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Change of viscosities of polymers on γ irradiation

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The change in viscosity of polymeric silicone fluids due to γ irradiation has been studied below the gel point using a sensitive differential viscometer. Using the correspondences between resistivity and viscosity of fluids, the random resistance network has been used to explain the increase in viscosity due to irradiation, and fairly good agreement with experiment has been obtained.

I. INTRODUCTION

Energetic radiation usually deposits energy in a material medium within a highly localized region. The energy deposition may cause excitations, ionizations, and chemical dissociations in polymeric liquids. Subsequent recombination or deexcitation produces newer species of polymers, thereby altering the physical properties of the liquid. The amount of change in physical properties usually depends on the amount of the dosage received by the solution and is hence often used as a measure of dose. One such physical property of liquids easily amenable to measurement is the dynamic viscosity.

In the early 1950s extensive efforts have been invested in studying the radiation-induced changes in different polymers. Most of the experiments were motivated to find the change in molecular weight (M), which was found by the measurement of intrinsic viscosity.[1-4] Experimental investigations were also made close to gel point with polydimethylsilicone (PDMS, commonly known as silicone fluid)—both linear and cyclic, by Charlesby.[5] The intrinsic viscosity of cyclic and linear PDMS fractions (M: 800–1700 amu) has been measured[6] in butanone at 0 °C and in toluene and cyclohexane at 25 °C. Preliminary results on the changes of viscosity of various grades of PDMS [200, 500, and 1000 cS (centistokes)] with γ dose were reported earlier by us.[7]

In this paper we present the experimental observations of damage produced in polymeric silicone fluids [$(\text{—Si(Me)}_2\text{O—})_n$, where Me denotes methyl] of different grades by γ irradiation by measuring the change of their dynamic viscosities. We also present a theoretical approach (model) to explain our observations on the basis of the random resistor network (RRN) model. To the best knowledge of the authors this approach has not been used earlier in explaining change in viscosity of Newtonian liquids due to irradiations by ionizing radiations.

II. PRINCIPLE OF VISCOSITY CHANGE DUE TO γ IRRADIATION

We presume that upon irradiation, short-lived excited complexes (S^{**}) are formed and they either dissociate in a very short time, ionize, or are quenched by transfer of energy. The ion-electron recombination rate would presumably be quite high, as expected in liquids, equilibrating the ionization–ion-electron recombination channel. Covalent bonds broken during dissociation would give rise to reactive sites, thus permitting the recombination of broken fragments at the active sites. Invoking a simple rate-kinetic picture

$$\begin{tikzcd} S \arrow[r, shift left, "\Gamma"] & (S^{**}) \arrow[l, shift left, "\Gamma_d"] \arrow[r, "\Gamma_n"] \arrow[d, shift left, "\Gamma_j"] & \{F_n\} \arrow[r, "k_{nn'}"] & \{P\} \\ & \{I_j\} \arrow[u, shift left, "k_{ij}"] & & \end{tikzcd}$$

we obtain

$$\begin{aligned} \dot{S} &= -\Gamma S + \Gamma_d (S^{**}) \\ (\dot{S}^{**}) &= \Gamma S - \left[\Gamma_d + \sum_n \Gamma_n \right] (S^{**}) , \\ \dot{F}_n &= \Gamma_n (S^{**}) - \sum_{n'} k_{nn'} F_{n'} F_n , \\ \dot{P} &= \sum_n \sum_{n'} k_{nn'} F_n F_{n'} , \end{aligned} \tag{1}$$

where S represents the concentration of the original silicone fluid, F_n the concentration of fractured molecule, P the concentration of the product polymer, and I_j the ionic species j. The rate kinetics may be worked out in abstraction using energy-dependent parameters Γ, Γ_d, Γ_n, Γ_j, k_{ij}, and $k_{nn'}$ representing the formation frequency (photon-atom reaction frequency), quenching frequency, frequency of dissociation into various fractures, frequency of formation of ions and electrons, ion-electron recombination rate, and the fracture-fracture association rate coefficient, respectively. Assuming that the radiation dosage, delivered at a constant rate for a time T, is sufficiently small so as not to change S appreciably and that the ionization channel has equilibrated in a time much less than the fragment-fragment recombination time $\tau = (\Gamma_d + \sum_j \Gamma_j + \sum_n \Gamma_n + \sum_j k_{ij} I_j)^{-1}$, one may obtain the concentration of the recombined polymers P as follows:

$$P(t)=\frac{S\sum_{n}\Gamma_n\Gamma T}{\left[\Gamma_d+\sum_{n}\Gamma_n\right]}-\sum_{n}F_n(t)-\frac{\sum_{n}\Gamma_n\Gamma S}{\left[\Gamma_d+\sum_{n'}\Gamma_{n'}\right]^2}\left\{1-\exp\left[-\left[\Gamma_d+\sum_{n}\Gamma_n\right]T\right]\right\}\exp\left[-\left[\Gamma_d+\sum_{n}\Gamma_n\right](t-T)\right] . \tag{2}$$

It should be noted that P refers to the number density of an ensemble of various kinds of recombined polymers of grossly unequal shapes and sizes. The first term in Eq. (2) is proportional to the dosage of radiation. The second and the third terms are found to be negligible compared to the first after a prolonged curing time $(t-T)$. This gives us the relation

$$P=\frac{S\Gamma_0 T}{\left[1+\Gamma_d\Big/\sum_{n'}\Gamma_{n'}\right]}\propto D , \tag{3}$$

indicating that the concentration P of the recombined polymers would be linearly proportional to the dosage D. The scenario at high dose rates (so as to have a large probability of multiple excitations in individual molecules) would be different. In such situations, instead of having several small-size clusters, a few very large clusters may be expected, resulting in gelation. The resulting liquid would be expected to be non-Newtonian, having elastic resistance to shear. The consequent increase in viscosity of such liquids has been formulated on the basis of the bond percolation model[8] leading to a divergence of average cluster size (mass).

Even though the viscosity has more than doubled, as demonstrated in Table I, the liquid of our interest remained Newtonian, as expected at low dose rates. In this situation the concentration of recombined clusters is expected to increase without the divergence of average cluster size (mass) and hence a different treatment is required to explain the increase in dynamic viscosity. In this article we attempt to develop a model suitable for such a situation considering the flow of the liquid to be Newtonian.

Viscosity would be changed by the presence of the recombined polymers either due to the change in their shape or size. This change in viscosity is conveniently represented by Einstein's formula for the viscosity of dilute suspensions

$$\eta=\eta_0(1+2.5vc) , \tag{4}$$

where η and η_0 are the viscosities of the solution with and without the suspensions, v is the volume of the sphere with an equivalent drag as experienced by a polymer of an average shape or size, and c is the concentration of polymers. However, this relation is strictly valid at low concentrations at which the assumption of the superposition of the fluid velocity fields due to individual suspension particles is valid. At higher concentrations of the suspensions, the boundary layers of different particles begin to overlap and due to the nonlinearity of the Navier-Stokes equation, the assumption of superposition is no longer valid. To overcome this difficulty at large concentrations, we replace the fluid by an array of tubes joining the neighboring vertices of a cubic or any other periodic three-dimensional lattice in which the suspended particles could be considered to block individual tubes randomly. Such a model can be solved by invoking the idea of a random resistor network. But this requires some similarity to be established between resistivity and viscosity of fluids. The Navier-Stokes equation for a stationary streamlined flow of an incompressible fluid can be rearranged [see the Appendix, Eq. (A3)] to obtain the force gradient along the streamline as given by

$$\frac{\partial F}{\partial \xi}=\eta\oint\frac{d\mu}{h_\xi h_\nu}\left[\frac{\partial}{\partial \nu}(h_\xi u)\right]+\int\rho\frac{\partial u}{\partial t}dA_\xi+\int\rho\frac{u^2}{h_\xi}\frac{\partial}{\partial \xi}[\ln(h_\mu h_\nu)]dA_\xi \tag{5}$$

(ξ, μ, and ν are coordinates with ξ along the streamline, μ in a nonmoving surface orthogonal to ξ, and ν is orthogonal to both at the surface; h_ξ, h_μ, and h_ν are scale factors; ρ and η are mass density and viscosity; and A_ξ is perpendicular to the flow). Here the first integral on the right-hand side is proportional (constant of proportionality being C_1) to the product of the cross-section-averaged flow velocity along the streamline and the viscosity. The second term is the product of the area-averaged acceleration along a streamline, the cross section and the mass density, while the third term is proportional to the square of the area-averaged velocity, the mass density ρ, and a system-dependent length parameter. If the third term is small compared to the other terms (as may happen for highly viscous fluids), one may compare this to Ohm's

TABLE I. Threshold dosage (D_0) and the viscosity exponent (γ) as obtained by the theoretical fit [Eq. (11)] of the experimental data for various grades of silicone fluid.

Kinetic viscosity (cS)	Viscosity exponent γ	Threshold dose D_0 (megarad)	Molecular weight (amu)
50	0.5155	441.28	3 600
200	0.3480	110.56	10 600
500	0.3602	76.95	18 000
1000	0.3884	62.16	26 500
2000	0.3750	53.55	34 000
3000	0.3575	44.64	38 700

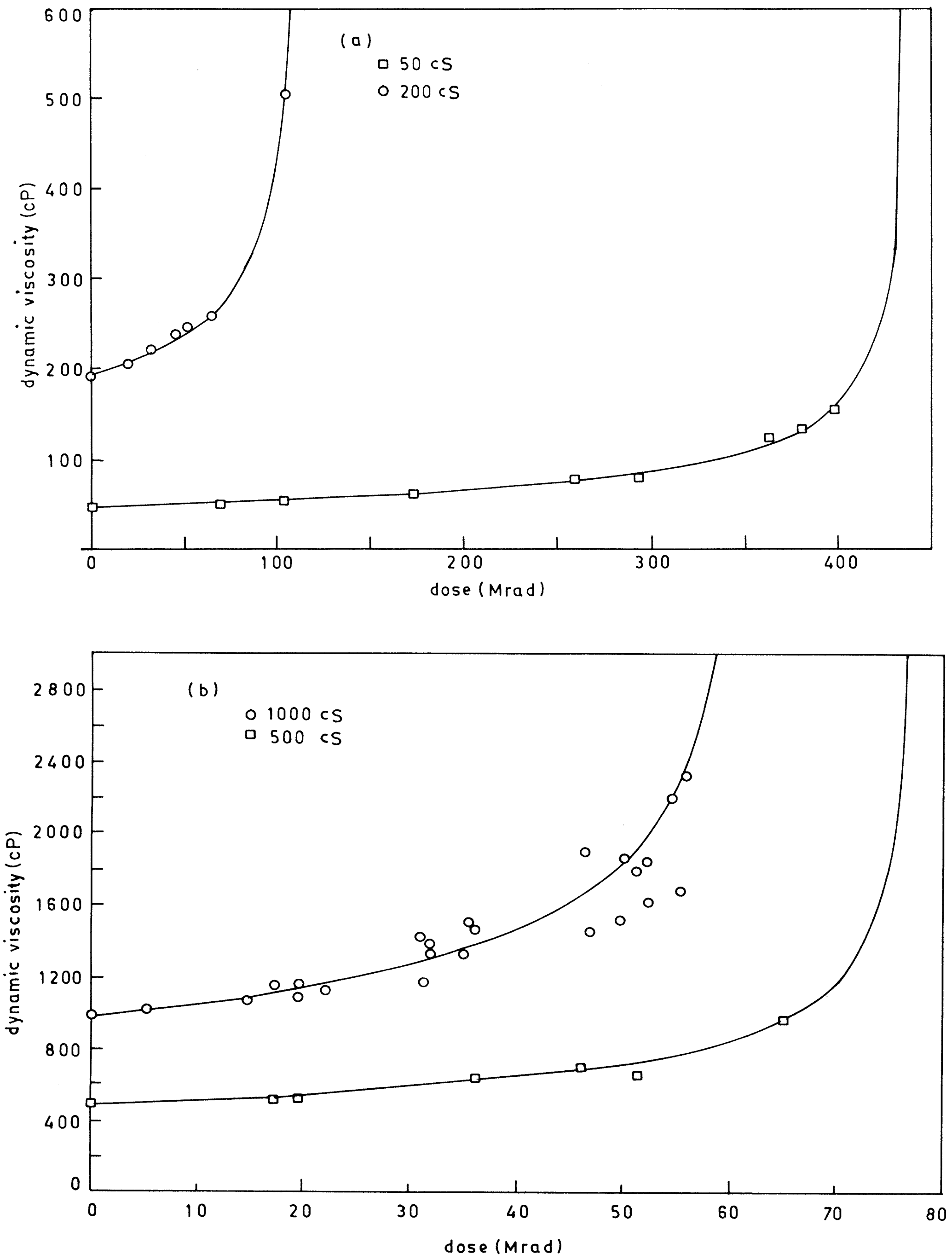

FIG. 1. Observed variation of viscosity of different grades of silicone fluid with γ dose. Solid line represents theoretical fit [Eq. (11)] to the experimental data.

law by mapping the electric-field strength to the force gradient along a streamline and the current density to the area-averaged streaming velocity. In that case $C_1\eta$ becomes equivalent to inverse of electrical conductivity and $C_2\rho$ to electrical inductance per unit length, thereby accounting for dissipative and inertial forces [see Eq. (A4) in the Appendix]. This allows the extension of the percolation (RRN) picture to understand the mechanism of changes in viscosity of concentrated polymeric solutions. The conductivity in the RRN model varies as

$$\sigma \propto (P' - P'_0)^{\gamma} , \tag{6}$$

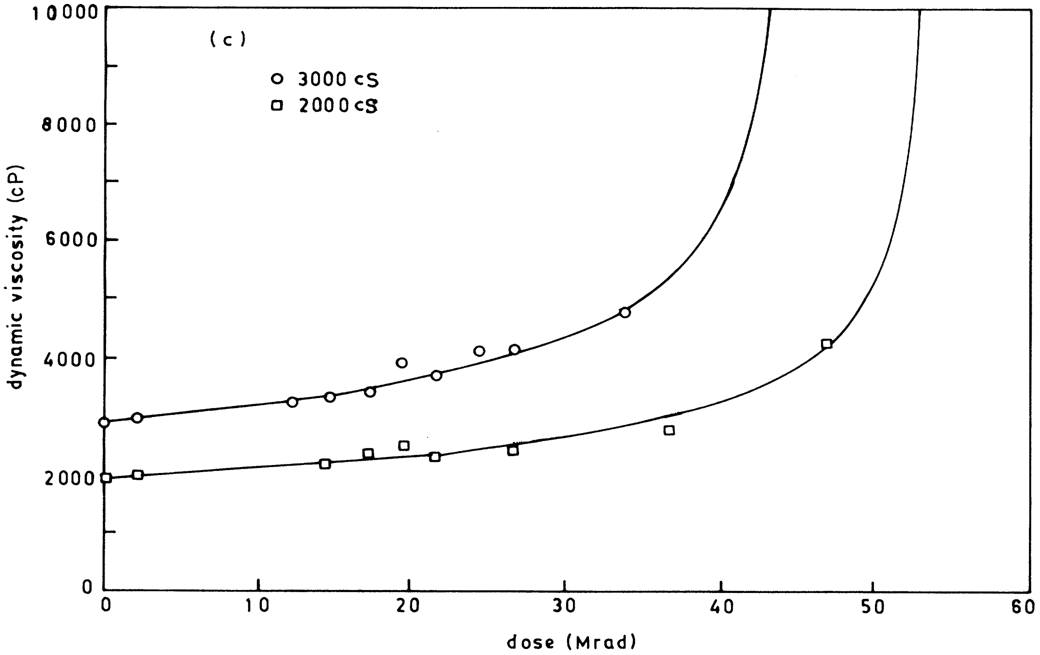

FIG. 1. (*Continued*).

where γ is the conductivity exponent, P' is the probability of resistive linkage between adjacent sites, and P'_0 is the threshold probability. This may alternatively be represented by the probability (P) of missing linkages from a complete circuit, as given by

$$P = 1 - P' . \tag{7}$$

Substituting this into Eq. (6), we obtain

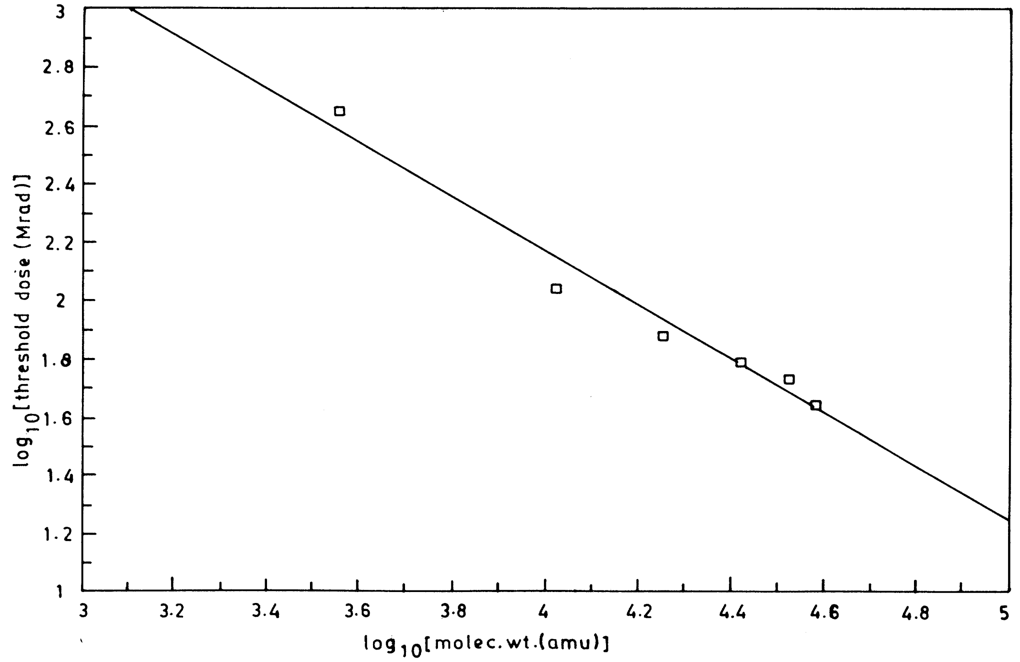

FIG. 2. Observed dependence of the threshold dosage on the mean molecular weight of silicone fluids. The straight line corresponds to a dependence of $D_0 = 147.74(10^4/M)^{0.921 \pm 0.0821}$ where M is the molecular weight and D_0 is the threshold dosage.

$$\sigma \propto (P_0 - P)^{\gamma} , \tag{8}$$

where P_0 is the corresponding threshold probability. As stated earlier, we replace the fluid flow by a three-dimensional array of tubes where the suspension affects the fluid flow by blocking individual tubes. With the probability of blocking individual tubes as P, the correspondence between $C_1\eta$ and σ^{-1} allows us to write

$$\eta \propto (P_0 - P)^{-\gamma} . \tag{9}$$

The probability (P) of tube blockage is proportional to the concentration (c) of the suspension and hence we may write

$$\eta = \eta_0 (1 - c/c_0)^{-\gamma} , \tag{10}$$

where η_0 is the suspension-free viscosity and c_0 is the threshold concentration at which the viscosity diverges. Since the concentration of recombined polymers varies linearly with the dosage (D) as shown in Eq. (3), we obtain

$$\eta = \eta_0 (1 - D/D_0)^{-\gamma} , \tag{11}$$

where D_0 is a threshold dosage.

III. EXPERIMENT

Silicone fluids (polydimethylsiloxanes—a linear polymer $[\mathrm{Si(Me)_2O}]_n$ from Metroark Pvt. Ltd.) of initial kinematic viscosities of 50, 200, 500, 1000, 2000, and 3000 cS were irradiated in glass containers using the γ irradiation facility of Saha Institute of Nuclear Physics, Calcutta. The source was a radioactive ^{60}Co and the measured dose rate was 2 Gy/s (100 rad = 1 Gy). The dose time varied from a few hours to about 100 h and since the half-life of ^{60}Co is about 5.3 yr, the dose rate during this time may be assumed to be a constant. After a minimum curing time of 5 to 6 h the dynamic viscosity was measured by using a sensitive differential viscometer. In the differential viscometer, the difference in viscosities of the two samples is determined by measuring the difference in torques with outer cylinders rotating in opposite directions with equal speed as described elsewhere.[9] Uncertainty associated with the measurement of change in viscosity is of the order of 5%.

Checks were made to ensure that the flow was Newtonian: (i) by noting that there is no time dependence of the viscous torque, (ii) by measuring the elastic shear resistance of the liquids in a separate experiment where no significant elastic resistance was found, and (iii) by measuring the viscosity of a given liquid at five different shear rates and no change in viscosity was observed. The temperature during the experiment was almost constant (25±2 °C) and furthermore the temperature coefficients of viscosity of silicone fluids are small. Added to this, the estimated average mechanical heating power (<1.81 mW) and the power density (<0.21 mW/cm^3) was small during the entire measurement.

IV. RESULTS AND ANALYSIS

The behavior of change in viscosity of silicone fluid with γ-ray dose is shown in Fig. 1. As observed, the viscosity increases smoothly with the dosage of γ irradiation as predicted by Eq. (11) and diverges at some asymptotic value of the dosage. The samples with small polymeric size, i.e., with smaller dynamic viscosity, diverge at a much higher dosage compared to the ones with a larger average polymeric size (or higher viscosities) and the curves are qualitatively similar. By fitting Eq. (11) to the experimental data, D_0 and the viscosity exponent (γ) were obtained. The values of D_0 and γ for silicone fluid of different viscosities are presented in Table I. As expected, the viscosity exponent (γ) is found to be fairly constant with liquids of different viscosities except for the 50-cS sample. The dependence of the threshold dose D_0 on the molecular weight as obtained from the present experiment is presented in Fig. 2. The observed dependence may be represented by an equation of the form $D_0 \sim M^{-0.92}$. This is in good agreement with the ($1/M$) dependence of D_0 as shown by Charlesby.[10]

V. CONCLUSION

We therefore conclude that the viscous flow of polymeric solutions may be interpreted in the framework of the RRN model. The observed exponent (γ) is quite different from that obtained from the RRN model (1.6 ± 0.1 in case of bond percolation and 1.5 ± 0.2 in case of site correlated percolation[11]), which is understandable to a certain extent from the following arguments. The analogy between the resistivity and the viscosity is not exact, as can be seen from the Eq. (5). The third term of the equation is nonlinear in fluid velocity (reflecting the inherent nonlinear nature of the Navier-Stokes equation) and may not always be negligible[12] as assumed in developing this model. It is to be noted in this connection that the scaled drag calculated numerically[13] by considering the flow fields within periodic arrays of cylinders arranged in hexagonal and square lattices has the same behavior as predicted by our model.

APPENDIX

The Navier-Stokes equation for incompressible fluid flows may be rearranged and the force on any fluid element may be obtained from the volume integral of the force density as

$$\mathbf{F} = -\eta \int\int\int \nabla^2 \mathbf{u}\, dV + \rho \int\int\int \dot{\mathbf{u}}\, dV + \rho \int\int\int (\mathbf{u}\cdot\nabla)\mathbf{u}\, dV . \tag{A1}$$

For a streamlined fluid flow in a transversely bounded region we may choose an orthogonal coordinate system with ξ along the direction of the local fluid flow ν such that it is orthogonal to both ξ and the transverse boundary and μ such that it is orthogonal to both ξ and ν. In such a coordinate system the force gradient along the fluid flow may be evaluated as

$$\frac{\partial F}{\partial \xi} = \eta \int\int [\nabla \times (\nabla \times \mathbf{u})] \cdot d\,\mathbf{A}_\xi + \rho \int\int \dot{\mathbf{u}} \cdot d\,\mathbf{A}_\xi + \rho \int\int (\mathbf{u}\cdot\nabla)\mathbf{u} \cdot d\,\mathbf{A}_\xi \tag{A2}$$

and the integrals are in the μ-ν surface. The first integral may be reduced using the Stokes theorem and the third using the fact that div $(\mathbf{u})=0$, enabling us to write them in the explicit form

$$\frac{\partial F}{\partial \xi}=\eta \oint \frac{d\mu}{h_\xi h_\nu}\left[\frac{\partial}{\partial \nu}(h_\xi u)\right]+\rho \int \dot{u}\, dA_\xi - \int\int \frac{\rho u^2}{h_\xi}\frac{\partial}{\partial \xi}[\ln(h_\mu h_\nu)]dA_\xi \ , \tag{A3}$$

where h_ξ, h_μ, and h_ν are the respective scale factors. These integrals may not be evaluated in general for any boundary condition, but since we are interested in drawing an analogy between viscosity and resistivity, their average values will serve our purpose. The first integral is proportional to the cross-section-averaged streaming velocity, the second integral is proportional to the cross-section-averaged acceleration, and the third integral is proportional to the square of the average streaming velocity:

$$\frac{\partial F}{\partial \xi}=C_1\eta\langle u\rangle+C_2\rho\langle \dot{u}\rangle-C_3\rho\langle u^2\rangle \ . \tag{A4}$$

The constant of proportionality in the third integral C_3 has the dimension of length and may vanish or become negligibly small under certain conditions, (e.g., for flow through any tube having translationally invariant cross sections C_3 vanishes). The constant of proportionality C_2 of the second integral has dimension of area. However, the second term itself vanishes if the flow is steady. The constant of proportionality C_1 of the first integral is dimensionless and is specific of various geometries (e.g., for cylindrical geometry $C_1=8\pi$). The interesting features of Eq. (A4) are that (i) it explicitly displays the various components of the Navier-Stokes equation corresponding to dissipative, inertial and nonlinear behavior; and (ii) it predicts the correct form of the Poiseuille relation from the resistance analogy (neglecting the second and third terms).

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