AC electrolyte conductivity in the $\omega \tau < 1$ regime

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Abstract

Details of the dynamic behaviour of different charged clusters in liquids are discussed. Their associated mass is considered which possesses a number of interesting features in a normal viscous liquid.

In the two previous papers [1, 2] the authors noted that the systematically observed [3–6] temperature dependence of the positive ions effective mass in superfluid helium has mainly normal (non-superfluid) origin. Formally, the point is that under non-stationary conditions the Stokes drag force $F(\omega)$ acting on a sphere moving in a normal fluid actually has both real and imaginary components. In the extreme case of low Reynolds numbers one has [7, 8]

$$F(\omega) = 6\pi \eta R \left(1 + \frac{R}{\delta(\omega)}\right) v(\omega) +$$

$$3\pi R^2 \sqrt{\frac{2\eta \rho}{\omega}} \left(1 + \frac{2R}{9\delta(\omega)}\right) i\omega v(\omega), \quad (1)$$

where $\rho$ is the liquid density, $\eta$ is its viscosity, $v$ is the sphere velocity, $\delta(\omega)$ is the so-called viscous penetration depth, and $R$ is the sphere radius (or effective radius of the ion or a different particle or cluster).
It is natural to identify the coefficient at $i\omega v(\omega)$ with the efficient associated mass of the cluster:

$$m_{\text{ass}}(\omega, R) = m_{id}(\rho, R) \left[ 1 + \frac{9 \delta(\omega)}{2R} \right],$$

$$m_{id}(\rho, R) = \frac{2\pi \rho R^3}{3} \quad (2)$$

The associated mass $m_{\text{ass}}$ proves to be frequency-dependent (the dependence being rather strong at low frequencies) and this circumstance should be actually taken into account when considering the ion (cluster) dynamics employing the Navier-Stokes equation.

Experiments [3–6] were carried out at finite frequencies, and the data of Ref. [3] were obtained in the range of $\omega \tau < 1$, where $\tau$ is the the particle velocity relaxation time. Here, according to Eq. (2), the following asymptotics arising due to the ion effective mass growth at low frequencies holds:

$$\frac{\text{Im } v}{\text{Re } v} \propto \omega^{1/2}, \quad (3)$$

As to the measurements reported in Ref. [3] they on the one hand reveal a substantial polaronic effect (the ion mass proves to be several times larger than $m_{id}$). On the other hand, at low frequencies Eq. (3) does not hold and instead the limiting behaviour

$$(\text{Im } v/\text{Re } v)_{\omega \to 0} \propto \omega, \quad (3a)$$

is observed which is typical of clusters with fixed mass. An acceptable trade-off between (2) and (3) is that the $m_{\text{eff}}(\omega \to 0) \propto \omega^{-1/2}$ dependence should reach a saturation in the vicinity of $\omega \tau \sim 1$, i.e. in the frequency range where $\text{Re } F(\omega) \simeq \text{Im } F(\omega)$. Bearing this in mind, it is easy to show [1] that the associated mass $m_{\text{ass}}(\rho_n, R_n)$ for the superfluid helium transforms to

$$m_{\text{ass}}(\rho_n, R_n) = 2.1\pi R_n^3 \rho_n, \quad (4)$$

which means that the mass becomes frequency independent and its observed temperature dependence is due to the factor $\rho_n(T)$ in Eq. (4) and its maximum value substantially exceeds the ideal associated mass $m_{id}$. However, the assumption $\text{Re } F(\omega) \simeq \text{Im } F(\omega)$ is not quite consistent with the conditions of the experiments reported in Ref. [3].
Actually the effective mass saturation in the limit $m_{eff}(\omega \rightarrow 0)$ is related to the divergency in the linear approximation of the integral

$$W = \int \rho(r)u^2(r)d^3r,$$

(5)

where $u(r)$ is the velocity field falling off anomalously slow (as $r^{-1}$) at large distances from the body moving with a constant velocity $v$ through the liquid. The details of this non-linear scenario clearly indicated in Ref. [1] have not yet been studied. It is the purpose of the present paper to consider this scenario and discuss its applicability to data of Ref. [3].

1. Divergency of Eq. (5), and hence of the quantity $m_{ass}^{st}$

$$m_{ass}^{st}v^2/2 = W,$$

(5a)

can be eliminated in the so-called Oseen approximation [1,7,8] which reveals that the behaviour $u(r) \propto r^{-1}$ following from the linearized Navier-Stokes equation and resulting into the divergency (5) is actually replaced by the exponential decay of the velocity field at distances $r > R/\Re$, $\Re = Rv/\eta \ll 1$. Because of this exponential decay the quantity $m_{ass}^{st}$ becomes finite but acquires a non-linear dependence on velocity $v$

$$m_{ass}^{st} \simeq \frac{m_{id}}{\Re} \ln (1/\Re), \quad \Re = Rv/\eta \ll 1,$$

(6)

where $m_{id}$ is defined in Eq. (2) and $\Re$ is the Reynolds number. The additional factor in (6) accounts (with the logarithmic accuracy) for the presence of a laminar trace generated by a sphere moving through a viscous liquid.

The result (6) is consistent with both the linear asymptotics $m_{eff}(\omega \rightarrow 0) \propto \omega^{-1/2}$ and the requirement of reaching a plateau in the limit. The same treatment reveals the physical reasons of the divergency and the mechanism of its elimination. However, the progress in understanding leads also to some formal “losses” here since the cluster dynamics in the most interesting domain $m_{ass}^{st}/m_{id} \gg 1$ becomes non-linear. In particular, the Fourier representation providing a transparent interpretation of the difference between (3) and (3a) can no longer be used. Analysis of dynamic properties of the cluster described by Eq. (6) requires an alternative approach. In the present paper we discuss with this aim the problem of a step-like external force $F$ acting on a particle in viscous liquid. An appropriate quantity for the efficient particle mass is the combination

$$\Delta(t) = \frac{\dot{v}}{v_\infty - v(t)},$$

(7)
Figure 1: Crossover from the $\Delta(t)$ curve defined by the asymptotics (12) (thick solid line) to the long-time behaviour described by Eq. (15). Thin solid, dotted, and dashed lines correspond to $b/a = 3, 2$ and $1.4$, respectively.

which is calculated below.

For the Drude dynamics

$$(m_0 + m_{id})(\dot{v} + v/\tau) = eE(t), \quad (8)$$

the problem of a step-like external force $eE$ applied to the particle leads to the velocity $v(t)$

$$v(t) = v_\infty[1 - \exp(-t/\tau)], \quad v_\infty = eE\tau/(m_0 + m_{id}),$$

$$\Delta_{Drude} = 1/\tau, \quad (9)$$

where $m_0$ is the cluster bare mass, $m_{id}$ is defined by Eq. (2), and $e, E = const$ are the ion charge and driving electric field.

On the other hand, the conventional Langevine equation

$$(m_0 + m_{id})\ddot{v} + 6\pi R\eta v(t) = eE(t) \quad (10)$$

yields

$$v(t) = v_\infty[1 - \exp(-t/\tau_s)], \quad v_\infty = eE\tau_s/(m_0 + m_{id}),$$

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Figure 2: Temperature dependence of the viscosity $\eta$ and inverse mobility of negative ions $\mu^{-1}$ in helium.
Figure 3: Experimental (full squares) and theoretical (solid line calculated according to Eq.(17)) effective mass of negative ions in helium

\[ \tau_*^{-1} = \frac{6\pi R\eta}{(m_0 + m_{id})}. \]  

(10a)

\[ \Delta_{Langev} = \frac{1}{\tau_*} \]

In both cases (Eqs. (9) and (10)) the combination \( \Delta \) does not depend on time, and for the Drude case it also does not depend on the ion mass.

It is natural to develop the Stokes dynamics which we are interested in on the basis of the linear approximation where the Fourier component \( F(\omega) \) of the efficient drag force acting on the sphere moving in a viscous liquid is given by Eq. (1). For the velocity \( v(t) \) this force yields [8,9]

\[ v(t) = \frac{\gamma}{q} + \frac{\gamma p}{s_1 - s_2} \frac{\exp(s_1^2 t)}{s_1} - \frac{\exp(s_2^2 t)}{s_2} - \frac{1}{\sqrt{\pi}} \int_0^t \frac{\exp[s_1^2(t-\tau)] - \exp[s_2^2(t-\tau)]}{\sqrt{\tau}} d\tau \]

(11)

\[ v(t = 0) = 0 \]

where \( s_1 \) and \( s_2 \) are roots of the equation

\[ s^2 + ps + q = 0, \]
\[ q = \frac{\kappa}{m_0 + m_{id}}, \quad p = 3\frac{\sqrt{\kappa m_{id}}}{m_0 + m_{id}}, \]
\[ \gamma = \frac{eE}{m_0 + m_{id}}, \quad \kappa = 6\pi R\eta. \]

In agreement with the initial condition the left-hand side of Eq. (11) turns into zero at \( t \to 0 \) (which is readily verified if one employs the formulae \( s_1 + s_2 = -p, s_1s_2 = q \)).

In the opposite limiting case (where \( |s_{1,2}^2|t \gg 1 \)) the asymptotics
\[ e^{s^2t}\left[ \frac{1}{s} - \frac{1}{\sqrt{\pi}} \int_0^t \frac{\exp(-s^2\tau)}{\sqrt{\tau}} \right] \simeq \frac{1}{s^2\sqrt{\pi}t}[1 + \sum_{n=1}^{\infty} \frac{n(2n - 1)!!}{(2s^2t)^n}] \] (12)
holds. The structure of Eq. (12) reveals that the velocity \( v(t) \) approaches its asymptotic value \( v(\infty) = \gamma/q \) following a square-root law. It is also interesting that this asymptotics is formed exponentially with the typical time
\[ \tau_{1,2} \sim s_{1,2}^{-2} \] (13)

The appearance of exponentials (13) has a transparent qualitative interpretation. At the initial stage of the adjustment of \( v(t) \) to its steady-state value the process (11) resembles the Langevine scenario (10) with the typical exponential relaxation to the stationary behaviour and the relaxation time inversely proportional to the constant cluster mass. Later, when the associated mass starts to compete with the bare mass (either \( m_0 \) or \( m_{id} \)), a specific square-root approach to the stationary regime develops which is absent in the traditional dynamics.

In addition to being of substantial interest in itself, the results (11–13) proves to be important for correct formulation of our main problem of the velocity relaxation for the ion with mass (6). The point is that this definition does not apply at the initial stage of the process where both \( v(t) \) and the associated mass are growing with time, i.e. \( (dm/dv) > 0 \) following the scenario correctly described by Eq. (11). On the contrary, in the situation described by Eq. (6) one has \( (dm/dv) < 0 \).

Therefore, at some intermediate stage of the relaxation process the quantity \( (dm/dv) \) should have an extremum. At present we are unable to determine its position on the time axis in a self-consistent way, for example by solving the harmonic problem in the Oseen approximation. Therefore, the suggested approximate solution consists of two parts. The initial stage is
described by linearized dynamics (11–13). Its final part serves as the initial condition for dynamics with mass (6). The matching time \( t^* \) and the corresponding ion velocity \( v^* \) are taken to be \( t^* \simeq \tau_1 \) and \( v^* \simeq v(\tau_1) \) where \( \tau_1 \) is the longer one of the two times \( \tau_{1,2} \) (13).

The equation of motion to be solved is

\[
m_* \ddot{v} + \frac{m_{id}}{\text{Re} \ln (1/\text{Re})} \dot{v} + 6\pi R \eta v(t) = eE(t),
\]

\[
m_* = m_0 + m_{id} \quad \text{Re} = Rv/\eta
\]

\[
v \geq v^*, \quad t \geq t^*,
\]

where \( v^* \) and \( t^* \) are the matching velocity and time. To find \( v^* \) and \( t^* \), one should solve Eq. (14) for arbitrary values of \( v^* \) and \( t^* \) and then to study the general conditions of the intersection of curves \( \Delta(t) \) resulting from Eqs. (11) and (14). Then the intersection domain should be used to determine the values of \( v^* \) and \( t^* \). In our approximate approach we adopt \( t^* \simeq \tau_1 \), \( v^* \simeq v(\tau_1) \).

In the most interesting limit \( \text{Re} \ll 1 \) Eq. (14) can be simplified and explicitly integrated to yield

\[
\frac{1}{b} \left[ \ln \frac{v(t)}{b - av(t)} - \ln \frac{v^*}{b - av^*} \right] = t - t^*,
\]

\[
a = \frac{6\pi R^2}{m_{id}}, \quad b = \frac{eER}{m_{id}\eta}.
\]

It is obvious that under the conditions \( b - av(\infty) \to 0 \) the process (15) approaches the stationary regime with the velocity

\[
v(\infty) = v_{max} = eE/6\pi R \eta
\]

The general behaviour of \( \Delta(t) \) for \( v(t) \) specified by Eqs.(11) (in the range where asymptotics (12) is valid) and (15) is presented in Fig. 1 where the choice of parameters \( v^* \) and \( t^* \) is also illustrated.

2. The above analysis allows two qualitative conclusions to be made. First, in the domain \( \omega \tau_1 \ll 1 \) the cluster associated mass indeed has the structure (6) with the efficient velocity \( v = v_{max} \) reached by the ion in a single cycle. In these estimates employing the results obtained for a semi-infinite time interval the role of \( \omega^{-1} \) is played by appropriate finite time.
interval containing the initial point. Second, in the same frequency range $v_{\text{max}}$ can be estimated using either the data on stationary ion mobility in the Stokes form (16), or direct experimental measurements of that mobility covering also the transitional (Knudsen-Stokes) domain.

Let us discuss the data of Ref. [3] within the framework provided by Eqs. (14–16). First of all one should estimate the extent to which the inequality $\omega \tau_s \ll 1$ is satisfied assuming that $\omega \leq 10^{-10}$ s and $\tau_s \geq \tau_1$ (13). The available experimental data on the helium viscosity and normal component density yield

$$\eta \simeq 2 \cdot 10^{-5} \text{ g/(cm s)}, \quad \tau_s = \frac{\rho_n R_s^2}{2\eta} \leq 10^{-11} \text{ s},$$

$$\omega \tau_s \sim 10^{-1} < 1.$$

Further, the Reynolds number

$$\text{Re} \sim \rho_n v_D R_s / \eta, \quad \text{Re} \ll 1$$

proves to be dependent on the driving electric field strength whose value was not given in Ref. [3]. It is only clear that, the field should be sufficiently weak so that the Reynolds number is small (since otherwise it is impossible to explain the observed mass enhancement). Under these conditions, bearing in mind that

$$l_\eta = \frac{R_s}{\text{Re}}, \quad M_{id} = 2\pi R_s^3 \rho_n / 3$$

and assuming that in all measurements the electric filed amplitude $E_D$ was kept constant,

$$v_D = \mu E_D, \quad E_D = \text{const}$$

one obtains

$$M_n^{\text{ass}} \simeq M_{id} \frac{l_\eta}{R_s} = \frac{2\pi R_s^2 \eta}{3v_D} = \frac{2\pi R_s^2 \eta}{3\mu E_D} = \text{const} \cdot \frac{\eta}{\mu} \quad (17)$$

where $\mu$ is the stationary ion mobility [3]. Thus, in contrast to Eq. (4) the arising interpretation of the efficient mass temperature dependence is related to the simultaneous effects of both $\eta(T)$ and $\mu(T)$. The corresponding plots together with the data of Ref. [3] are presented in Figs. 2 and 3.

To sum up, one can say that the complicated temperature dependence of the Stokes associated cation mass is a manifestation of a rather general
phenomenon inherent to motion of various mesoscopic clusters through viscous liquid. In the extreme case of small Reynolds numbers their efficient mass proves to possess a substantial velocity dependence. The outlined effect should be taken into account in the ion dynamics in various electrolytes as well as in the calculations of equilibrium and dynamic properties of colloid systems, etc.

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