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Universal interrelation between measures of particle and polymer size

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The characterization of many objects involves the determination of a basic set of particle size measures derived mainly from scattering and transport property measurements. For polymers, these basic properties include the radius of gyration \( R_g \), hydrodynamic radius \( R_h \), intrinsic viscosity \( [\eta] \), and sedimentation coefficient \( S \), and for conductive particles, the electric polarizability tensor \( \alpha_E \) and self-capacity \( C \). It is often found that hydrodynamic measurements of size deviate from each other and from geometric estimates of particle size when the particle or polymer shape is complex, a phenomenon that greatly complicates both nanoparticle and polymer characterizations. The present work explores a general quantitative relation between \( \alpha_E \), \( C \), and \( R_g \) for nanoparticles and polymers of general shape and the corresponding properties \( [\eta] \), \( R_h \), and \( R_g \) using a hydrodynamic-electrostatic property interrelation. [http://dx.doi.org/10.1063/1.4991011]

I. INTRODUCTION

The shape discrimination of objects on length scales ranging from nanoparticles and polymers to people and aircraft involves a primitive set of object properties derived from scattering or transport property measurements.¹ These properties include the electric polarizability tensor \( \alpha_E \) important for the far-field/low frequency scattering of particles by electromagnetic radiation in the Rayleigh limit where the conductive particles are small in comparison with the radiation wavelength, the radius of gyration \( R_g \) also derived from light scattering or imaging, the hydrodynamic radius \( R_h \) from dynamic light scattering or sedimentation coefficient \( S \) from centrifugation measurements, and the intrinsic viscosity \( [\eta] \) particle suspensions and polymer solutions at low concentrations. The self-capacitance \( C \) of particles is also important in relation to understanding the potential energy of conducting objects and the rate of diffusion-limited reaction because the Smoluchowski rate constant is proportional to \( C \).² The self-capacitance also arises in connection to the scattering length in acoustics,³ quantum mechanics,⁴ and other diverse applications.⁵ Finally, we mention that \( \alpha_E \) emerges in continuum property calculations of changes in many material properties such as electric conductivity, thermal conductivity, dielectric constant, and magnetic permeability, among others, when a small concentration of particles is added to another medium⁶–⁸ so that \( \alpha_E \), as in the case of \([\eta]\), has a significant potential for particle shape characterization.

Although the value of these “shape functionals” for shape characterization has long been appreciated in the mathematical community⁹ and the calculation of these properties has been the preoccupation of many great scientists such as Poisson, Laplace, Kelvin, Maxwell, and Einstein, this field has been slow to develop because of the intrinsic difficulty of the calculation of these measures of particle shape beyond a few simple geometries such as the ellipsoid, torus, spindle, and lens shapes. The challenge of calculating these properties has generated a large body of mathematical methods such as the Kelvin inversion method, but even great mathematicians of the twentieth century, such as Pólya, had to conclude that the analytic calculation of \( C \) of even such “simple” objects as a cube is basically impossible.⁹

The computational situation has changed in recent years because of the confluence of two developments, large scale computational facilities and probabilistic potential theory, that allow for a formulation of problems with complex-shaped boundaries in terms of averaging over random walk paths. This path-integral method allows for the calculation of the properties of polymers and particles having essentially an arbitrary shape to unprecedented accuracy and with high computational efficiency.¹⁰,¹¹ We are then in the position to explore shape-property interrelations that were not previously feasible.

In this work, we focus on the relation between \( \langle \alpha_E \rangle \), \( C \), and \( R_g \) of polymer and particles having complex morphologies. Electrostatic-hydrodynamic analogies extend these relations to those between \( R_h \), \([\eta]\), and \( R_g \). We validate this relation against data for a large variety of particle shapes, where these property measurements lead to rather distinct size estimates. These property interrelations should be useful in particle and polymer characterization and in the design of new materials because of the significance of \( \langle \alpha_E \rangle \) for estimating property changes in materials with additives.

II. SCALING RELATIONSHIP BETWEEN \( \langle \alpha_E \rangle \), \( C \), AND \( R_g \)

The calculation of measures of particle size from Laplace’s equation, such as the electric polarizability \( \langle \alpha_E \rangle \),
the magnetic polarizability $\langle \alpha_M \rangle$, the self-capacitance $C$, and the hydrodynamic virtual mass $[M]$, is a problem of long standing mathematical and physical interest. Correspondingly, the Stokes friction coefficient $f_i$ and the intrinsic viscosity $[\eta]$ provide basic measures of particle size associated with the solution of the Stokes equation.\(^6,^9\) Hydrodynamic-electrostatic analogies interrelating these properties are a source of physical insight and highly useful approximations.\(^1\)

The origin of these correspondences can be appreciated from the observation that the angular averaging of the Oseen tensor, the free space Green’s function of the Stokes equation, is the free-space Green’s function of Laplace’s equation.\(^12\) We do not discuss the details of these relationships here but simply note that the knowledge of $\langle \alpha_E \rangle$ and $C$ for objects of general shape allows for an estimation of $[\eta]$ and the Stokes friction coefficient to an accuracy of about 1%, which is usually far less uncertain than experimental estimates of these quantities.\(^13\) The problem of estimating $\langle \alpha_E \rangle$ and $C$ then pertains to the practically important problem of determining $[\eta]$ and $R_h$ of complex shape particles and to the problem of understanding how these size measurements are interrelated.

As noted above, the number of object shapes allowing for the analytic calculation of these measures of particle shape is rather limited, and for mathematical expediency, it is often assumed that complex particles or polymers are effective ellipsoids or some other mathematically tractable form. The pressing practical need for polymer and particle characterization has led established mathematical frameworks for treating more complicated particle shapes and we may draw on these frameworks to deduce our general relationship between $\langle \alpha_E \rangle$, $C$, and $R_h$ given the hydrodynamic-electrostatic analogy mentioned above.

There are two approximate frameworks for calculating polymer hydrodynamic properties, the Kirkwood–Riseman (KR)\(^14\) “bead” or “slender-body” model and the Debye–Bueche (DB)\(^15\) “porous sphere” model. Each of these models have their shortcomings,\(^15\) but both models remain of enduring interest because they make predictions for the hydrodynamic properties of polymers that have at least qualitative validity. The main approximation of the KR and DB theories is a configurational preaveraging approximation that can lead to an appreciable error as large as $O(20\%)$ in the estimation of the hydrodynamic properties of flexible polymers.\(^16,^17\) We are not interested in these shortcomings in the present work, but rather on what these approximate theories have to say qualitatively about how shape influences the variable hydrodynamic interaction in the determination of $[\eta]$ and $R_h$. The self-interaction strength is also at the heart of calculating $\langle \alpha_E \rangle$ and $C$, and we use these hydrodynamic models for qualitative guidance in developing a scaling relation connecting these fundamental measures of particle shape. The path-integration program ZENO\(^7,^13\) can then be used to numerically calculate $\langle \alpha_E \rangle$ and $C$ to low uncertainty to validate the proposed relationship for diverse classes of objects listed in Sec. III.

Our scaling relation is derived from a consideration of the limiting case, when the particle is imagined to be broken apart into segmental fragments separated at a great distance from each other and the other extreme limit where the particle components form a compact particle. We are looking here for a relation that subsumes these limits, and everything in between, without any assumption of particle sphericity, configurational preaveraging, etc.

Both the KR and the DB framework indicate that the Stokes friction coefficient $\zeta$ of a collection of well-separated particles scales as the number of particles $n$ times the Stokes friction coefficient of each particle, $n\zeta$, and the self-capacity $C$ also exhibits the same simple additive relation in the limit where the particles have no interactions. If instead, the particles are connected into a linear array in three dimensions, $f_i$ scales as $n\zeta/\ln(n)$, which is similar to the ideal “free-draining” limit, $f_i \sim n\zeta$.\(^18\) On the other hand, if we compress all our particles into a sphere of radius $R$, then the number of subparticles is clearly irrelevant since the hydrodynamic field does not penetrate into the particle cluster.\(^19\) The same situation is true, a sphere where $C$ equals the sphere radius $R$, so that $C = R_h$. The equality between $C$ and $R_h$ also holds exactly for triaxial ellipsoids\(^6\) and is approximately true (±1% uncertainty) for the average friction coefficient of particles having essentially an arbitrary shape.\(^7,^13\) $C$ and $R_h$, respectively, describe how the particle shape alters the flux of mass and momentum into the surrounding medium, so at equilibrium, these measures of shape are naturally deeply interrelated.

Now, we extend some basic considerations to the less obvious case of the intrinsic viscosity $[\eta]$ where previous hydrodynamic modeling provides a reference for our scaling argument. The application of a shear field to dilute suspension creates a dipolar stress response from the particles in a fashion similar to an electric field on a suspension of conducting particles in an insulating medium.\(^20\) Since, $\langle \alpha_E \rangle$ for rod-like particles exhibits the well-known asymptotic scaling,\(^6\)

$$\langle \alpha_E \rangle \sim n^3/\ln(n),$$

both the KR and DB theories indicate that $[\eta]$ for rod-like polymers follows the scaling relationship,

$$[\eta] \sim \langle \alpha_E \rangle/V_p,$$

reflecting the hydrodynamic-electrostatic analogy mentioned above. Here, $V_p$ is the polymer volume. In terms of the length $n$ of the rod, $[\eta]$ then scales as\(^21\)

$$[\eta] \sim n^2/\ln(n),$$

and the electric polarizability of a sphere scales proportionally to the sphere volume.\(^6\) These limiting scaling relations are recovered by both the KR and DB theories, which both indicated a general scaling expression for polymers,

$$[\eta] \sim R_h R_h^2/V_p,$$

where $R_h$ is the polymer radius of gyration which suggests an approximation for $\langle \alpha_E \rangle$. As mentioned before, both the KR and DB theories involve severe approximations.

In the polymer science field, Eq. (4) is known as the Weill–des Cloizeaux approximation,\(^22\) and this scaling relationship has often been applied to rationalize the mass-scaling of $[\eta]$ for flexible polymers with and without excluded volume
interactions. Unfortunately, an extensive test of Eq. (4) using ZENO has revealed that it is simply inadequate for flexible polymers.\textsuperscript{10} This relation only holds for slender thread-like and compact bodies where hydrodynamic interactions within the particle and conformational fluctuation effects are weak. There has been a long-standing need for a better approximation for the intermediate case between thread-like polymers and compact objects since most real polymers, and many nanoparticles requiring characterization, are objects of this kind.

Since \( C \) arises in so many physical contexts beyond electrostatics, and because electromagnetic units can be confusing due to the multiple systems of units in use, we have followed standard usage in the mathematical/physics literature of introducing “reduced units” that emphasize the dependence of capacity and polarizability on the particle size. In particular, we have used reduced units in which \( C \) of a sphere equals its radius \( R \), corresponding to taking \( 4\pi\varepsilon_0 = 1 \), where \( \varepsilon_0 \) is the permittivity of the medium in which the conductive particle is placed, so that the standard definition of \( C \) in terms of farads reduces to \( C = R \) for a sphere, and more generally \( C \) has units of length. In the same units, \( \langle \sigma_E \rangle \) has units of volume, and specifically \( \langle \sigma_E \rangle \) for a highly conductive sphere is equal 3 times its volume.

In the absence of any tractable analytic approach to interrelate \( \langle \sigma_E \rangle \) to other measures of polymer/particle size, we consider a scaling approach that respects all limiting known results as special cases and reflects our knowledge of \( \langle \sigma_E \rangle \) and \( C \) gained by recent computational studies. We estimate the average electric polarizability tensor, \( \langle \sigma_E \rangle = \text{trace}(\langle \sigma_E \rangle)/3 \), with the requirement that the expression interpolates exactly between the slender body and compact particle scaling limits, but we do not make the particular choice indicated in the scaling expression given in Eq. (4). We instead take \( \langle \sigma_E \rangle \) to equal,

\[
\langle \sigma_E \rangle = [\sigma_{\text{sphere}}^e]_0 \left( 4\pi C^3/3 \right) \Psi_C^{(d - 3)},
\]

where the field “penetration function,” \( \Psi_C = C/R \_g \), describes the extent to which the exterior field penetrates into the polymer and \( d_1 \) is the fractal dimension of the particle. In particular, \( d_1 = 1 \) for a rod, \( d_1 = 2 \) for a random coil, \( d_1 = 3 \) for a sphere, etc. Here, \( \Psi_C \) plays a central role in both the KR and DB models,\textsuperscript{14,15} but the power \( (d_1 - 3) \) in Eq. (5) is new to modeling this hydrodynamic self-interaction crossover. It is apparent that the slender body scaling limit of Onsager\textsuperscript{21} is recovered, the case from Eq. (5) when taking the slender rod limit \( (d_1 = 1) \) and for a spherical particle where \( d_1 = 3 \), and we recover the exact relation of Maxwell\textsuperscript{21}

\[
\frac{\langle \sigma_E \rangle}{(4\pi C^3/3)} = [\sigma_{\text{sphere}}^e]_0 = 3.
\]

Note that Eq. (5) specifies the prefactor so this relation has no free parameters. Basic scaling consistency then suggests that we can approximate \( \langle \sigma_E \rangle \) by a generalized geometrical mean of \( C \) and \( R_g \) where the exponent involves the fractal dimension of the object.

Of course, fractal objects are idealizations of real objects that never conform exactly to self-similar geometrical structures, just as spheres, cubes, tetrahedra, and octahedra exist as ideal Platonic forms used to model real structures. While true fractal objects exhibit a characteristic mass scaling relationship between their radius of gyration and mass \( M \),

\[
R_g \sim M^{1/d_2},
\]

many non-fractal objects exhibit this type of mass scaling relationship to a good approximation. This situation arises for many polymeric structures, so we define an effective “mass scaling exponent” \( v^{\text{eff}} \) by the mass scaling relationship,

\[
R_g \sim M^{v^{\text{eff}}}. \tag{8}
\]

The effective exponent \( v^{\text{eff}} \) depends on the object geometrical parameters. For instance, \( v^{\text{eff}} \) is a function of the aspect ratio \( r \) for oblate and prolate ellipsoids, where \( r \) is the ratio between the largest to the smallest ellipsoid axis.\textsuperscript{34} The same situation arises for dendrimers,\textsuperscript{25,26} duplex DNA,\textsuperscript{27} carbon nanotube domains,\textsuperscript{8} nanoparticle with grafted layers of DNA chains,\textsuperscript{28,29} etc. In each case, the molecular parameters describing the object must be prescribed over which the mass scaling relation is exhibited. Numerical or analytically estimated \( v^{\text{eff}} \) values corresponding to the objects explored in this study are tabulated in the supplementary material and values are also summarized in Tables I and II.

We thus arrive at a general scaling relation between \( \langle \sigma_E \rangle \), \( C \), and \( R_g \),

\[
\langle \sigma_E \rangle = [\sigma_{\text{sphere}}^e]_0 \left( 4\pi C^3/3 \right) \Psi_C^{(1/v^{\text{eff}} - 3)}, \tag{9}
\]

that is not restricted to fractal objects. We note that a similar relation holds for objects in two dimensions,\textsuperscript{9}

\[
\langle \sigma_E \rangle = [\sigma_{\text{disc}}^e]_0 \left( \pi C_L^2 \right), \tag{10}
\]

where \( [\sigma_{\text{disc}}^e]_0 = 2 \) and \( C_L \) is the logarithmic capacity (an extension of the capacity to two dimensions where random walks are recurrent). Reciprocity\textsuperscript{30} implies \( \langle \sigma_M \rangle = -\langle \sigma_M \rangle \) in two dimensions, and we note that \(\sigma_M\) in three dimensions is exactly equal to a hydrodynamic virtual mass tensor \( M \), up to a constant of proportionality defined by mathematical convention.

The estimation of \( \langle \sigma_E \rangle \) and \( C \) can be immediately translated into estimating \( \lbrack \eta \rbrack \) and \( R_g \) for polymer and nanoparticles.


<table>
<thead>
<tr>
<th>( g_i )</th>
<th>( R_g )</th>
<th>( C )</th>
<th>( v^{\text{eff}} )</th>
<th>( \langle \sigma_E \rangle )</th>
<th>( \langle \sigma_E \rangle^c )</th>
<th>( \text{dev}(%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>13.3</td>
<td>13.91</td>
<td>0.220</td>
<td>36.256</td>
<td>36.248.5</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>16.81</td>
<td>18.60</td>
<td>0.292</td>
<td>84.393</td>
<td>84.413.2</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>20.92</td>
<td>24.27</td>
<td>0.315</td>
<td>184.500</td>
<td>184.566.7</td>
<td>0.07</td>
</tr>
<tr>
<td>6</td>
<td>25.82</td>
<td>31.07</td>
<td>0.325</td>
<td>382.600</td>
<td>382.311.3</td>
<td>0.08</td>
</tr>
<tr>
<td>7</td>
<td>31.55</td>
<td>39.07</td>
<td>0.328</td>
<td>757.200</td>
<td>757.302.0</td>
<td>0.01</td>
</tr>
<tr>
<td>8</td>
<td>38.28</td>
<td>48.55</td>
<td>0.331</td>
<td>1444.000</td>
<td>1445.308.0</td>
<td>0.09</td>
</tr>
<tr>
<td>9</td>
<td>45.76</td>
<td>59.13</td>
<td>0.332</td>
<td>2609.000</td>
<td>2609.038.4</td>
<td>0.01</td>
</tr>
<tr>
<td>10</td>
<td>53.95</td>
<td>70.81</td>
<td>0.332</td>
<td>4474.000</td>
<td>4476.273.1</td>
<td>0.05</td>
</tr>
<tr>
<td>11</td>
<td>62.37</td>
<td>82.71</td>
<td>0.333</td>
<td>7120.000</td>
<td>7116.263.8</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Percentage average deviation \( \text{dev}(\%) \) \( \text{dev}(\%) \)
TABLE II. List of objects, their effective mass scaling exponents $\nu_{\text{eff}}$, and percentage deviation of predictions and simulation estimates, $\text{dev}(%)$.

<table>
<thead>
<tr>
<th>Object</th>
<th>$\nu_{\text{eff}}$</th>
<th>$\text{dev}(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swollen random coils</td>
<td>0.559</td>
<td>1.0</td>
</tr>
<tr>
<td>Flexible capped cylinders</td>
<td>0.516</td>
<td>0.7</td>
</tr>
<tr>
<td>Worm-like chains</td>
<td>0.535</td>
<td>0.7</td>
</tr>
<tr>
<td>Rods ($8 &lt; L &lt; 1900$)</td>
<td>$\left( \frac{6.1}{3} \right)^2 + \frac{0.49}{L^{0.0323}}$</td>
<td>0.7</td>
</tr>
<tr>
<td>Oblate ($1 &lt; r &lt; 100$)</td>
<td>$\frac{\sqrt{\text{dev}}}{\text{dev}}$</td>
<td>0.9</td>
</tr>
<tr>
<td>Prolate ($6 &lt; r &lt; 100$)</td>
<td>$\left( \frac{4.6}{3} \right)^2 + \frac{0.6}{r^{0.0323}}$</td>
<td>0.3</td>
</tr>
<tr>
<td>Flat sheets</td>
<td>0.565</td>
<td>1.2</td>
</tr>
<tr>
<td>Flexible sheets</td>
<td>0.553</td>
<td>1.3</td>
</tr>
<tr>
<td>Eden clusters</td>
<td>0.330</td>
<td>0.7</td>
</tr>
<tr>
<td>Diffusion-limited aggregates</td>
<td>0.32</td>
<td>0.8</td>
</tr>
<tr>
<td>Lattice animals</td>
<td>0.510</td>
<td>3.6</td>
</tr>
<tr>
<td>Percolation clusters</td>
<td>0.250</td>
<td>0.8</td>
</tr>
<tr>
<td>Tori ($5 &lt; r &lt; 1000$)</td>
<td>$\frac{0.52}{r^{0.2}}$</td>
<td>0.6</td>
</tr>
<tr>
<td>Star-like polymers</td>
<td>$\frac{400}{r^2}$</td>
<td>0.8</td>
</tr>
<tr>
<td>Dendrimers</td>
<td>Table I</td>
<td>0.05</td>
</tr>
<tr>
<td>Knots</td>
<td>$\nu_{\text{eff}}(m)$</td>
<td>0.60</td>
</tr>
<tr>
<td>Platonic solids</td>
<td>$\frac{1}{3}$</td>
<td>1.0</td>
</tr>
<tr>
<td>Polymer-grafted particles</td>
<td>0.333</td>
<td>0.8</td>
</tr>
<tr>
<td>CNT tumbleweed structures</td>
<td>$\frac{1}{3}$</td>
<td>0.6</td>
</tr>
<tr>
<td>Globular proteins</td>
<td>$\nu_{\text{eff}}$</td>
<td>1.2</td>
</tr>
</tbody>
</table>

In particular, there are hydrodynamic-electrostatic approximations linking these properties, $\nu_{\text{eff}}$, and $\{\eta\} = \nu_{\text{eff}}(\alpha_E)/\nu_E$. In general, $\nu_{\text{eff}} \approx 1$ to a high approximation [O(1%)] and $\nu_{\text{eff}} \approx 0.79$ with uncertainty O(5%) having a general shape, so that we also estimate hydrodynamic properties to within low uncertainty. This uncertainty can be reduced to O(1%) by using the components of the polarizability tensor to further specify $\nu_{\text{eff}}$. Below, we focus on interrelating $\langle \alpha_E \rangle$ to $C$ and $R_E$ since the interrelation is “equivalent” to the one between $\{\eta\}$ to $R_0$ and $R_E$.

III. NUMERICAL SUPPORT FOR PROPERTY INTERRELATION

Recent experimental and theoretical studies have indicated the failure of scaling arguments to describe measures of polymer and nanoparticle size. In particular, the mass scaling exponents defining size depend on the property, i.e., $R_E$, $R_0$, $\{\eta\}$, and $S$. This failure of scaling arguments has been discussed extensively in the case of DNA. We next validate our predicted relationship between these measures of polymer and nanoparticle size.

In this section, we test Eq. (9) for linear and branched polymers, non-fractal particles and particle clusters, and other complex non-fractal structures such as globular proteins and tumbleweed carbon nanotube domains. For each group of objects, we plot $\langle \alpha_E \rangle$ versus $\langle \alpha_E \rangle$ in Figs. 1–5, where $\langle \alpha_E \rangle$ is either determined from ZENO or an analytic result and $\langle \alpha_E \rangle$ is the value of the electric polarizability calculated by using Eq. (9). Here, the symbols represent the data and the red lines are generated from the linear relation between these quantities, for comparison purposes. The insets are representative configurations for each object. More information about

FIG. 1. Linear polymeric structures. (a) Flexible polymers with repulsive excluded volume interactions (swollen random coils) generated via Monte Carlo simulations (b) flexible capped cylinders generated via MD (c) Worm-like chains obtained from the fit functions given in Ref. 10. The rods have lengths ($L$) in the range $10 < L < 1900$. Calculations for rods having a rectangular cross section fit our scaling just as well, but we do not show these data here.

the objects and their properties is given in the supplementary material.

The uncertainty estimates are calculated from the percent deviation between the directly computed value, $\langle \alpha_E \rangle$, and the theoretical estimate from Eq. (9), $\langle \alpha_E \rangle^\ast$.

$$\text{dev}_{\nu}(%) = \left| \frac{\langle \alpha_E \rangle - \langle \alpha_E \rangle^\ast}{\langle \alpha_E \rangle^\ast} \right| \times 100.$$ (11)

For a family of $N$-objects, we report the percentage average deviation value,

$$\overline{\text{dev}}(%) = \frac{\sum_{j=1}^{N} \text{dev}_{\nu}(\%) }{N}. \quad (12)$$

FIG. 2. Model oblate and prolate structures. The functional forms for calculating $\langle \alpha_E \rangle$ for oblate and prolate ellipsoids presented in (a) and (b), respectively, are provided in Ref. 7. Here, $\nu_{\text{eff}}$ is a function of the aspect ratio $r$. The flexible and flat sheets were generated to study the electromagnetic properties of graphene, Ref. 8, from which we drew our conformational data in (c) and (d).
FIG. 3. Equilibrium and non-equilibrium randomly branched polymer structures. In (a) and (b), we show non-equilibrium and equilibrium Eden clusters and diffusion-limited aggregate clusters, respectively, in (c), we show lattice animals or swollen branched equilibrium polymers, and in (d), we show “percolation clusters” or equilibrium branched polymers having screened excluded volume interactions.

Table I shows an example calculation of \( \text{dev}(\%) \) for dendrimers having different generation number. Here, \( \langle \alpha_E \rangle_c \) in column 6 has been computed using the columns 2, 3, and 4 on Eq. (9). The \( \text{dev}(\%) \) values for all the objects analyzed in this study are reported in Table II.

A. Flexible worm-like and rod-like polymers and particles

In Fig. 1, we consider rod-like nanoparticle and semi-flexible and flexible polymer models that have been used to model a flexible polymer such as polystyrene and rod structures such as carbon nanotubes and semi-flexible double-stranded DNA molecules (details of these calculations are described in supplementary material). In all cases, Eq. (9) holds to a good approximation, and we provide the effective scaling exponents \( \nu_{\text{eff}} \) in Table II. The flexible and semi-flexible polymer chains were generated by molecular dynamic simulations, as described in Ref. 8. We also varied the polymer cross-sectional shape and the shape of the rod-end to ensure that these morphological changes do not affect the quality of the property interrelationship. In Table I, we report the percent deviation between the calculated result and the theoretically estimated value.

B. Platelets and two-dimensional flexible polymers

Figure 2 considers model oblate and prolate shaped particles. Exact results are available for the ellipsoids, and they are used to test Eq. (9). We have also shown square plates and crumpled sheet particles that have been used to model graphene nanoparticles. Again, deviations between exact calculations and the numerical values for \( \langle \alpha_E \rangle \) are \( \approx 1\% \).

C. Equilibrium and non-equilibrium branched polymers

In Fig. 3, we investigate randomly branched polymers. In (a) and (b), we show perhaps the most commonly encountered non-equilibrium branched polymeric structures,12,6,8 Eden clusters,12,13 and diffusion-limited aggregate clusters. These cluster types are well known and the conformational data used in the computations are taken from the study of Mansfield and Douglas,26 who also provide illustration of representative clusters. Eden clusters are rather compact clusters while diffusion-limited aggregates DLA clusters are rather diffuse fractal-like clusters because they exhibit a non-trivial mass scaling over a large mass range. Both types of non-equilibrium cluster are rather spherical on average. In (c), we show lattice animals or swollen branched equilibrium polymers from the recent study of Audus et al.35 We contrast these results for swollen branched polymers with “percolation clusters” and...
equilibrium branched polymers with screened excluded volume interactions. Percolation clusters have been extensively studied before, and we refer to the work of Mansfield and Douglas for illustrative images of the percolation clusters utilized in the present analysis. The apparent mass scaling exponents are given in the supplementary material.

D. Polymers and particles having different topology

Polymer structures come in a wide range of topologies and it has traditionally been very difficult to account for topological effects on polymer transport properties. Figure 4 shows several important topological types. In Fig. 4(a), ring polymeric structures (as observed in some carbon nanotube materials) are one of the non-trivial shapes for which exact calculation can be made, and direct calculation of \( \nu_{\text{eff}} \) from these results shows that \( \nu_{\text{eff}} \) depends on the ratio \( r = r_1/r_2 \), \( r_1 \) and \( r_2 \) being the inner and outer radius. In (b), worm-like star polymer configurations having fixed arm length \( L = 18 \) beads and persistence length of the chains of each arm equals \( l_g = 3 \) beads in our coarse-grained model. A variable number of arms, \( f \), is considered in this plot where \( f \) varies from 10 to 35. The star polymer model uses the same chain model as studied in Refs. 28 and 29. Dendrimers involve a cascade of branching of fixed units so that this molecular has a hierarchical topology. Here, we draw upon dendrimer simulations ranging from dendrimer generation \( g_l = 3 \) to \( g_l = 11 \), where \( \nu_{\text{eff}} \) varies significantly with molecular mass in this type of polymeric structure. We are not aware of any previous molecular dynamics simulations of the hydrodynamic properties of semi-flexible rings having a large range of knot complexity, \( 0 \leq m \leq 8 \), the range encountered in practice with DNA samples, and we provide estimates of \( \langle \alpha_g \rangle \) in Fig. 4(d).

We model our polymer by a semi-flexible chain having a persistence length of 50.2 nm and a diameter of 2.8 nm, appropriate for dsDNA in solution containing 1M NaCl.

E. Polymers and particles having compact shape

In Fig. 5, we consider model polymers and nanoparticles that have a relatively compact structure. In particular, we test Eq. (9) for (a) ideal platonic solids, which are realized by mineral crystals, viruses, and many other natural forms. (b) Spherical inorganic nanoparticle with grafted chains. The polymer-grafted nanoparticle configurations were generated using MD and their properties were obtained by using ZENO. (c) Dense cluster of multi-walled carbon nanotubes or “tumbleweeds.” These complex-shaped particles are often observed in commercial nanotube materials, and the simulated tumbleweed structures are derived from molecular dynamics simulations of \( N \) worm-like tubes confined to a sphere. Here, we vary the number of carbon nanotubes (CNTS) in the range \( 20 \leq N \leq 240 \). (d) A sampling of globular proteins from the protein database. The ZENO protein property calculations were taken from Ref. 42.

As before, we find the deviation between the computed and directly estimated properties or the chosen globular proteins to be on the order of \( \approx 1\% \). The conformational data for the spherical nanoparticles with flexible chains is obtained from a previous study of single-stranded DNA grafted to nanoparticle surfaces having fixed length \( L = 10 \) beads and different number of strands \( N_s \), where \( N_s \) ranges from 5 to 100.

IV. DIRECT ANALYTIC ESTIMATION OF \([\eta]\) FROM \( R_g \) AND \( R_h \) DATA AND EXPERIMENTAL VALIDATION

We now combine Eq. (9) with the hydrodynamic-electrostatic relationships described in Sec. II to connect \([\eta]\), \( R_g \), and \( R_h \),

\[
[\eta] = \frac{q^2}{V_p} 4\pi(q R_h)^{1/\nu_{\text{eff}}} R_g^{(3\nu_{\text{eff}} - 1)/\nu_{\text{eff}}}. \tag{13}
\]

For the particular case of a spherical particle, \( q = 5/6 \), \( q_{\text{h}} = 1 \), \( V_p = 4/3\pi R_h^3 \), \( R_g = \sqrt[3]{5/3} R_h \), and \( \nu_{\text{eff}} = 1/3 \), we have \([\eta] = (5/2)\), which is consistent with the value determined by Einstein. More generally, \( q_{\text{h}} \) depends weakly of particle or polymer shape and it is determined from the classic components of the polarization tensor. First of all, if we take the simple approximation, \( q_{\text{h}} \approx 0.79 \) and \( q_{\text{h}} = 1 \), which is suitable for many complex shaped particles, and if we express \([\eta]\) in terms of polymer mass concentration, then Eq. (13) can be written as

\[
[\eta] = \frac{0.79N_A}{M} 4\pi\left(\frac{q R_h}{R_g}\right)^{1/\nu_{\text{eff}}} R_g^{(3\nu_{\text{eff}} - 1)/\nu_{\text{eff}}}. \tag{14}
\]

Combining Eq. (14) with the mass-scaling relationship for \( R_g = a_g M^{\alpha} \) which is equivalent for \( R_h = a_h M^{\alpha} \) provides an explicit and novel expression for the Mark–Houwink exponent relationship,

\[
[\eta] = \frac{0.79N_A}{M} \left(\frac{4\pi a_h}{a_g}\right)^{1/\nu_{\text{eff}}} R_g^{(3\nu_{\text{eff}} - 1)/\nu_{\text{eff}}} M^{(\nu_{\text{eff}} - 1)/3\nu_{\text{eff}} - 2}. \tag{15}
\]

defined by the scaling relation, \([\eta] = K M^\alpha \), where \( K \) is a precisely specified constant and the exponent \( \alpha \) equals \( a = \nu_{\text{eff}}/\nu_{\text{eff}} + 3\nu_{\text{eff}} - 2 \). For spherical particles, \( \nu_{\text{eff}} = \nu_{\text{eff}} = 1/3 \), so that \( a = 0 \), and for the particular case of polymers in a theta-solvent, \( \nu_{\text{eff}} = \nu_{\text{eff}} = 1/2 \), so that \( a = 1/2 \), as expected.

We next validate our proposed universal relationship between \([\eta]\), \( R_g \), and \( R_h \) based on experimental results. We first consider duplex DNA for this test since there is large and internally consistent experimental data base for \([\eta]\), \( R_g \), and \( R_h \) of this polymer because of the fundamental biological significance of this class of biopolymers. This class of polymers is also especially significant since scaling arguments that assume one scale governs polymer size have been shown to fail in this class of polymers. Finally, polydispersity of the chain length does not contribute greatly to experimental uncertainty in these biological macromolecules.

We may express \([\eta]\) in common polymer science concentration units, \((dl/g)\), as

\[
[\eta] (dl/g) = \frac{59.7844}{M(g)} R_h(nm)^{1/\nu_{\text{eff}}} R_g(nm)^{(3\nu_{\text{eff}} - 1)/\nu_{\text{eff}}}. \tag{16}
\]

Figure 6(a) shows a direct comparison between experimental measurements \([\eta]\) and analytic estimations obtained from
Eq. (16) denoted as $\eta^2$ as a function of the DNA molecular mass $M$. The $[\eta]_c$, $R_g$, and $R_h$ experimental data were taken from Ref. 32; further information about the calculation can be found in the supplementary material. We find that the average deviation between the computed and directly measured properties for DNA is $\text{dev}(\%) = 9.8\%$. This order of magnitude deviation for $[\eta]$ between the estimates and experimental measurements is comparable to the deviation between experimental estimates from the mass scaling relationships for $R_g$ and $R_h$ that describes DNA studies from different experimental groups and this higher uncertainty deviations can be traced to the high uncertainties in the experimental measurements of the radius of gyration (see the supplementary material). The black circles in Fig. 6 are experimental measurements and the red squares are calculated values by using Eq. (16).

We also consider the mass scaling of polystyrene in toluene in Fig. 6(b), another polymer for which tabulations of $[\eta]$, $R_g$, and $R_h$ have been made. The comparison of our analytic estimate from Eq. (16) to experiments reported by Roovers and Toporowski is also in good agreement, $\text{dev}(\%) = 3.0\%$. We again find that our analytic estimate of $[\eta]$ performs rather well without any free parameters.

FIG. 6. Comparison between experimental measurements $[\eta]$ and calculations $[\eta]^2$ for (a) double-stranded DNA and (b) polystyrene in toluene. Inset shows a direct comparison between our analytic estimates and the measured values of $[\eta]$.

V. CONCLUSIONS

We provide a general relationship that connects the properties, $C, R_g, \text{ and } (\langle \sigma_E \rangle)$ for particles having complex shape with no free parameters. This relationship has been tested for a variety of objects showing deviations from simulation estimates on the order $O(1\%)$. In contrast, expressions developed in the context of the approximate Kirkwood–Riseman and Debye–Bueche models have previously shown much larger deviations in general.\textsuperscript{3,32} Comparison of hydrodynamic theory to polymers and nanoparticles involves additional uncertainties, such as hydration in the case of DNA and chain polydispersity in polystyrene solution, but we find that we can estimate the properties to an uncertainty close to inherent experimental uncertainties.

Our universal relationship appears to explain the often observed difference in the mass scaling of polymer and nanoparticle properties. This new relation should allow for self-consistent estimates of polymer and nanoparticle size and a better characterization of the structure of polymers and nanoparticles based on precise static and dynamic light scattering measurements, in conjunction with solution viscosity and sedimentation measurements. Equation (9) can be used in conjunction with precise $[\eta]$, $R_h$, and $R_g$ observations, to estimate $\nu_{\text{eff}}$ for particular objects where no variable mass structures exist. This relation provides a measure of relative shape “irregularity” of particles that are not truly fractal and that in combination with other measures of polymer shape anisotropy, such as $R_h/R_g$, should have applications in classifying polymers and nanoparticles. Finally, Eq. (9) provides a useful consistency relationship among $[\eta]$, $R_h$, and $R_g$ measurements.
SUPPLEMENTARY MATERIAL

See supplementary material for more information about the computational models used to generate some of the nanoparticle and polymer configurations utilized to test the general relationship described in the main manuscript. We also include tables with the property values, their estimations, and their corresponding uncertainties.

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