\Delta I_2 = 2/\pi \int [C(\omega) - C(\infty)]d\omega = -b\tau$ from the $\omega$-dependent $C$ alone. The high nonlinearity as well as limited data resolution in previously published data, unfortunately, makes a full identification difficult.\textsuperscript{8,12,13,15} In some cases (such as the impact ionization of gas in Ref. 5), such a plasma interpretation is obviously an oversimplified approximation. Here we report the NC below 1 Hz in a giant electrorheological (ER) fluid.\textsuperscript{8} The $I - V$ characteristic is linear across a broad $V_{ac}$ range, and all features, e.g. $C(\omega)$, $\Delta I$, and the $R(\omega)$ contribution to it, are consistent with a plasma-like excitation with an extremely long $\tau$.

The ER fluid is a colloid of silicone oil and 20 nm urea-coated Ba$_8$Rb$_4$TiO(C$_2$O$_4$)$_2$ nanoparticles. The nanoparticle to oil ratio is 10 g: 3 ml. The capacitor cells were constructed of two parallel gold or copper electrodes with dimensions of 6 mm $\times$ 13 mm and a gap distance of 0.1 mm. The $ac$ measurements were performed via a serial connected $ac$ voltage source, capacitor cell, and current meter. Only $dc$ couplings were present. The phase angle was verified with resistors and capacitors of known values. Both the systematic error and the resolution of the phase angle are within 0.05$\deg$. Details of both the $ER$ fluid preparation and the measurements have been reported before. The same hardware was used in the transient measurements with the pulse output and the voltage reading being synchronized within $10^{-4}$ sec.

The effective $R(f)$ and $C(f)$, where $f = \omega/2\pi$, with an $ac$ excitation signal $V_{ac}$ of 1 V between 0.0005 and 100 Hz is shown in Fig. 1a and b under various $dc$ biases $V_{dc}$. With zero bias, the capacitance increases with the decrease of $\omega$. This behavior is typical of a disordered system and is referred to as the universal dielectric response (UDR).\textsuperscript{10} With the application of a $dc$ bias, the low frequency capacitance becomes negative while the UDR characteristics are retained at higher frequencies. The capacitance changes from positive to negative around 0.1 Hz and is independent of the bias for $V_{dc} \geq 300$ V. This excellent linearity is verified by the $V_{ac}$-independence of $C$ up to 100 V peak-to-peak (inset, Fig. 1a). It is interesting to note that the observed dispersion can be roughly separated into two parts: a relatively small UDR-like $C(\omega) > 0$ above 1 Hz and a plasma-like NC (solid line in Fig. 1b), which dominates the off-phase part below 0.01 Hz. Presently, the exact role of the $dc$ bias in the induced NC is unclear. It is believed that excess carriers are injected into the system with the application of bias, resulting in the plasma-like characteristics.

The transient current should be negative around and after 0.1 sec. based on the measured $C(\omega)$ and linearity.
We demonstrated this by directly measuring $\Delta I(t)$ for a voltage sequence of 340 V/350 V/360 V/350 V with a uniform time interval of 1032 sec. The trend can even be observed in the raw data, although with a significant baseline shift (inset, Fig. 2). To obtain a quantitative result, a smooth fit of $I_{\text{base}} = \sqrt{m + n \cdot t^2}$ (the thick line in the inset) was used as the baseline, where $m$ and $n$ are fitting parameters. The transient currents at 350 V during a 10 hr period (about 7 cycles) are then realigned by subtracting the start times of each cycle (grey traces in Fig. 2), and the average is plotted as the black line (the thick line with its width representing the standard error. The $\Delta I$ is indeed negative after 1–2 ms, and the baseline shifts do not affect the conclusion (Fig. 2).

For further comparison with the plasma model, both the nonlinearity and the $\omega$-dependence in the $R$-section were carefully reviewed. The relatively small $\Delta I(t)$, < 1% of the corresponding $I(\infty)$, requires better resolution than the data in Fig. 1, where the long-time shift limits the data accuracy (the data acquisition requires a few-week period). Local ac $I(V)$ loops with the same $V_{dc}$ of 350 V and a peak-to-peak $|V_{ac}|$ of 20 V, therefore, were measured at 0.3 and 0.001 Hz, respectively (Fig. 3). It should be pointed out that the contributions from both the $\omega > 0.3$ Hz and the $\omega < 0.001$ Hz parts should be negligible within the time window of 1–1000 sec. The relevant contributions from the passive $R$-channel at $t = 0^+$ and $\infty$, therefore, may be deduced from $R(0.3 \text{ Hz})$ and $R(0.001 \text{ Hz})$, respectively. The passive and reactive components, i.e., the $R$ and the $C$ of the sample, are represented by the non-hysteretic and the hysteretic parts of the $I - V$ loops, respectively (lower inset, Fig. 3). The $R$ component, therefore, is taken as the average of the $V$ increase- and $V$ decrease-branches (Fig. 3). Two features immediately emerge: a) the $I - V$ is rather linear within the experimental resolution of a few tenths of a percent over a 20 V range; and b) there is a significant $\omega$-dependence of $R$, which contributes to $\Delta I$. The observed $\Delta V \cdot (1/R_{0.3 \text{ Hz}} - 1/R_{1 \text{ mHz}}) \approx 0.08 \mu\text{A}$ (Fig. 3) is roughly half of the transient current directly measured (Fig. 3). It is interesting to note that this is exactly what is expected from the plasma model: $\Delta I_1 = -b r = \Delta I_2 = \Delta I/2$. Despite the large background, the plasma-like $R$-contribution is demonstrated in the observed NC.

Another interesting issue is the energy balance in such a system. The negative transient current $\Delta I$ actually flows against the field for a positive $\Delta V$, corresponding to an energy storage/conversion in the linear system (Fig. 3). Unlike ordinary capacitors, energy is released from the material in the $V$-increase branch, but stored during the $V$-decrease branch. This is, again, a characteristic of a plasma-like excitation. The extremely long phase coherence period, $\tau \sim 141 \text{ s}$, however, suggests that the excitation may be soliton-like in nature. An unusual surface plasma and quantum capacitance are possible candidates.

In summary, we have observed a negative capacitance in an ER fluid. Linearity is observed over broad ranges of $V_{dc}$ and $V_{ac}$. The dispersions in both $C$- and $R$-channels and the associated energy storage/conversion demonstrate that plasma-like excitations are present. This demonstrates that dielectric properties can be drastically changed through mesostructures, and opens the door for novel nano-materials.

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FIG. 1: a) $C(f)$ at $V_{dc}$ of 0 (circles), 3.5 (squares) and 5 kV/mm (triangles). The line is the fit for free carrier plasma with $b = 7.2 \cdot 10^{-11} \text{ s}^{-2}$ and $\tau = 141 \text{ s}$. Inset: the deduced $C$ vs. $V_{ac}$ at $V_{dc} = 350$ V and 10 mHz. b) Differential $R$ at $V_{dc}$ of 500 (squares) and 350 V (triangles).

FIG. 2: $\Delta I$ during a voltage serial of 340 V/350 V/360 V/350 V... Inset: the raw data of $I$. Thick solid line: the assumed base line. The positive part associated with the geometric capacitance is absent due to the time window used.

FIG. 3: The non-hysteretic parts of the $ac$ loop at $V_{dc} = 350$ V and $V_{ac} = 10$ V. Solid line: at 1 mHz; dashed line: 0.3 Hz. Bottom inset: the raw I-V loops at 1 mHz. Top inset: The power output after a positive 10 V jump.
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