Gaussian Statistics of Linear Chain Molecules and Crosslinked Elastomers

Summary of three-dimensional Gaussian chain statistics. In the absence of polymer-solvent interactions that typically induce chain expansion, the conformational characteristics of a single polymer chain can be described by three-dimensional random walk statistics. The following assumptions are appropriate.

(1) Long chain molecules act independently of each other when the polymer solution is very dilute. Except for the analysis of chain conformations in the solid state, it is necessary to dissolve polymers in an appropriate solvent to study their conformational characteristics in dilute solution. Under “Θ-solvent conditions”, which correspond to a particular temperature that depends on the polymer-solvent combination, the solvent does not induce chain expansion and the polymer, which is on the verge of precipitating from solution, exhibits unperturbed chain dimensions. Hence, in the presence of a solvent, properties of dilute polymer solutions can be measured by conventional techniques, but the conformation of long chain molecules in Θ-solvents is the same as their conformation in vacuo. “Good solvents” interact significantly with segments of the polymer chain, yielding dimensions from one end of the chain to the other end that are much larger than the “end-to-end” distance in a Θ-solvent.

(2) A single chain is described by \( n \) random steps, or chain segments, each of length \( \lambda \), where \( \lambda \) represents the length of a carbon-carbon single bond or the effective length of a monomeric repeat unit, sometimes referred to as the “Kuhn statistical segment length”.

(3) Freely jointed chains exhibit no bond angle or valence cone restrictions. Each conformation exhibits the same energy. Furthermore, it is perfectly acceptable for a chain segment to “fall back” on the previous segment such that both segments occupy the same region of space. This freedom is not enjoyed by real chains, as described by the principle of “excluded volume”, which increases the end-to-end distance of a real chain relative to a freely jointed chain.

One-dimensional random walk statistics of a freely jointed chain, via the formalism of Bernoulli trials and the binomial distribution, suggest that the conformational characteristics in three-dimensional space should follow a Gaussian distribution. The probability density distribution function, with dimensions of inverse volume, for finding an end-to-end chain vector \( \mathbf{r} \) after \( n \) steps, each of length \( \lambda \), is given by;
\[ P(r;n) = A \exp(-\beta^2 r^2) \]

where \( r^2 \) is the square of the magnitude of the end-to-end chain vector \( r \). This result implies that if one end of the polymer chain is anchored at the origin of a three-dimensional coordinate system, then it is most probable to find the other end at the origin also, but one must realize that there is no volume at \( r=0 \) to accommodate the end of the chain even if excluded volume is not considered. Analogously, if one flips a coin and take one step to the right each time the coin lands on its head, and one step to the left when the coin lands on its tail, then after a sufficient number of trials that justifies statistical analysis, the probabilities of obtaining heads and tails are 50:50 and the final position coincides with the initial position on a one-dimensional lattice. The Gaussian distribution parameters \( A \) and \( \beta^2 \), that characterize unperturbed chain dimensions in a \( \Theta \)-solvent, are calculated from (i) normalization of the distribution function, and (ii) evaluation of the mean-square end-to-end chain length, \( <r^2> \). If end-to-end chain vector \( r \) is measured from the origin of a rectangular Cartesian coordinate system and \( P(r;n)dr \) represents the probability that the end-to-end vector lies within the range from \( r \) to \( r+dr \), where orientation is an important consideration, then the normalization condition is written as follows;

\[
\int_{-\infty}^{+\infty} P(r;n)dr = 1
\]

where \( dr \) represents a differential volume element. In terms of the probability distribution function that is insensitive to orientation of the end-to-end chain vector, one expresses the differential volume element \( dr \) in spherical coordinates, such that;

\[
dr = r^2 \sin \Theta dr \ d\Theta \ d\phi
\]

and integrates over all possible angles \( \Theta \) and \( \phi \) (i.e., \( 0 \leq \Theta < \pi, \ 0 \leq \phi \leq 2\pi \)) to yield an end-to-end chain vector with length \( r \), where \( r \) is the magnitude of \( r \). Now, since the Gaussian distribution function depends only on the square of the magnitude of the end-to-end chain vector, one factors the normalization expression and obtains the probability density distribution function \( P(r;n) \) that does not depend on orientation, with dimensions of inverse length, such that \( P(r;n)dr \) represents the normalized probability of finding the end-to-end chain vector \( r \) on the surface of a spherical shell of radius \( r \) about the origin with thickness \( dr \). Hence;

\[
\int_{-\infty}^{+\infty} P(r;n)dr = \int_0^{2\pi} d\phi \int_0^{\pi} \sin \Theta d\Theta \int_0^{\infty} r^2 P(r;n)dr = 4\pi A \int_0^{\infty} r^2 \exp(-\beta^2 r^2)dr = 1
\]
The distribution function \( P(r;n) \) is given by \( 4\pi Ar^2 \exp(-\beta^2 r^2) \), and the previous statement of normalization yields the following result for the pre-exponential factor \( A \):

\[
A = \frac{\beta^3}{\pi^{3/2}}
\]

The mean-square end-to-end chain length is defined as the second moment of \( P(r;n) \);

\[
\langle r^2 \rangle = \int_{0}^{\infty} r^2 P(r;n) dr = 4\pi A \int_{0}^{\infty} r^4 \exp(-\beta^2 r^2) dr
\]

The second moment calculation, together with normalization, yields the following results;

\[
\langle r^2 \rangle = \frac{3}{2\beta^2}, \quad \beta^2 = \frac{3}{2\langle r^2 \rangle}, \quad A = \left\{ \frac{3}{2\pi\langle r^2 \rangle} \right\}^{3/2}
\]

\[
P(r;n) = 4\pi r^2 \left\{ \frac{3}{2\pi\langle r^2 \rangle} \right\}^{3/2} \exp\left( -\frac{3r^2}{2\langle r^2 \rangle} \right)
\]

**Vector analysis of the mean-square end-to-end chain distance.** Initially, one constructs an expression for the end-to-end chain vector \( \mathbf{r} \) by summing all \( n \) segment vectors \( \mathbf{h}_i \) as follows;

\[
\mathbf{r} = \sum_{i=1}^{n} \mathbf{h}_i
\]

where \( \mathbf{h}_i \) represents the segment vector from the \((i-1)^{\text{st}}\) mass point to the \(i^{\text{th}}\) mass point. Now, it is necessary to evaluate the scalar “dot” product of \( \mathbf{r} \) with itself by accounting for all dot products among the individual segment vectors. Hence;

\[
\mathbf{r} \cdot \mathbf{r} = \sum_{i=1}^{n} \mathbf{h}_i \cdot \sum_{k=1}^{n} \mathbf{h}_k
\]

There are \( n \) terms in the previous expression that contain the dot product of an individual segment vector with itself. Since each segment vector has the same length \( \lambda \), these \( n \) terms contribute \( n\lambda^2 \) to the square of the end-to-end chain distance. The previous
expression also contains \( n(n-1) \) (i.e., an even number of) dot products of two different segment vectors. Since \( \mathbf{h}_i \cdot \mathbf{h}_k \) is the same as \( \mathbf{h}_k \cdot \mathbf{h}_i \) and the \( n \) terms in which \( i = k \) have already been considered, the previous expression for the square of the end-to-end chain distance of a particular conformation reduces to:

\[
r \cdot r = \sum_{i=1}^{n} h_i \cdot \sum_{k=1}^{n} h_k = n \lambda^2 + \sum_{i,k=1 \,(i \neq k)}^{n} h_i \cdot h_k
\]

The previous expression for the square of the end-to-end chain distance \( r^2 \) of a particular conformation must be averaged with respect to the distribution of end-to-end chain vectors \( r \), where orientation is a necessary consideration due to the presence of the dot product of dissimilar segment vectors on the right side of the previous equation. In other words, a weighted average is required to calculate the mean-square displacement, where the weighting factor for a particular conformation with end-to-end chain vector \( r \) is given by \( P(r;n)dr \), which represents the normalized probability that this conformation exists. The mean-square end-to-end chain distance is constructed as follows;

\[
\langle r^2 \rangle = \int_{-\infty}^{\infty} \{r \cdot r\} P(r;n)dr = n \lambda^2 \int_{-\infty}^{\infty} P(r;n)dr + \sum_{i,k=1 \,(i \neq k)}^{n} \int_{-\infty}^{\infty} \{ h_i \cdot h_k \} P(r;n)dr
\]

The first term on the right side of the previous equation is simply \( n \lambda^2 \), due to the fact that \( P(r;n) \) is normalized. If \( \alpha_{ik} \) represents the orientation angle between segment vectors \( \mathbf{h}_i \) and \( \mathbf{h}_k \), then the dot product of these two vectors in the previous expression yields;

\[
\mathbf{h}_i \cdot \mathbf{h}_k = \lambda^2 \cos \alpha_{ik}
\]

and one must average the cosine of this orientation angle with respect to the angular part of the distribution of chain vectors. One obtains the following result;

\[
\langle r^2 \rangle = n \lambda^2 + \lambda^2 \left( \frac{\beta^3}{\pi^{3/2}} \right) \sum_{i,k=1 \,(i \neq k)}^{n} \int_{0}^{\pi} \{ \cos \alpha_{ik} \} \sin \Theta d\Theta d\varphi \int_{0}^{\infty} r^2 \exp(-\beta^2 r^2)dr
\]

Integration of the radial part of the distribution function over all possible chain lengths \( r \) yields;

\[
\int_{0}^{\infty} r^2 \exp(-\beta^2 r^2)dr = \frac{\sqrt{\pi}}{4 \beta^3}
\]
This is obtained rather quickly via differentiation of the following result with respect to the parameter \( a \), and then letting \( a = \beta^2 \);

\[
\int_0^\infty \exp(-ax^2)dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}
\]

The final result for the mean-square end-to-end chain distance via this analysis is;

\[
\langle r^2 \rangle = n\lambda^2 \left[ 1 + \frac{1}{4n\pi} \sum_{i,k=1}^{n} \int_0^{2\pi} \int_0^{\pi} \{ \cos \alpha_{ik} \} \sin \Theta d\Theta d\varphi \right]
\]

where the second term in large brackets \([\cdot]\) on the right side of the previous equation represents the expansion of real chains relative to unperturbed “ideal” chains due to bond angle restrictions, valence cone restrictions, and polymer-solvent interactions at temperatures that are above the \( \Theta \)-point. For freely jointed chains with no bond angle or valence cone restrictions, \( h_i \) and \( h_k \) are uncorrelated, unless \( i=k \), and there is no preferred orientation for \( \cos \alpha_{ik} \). Hence, the average value of \( \cos \alpha_{ik} \) with respect to the orientation part of the distribution of chain vectors vanishes and one finds that the mean-square end-to-end chain distance reduces to \( n\lambda^2 \).

**One-dimensional random walk statistics via Bernoulli trials and the binomial distribution.** If one flips an “ideal coin” that exhibits an equal probability of landing on its head or tail, then the sequential probability that the coin will land on its head \( x \) times after \( n \) trials is given by \( P(x;n) \). For example, when both elemental probabilities are equal (i.e., 50:50);

\[
P(x;n) = \frac{n!}{x!(n-x)!} \left( \frac{1}{2} \right)^n
\]

where \( x \) ranges from 0 to \( n \). This result based on Bernoulli trials with equal elemental probabilities is a subset of the binomial distribution with unequal elemental probabilities \( p \) for the coin landing on its head and \( q \) when it lands on its tail (i.e., \( p+q=1 \)). Now, the sequential probability that a real coin will land on its head \( x \) times after \( n \) trials is given by;

\[
P(x;n) = \frac{n!}{x!(n-x)!} p^x (1-p)^{n-x}
\]
where, once again, \( x \) ranges from 0 to \( n \). In both cases, the coefficient of the elemental probabilities corresponds to the \( x^{th} \) coefficient in the binomial expansion of \((p+q)^n\). The moments generating function for \( P(x;n) \) is useful, in general, to calculate average chain dimensions (i.e., end-to-end chain distance and mean-square displacement). For a discrete distribution function, like \( P(x;n) \), the moments generating function \( F(z) \) is defined by the “\( z \)-transform” of \( P(x;n) \);

\[
F(z) = \sum_{x=0}^{n} z^x P(x;n) = \sum_{x=0}^{n} \frac{n!}{x!(n-x)!} (pz)^x q^{n-x} = (pz + q)^n
\]

The first moment, or the average value, of this normalized distribution function \( P(x;n) \) is given by;

\[
\langle x \rangle = \left( \frac{dF}{dz} \right)_{z=1} = \left\{ np(pz + q)^{n-1} \right\}_{z=1} = np
\]

which can be interpreted as the average number of times that a real coin lands on its head. For completeness, in terms of evaluating the second moment of a distribution function;

\[
\langle x^2 \rangle = \left\{ \frac{z}{d^2z} \left( \frac{z}{dz} \left( \frac{dF}{dz} \right) \right) \right\}_{z=1} = np + n(n-1)p^2
\]

The \( k^{th} \) moment of the distribution function \( P(x;n) \) is obtained by subjecting the moments generating function \( F(z) \) to the operator \( \{ z \; d/dz \} \) \( k \) times and then evaluating the result at \( z=1 \). By definition of the \( z \)-transform of \( P(x;n) \), the zeroth moment of \( P(x;n) \) is obtained by evaluating the moments generating function \( F(z) \) at \( z=1 \), which yields unity for a normalized distribution. Random walk statistics on a one-dimensional lattice can be analyzed via Bernoulli trials when there are equal elemental probabilities that each step is taken toward the right (i.e., the coin lands on its head) or toward the left (i.e., the coin lands on its tail). The path followed by drunken sailors is analogous to random flight statistics. Furthermore, the concentration profile that satisfies the unsteady state one-dimensional diffusion equation (i.e., Fick’s second law of diffusion), subjected to a “spike input” initially at the edge of a semi-infinite rectangular slab, is analogous to the probability density distribution function for random flight statistics of freely jointed chains in the continuous limit. Begin at the origin of a one-dimensional lattice. After \( n \) random steps of unit length, \( n_R \) steps occur to the right and \( n_L \) steps are taken to the left. Hence, \( n_R + n_L = n \) and the net displacement to the right is \( n_R - n_L = m \), where \( n_R = (n+m)/2 \) is analogous to \( x \) in the previous examples. The sequential probability of obtaining a net displacement of \( m \) units to the right of the origin after \( n \) independent random steps of unit length is given by;
The previous expression for the probability density distribution function $P(m;n)$ is discrete in terms of the number $n$ of Bernoulli trials. The range of $m$ is from $-n$ (i.e., when $n_L=n$ and $n_R=0$) to $+n$ (i.e., when $n_L=0$ and $n_R=n$). Furthermore, the minimum change in $m$ is 2 units because $n_L$ and $n_R$ change by a minimum of 1 unit each, $n_L$ and $n_R$ must sum to $n$, which represents a constant number of discrete random steps, and $m = n_R - n_L = 2n_R - n$. One obtains a Gaussian distribution for $P(m;n)$ in the continuous limit for an exceedingly large number of random steps.

**Asymptotic expression for $P(m;n)$ via Bernoulli trials.** The following steps are required to obtain a Gaussian distribution for $P(m;n)$ after a very large number of random steps with equal elemental probabilities.

1) Take the natural logarithm of the discrete Bernoulli trials result for $P(m;n)$;

\[
\ln P(m;n) = \ln n! - \ln \left(\frac{(n+m)!}{2}\right) - \ln \left(\frac{(n-m)!}{2}\right) - n \ln 2
\]

2) Use Sterling’s approximation for the factorial, given by;

\[
n! \approx n^n \sqrt{2\pi n} \exp\left(-n\right) \left\{1 + \frac{1}{12n} + \frac{1}{288n^2} - \ldots\right\}
\]

\[
\ln n! \approx \frac{1}{2} \ln(2\pi) + (n + \frac{1}{2}) \ln n - n
\]

3) Obtain the following result after combining terms without invoking any other approximations;

\[
\ln P(m;n) \approx -\frac{1}{2} \ln(2\pi) + n \ln n + \frac{1}{2} \ln n - n \ln 2 - \frac{1}{2} (n + m + 1) \ln \left(\frac{n}{2}\left(1 + \frac{m}{n}\right)\right) - \frac{1}{2} (n - m + 1) \ln \left(\frac{n}{2}\left(1 - \frac{m}{n}\right)\right)
\]

4) Use a Taylor series expansion for $\ln (1 \pm x) \approx \pm x - x^2/2 \pm \ldots$ to evaluate the last two terms on the right side of the previous equation, truncating each series after the quadratic term since $m < n$;
\[
\ln \left( \frac{n}{2} \left( 1 + \frac{m}{n} \right) \right) = \ln n - \ln 2 + \ln \left( 1 + \frac{m}{n} \right) = \ln n - \ln 2 + \frac{m}{n} - \frac{m^2}{2n^2} + ... \\
\ln \left( \frac{n}{2} \left( 1 - \frac{m}{n} \right) \right) = \ln n - \ln 2 + \ln \left( 1 - \frac{m}{n} \right) = \ln n - \ln 2 - \frac{m}{n} - \frac{m^2}{2n^2} - ... 
\]

5) Further analysis of the last two terms on the right side of step (3), with assistance from the Taylor series expansions in step (4) yields:

\[
-\frac{n+1}{2} \left[ \ln \left( \frac{n}{2} \left( 1 + \frac{m}{n} \right) \right) + \ln \left( \frac{n}{2} \left( 1 - \frac{m}{n} \right) \right) \right] = -\frac{n+1}{2} \left( 2 \ln n - 2 \ln 2 - \frac{m^2}{n^2} \right) = -n \ln n + n \ln 2 + \frac{m^2}{2n} - \ln n + n \ln 2 + \frac{m^2}{2n^2} \\
-\frac{m}{2} \left[ \ln \left( \frac{n}{2} \left( 1 + \frac{m}{n} \right) \right) - \ln \left( \frac{n}{2} \left( 1 - \frac{m}{n} \right) \right) \right] = -\frac{m}{2} \left( \frac{2m}{n} \right) = -\frac{m^2}{n}
\]

6) Combining terms in steps (3) and (5) for an exceedingly large number of random steps implies that \( n \gg 1 \) and it is reasonable to neglect \( m^2/2n^2 \) relative to \( m^2/2n \) in step (5);

\[
\ln P(m; n) = -\frac{1}{2} \ln(2\pi) + n \ln n + \frac{1}{2} \ln n - n \ln 2 - n \ln n + n \ln 2 + \frac{m^2}{2n} - \ln n + n \ln 2 + \frac{m^2}{2n^2} - \frac{m^2}{n} \\
= -\frac{1}{2} \ln(2\pi) - \frac{1}{2} \ln n + \ln 2 - \frac{m^2}{2n}
\]

7) In the continuous limit where \( n \gg 1 \), one obtains a Gaussian distribution function for the probability of obtaining a net displacement of \( m \) units to the right of the origin on a one-dimensional lattice after \( n \) independent random steps of unit length with equal elemental probabilities forward and backward;

\[
P(m; n) \approx \sqrt{\frac{2}{\pi n}} \exp \left\{ -\frac{m^2}{2n} \right\}
\]

This distribution function must be divided by 2 to achieve normalization because the minimum change in \( m \) is 2 units via the discrete formulation, and \( m \) ranges from \( -\infty \) to \( +\infty \) in the continuous limit.
Extrapolation of one-dimensional Gaussian statistics to three dimensions.

On a one-dimensional lattice, the statistical problem focuses on anchoring one end of a long-chain molecule to the origin and evaluating the probability of finding the other end at position \( r_x \) to the right (i.e., in the positive \( x \)-direction) after \( n \) random steps, each of length \( \lambda_x \), where \( r_x = m \lambda_x \). Hence, one sets \( m = r_x / \lambda_x \) in the previous expression for \( P(m;n) \), divides \( P(m;n) \) by 2 to insure normalization in the continuous limit, as described above, and equates probabilities in terms of both distribution functions to yield the final expression for \( P(r_x;n) \);

\[
P(r_x;n) dr_x = P(r_x;n) \lambda_x dm = \frac{1}{2} P(m;n) dm
\]

\[
P(r_x;n) = \frac{1}{2 \lambda_x} P(m;n) = \sqrt{\frac{1}{2 \pi n \lambda_x^2}} \exp \left\{ - \frac{r_x^2}{2 n \lambda_x^2} \right\}
\]

It is rather straightforward to verify that \( P(r_x;n) \) is, indeed, normalized. The average displacement on the one-dimensional lattice, given by \( \langle r_x \rangle \), or the first moment of the distribution \( P(r_x;n) \) vanishes because the integrand of the following expression is an odd function;

\[
\langle r_x \rangle = \int_{-\infty}^{\infty} r_x P(r_x;n) dr_x = \sqrt{\frac{1}{2 \pi n \lambda_x^2}} \int_{-\infty}^{\infty} r_x \exp \left\{ - \frac{r_x^2}{2 n \lambda_x^2} \right\} dr_x = 0
\]

Hence, the average position of the end of a freely jointed long-chain molecule that exhibits Gaussian statistics on a one-dimensional lattice is at the origin, exactly where the other end is anchored. The second moment of the distribution \( P(r_x;n) \), or the mean-square displacement on a one-dimensional lattice is calculated as follows;

\[
\langle r_x^2 \rangle = \int_{-\infty}^{\infty} r_x^2 P(r_x;n) dr_x = 2 \sqrt{\frac{1}{2 \pi n \lambda_x^2}} \int_{0}^{\infty} r_x^2 \exp \left\{ - \frac{r_x^2}{2 n \lambda_x^2} \right\} dr_x = n \lambda_x^2
\]

This is the one-dimensional analog of the three-dimensional result for chain dimensions in which contributions from chain conformations to the left of the origin do not cancel those to the right. The final result for \( P(r_x;n) \) is completely analogous to the solution of the following unsteady state one-dimensional diffusion equation in which a homogeneous semi-infinite rectangular medium is subjected to a spiked tracer input at \( y=0 \) and \( t=0 \);
\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2}
\]

\[
C(y, t) = \sqrt{\frac{1}{4\pi Dt}} \exp\left\{-\frac{y^2}{4Dt}\right\}
\]

when the mean-square displacement \(<(r_x)^2>\) is given by 2Dt, where \(t\) accounts for time and \(D\) is the tracer diffusion coefficient in the medium. The final solution for \(P(r_x; n)\) can be extended to analyze random flight statistics of isotropic freely jointed chains in three dimensions. The following conditions apply:

1) The polymer chain consists of \(n\) random flight steps in three-dimensional space, where each step has length \(\lambda\). The mean-square end-to-end chain distance is \(<r^2> = n\lambda^2\) when there are no bond angle or valence cone restrictions of a freely jointed chain with no polymer-solvent interactions in a \(\Theta\)-solvent.

2) This three-dimensional problem is equivalent to three simultaneous one-dimensional problems where:

(i) \(n\) random steps, each of length \(\lambda_x\), occur with equal probability forward and backward in the \(x\)-direction such that the net displacement in the positive \(x\)-direction is \(r_x\) and the mean-square displacement is \(<(r_x)^2> = n(\lambda_x)^2\)

(ii) \(n\) random steps, each of length \(\lambda_y\), occur with equal probability forward and backward in the \(y\)-direction such that the net displacement in the positive \(y\)-direction is \(r_y\) and the mean-square displacement is \(<(r_y)^2> = n(\lambda_y)^2\)

(iii) \(n\) random steps, each of length \(\lambda_z\), occur with equal probability forward and backward in the \(z\)-direction such that the net displacement in the positive \(z\)-direction is \(r_z\) and the mean-square displacement is \(<(r_z)^2> = n(\lambda_z)^2\)

The sequential probability of finding an end-to-end chain vector \(r\) after \(n\) random steps is;

\[
P(r; n)dr = \{P(r_x; n)dr_x\} \{P(r_y; n)dr_y\} \{P(r_z; n)dr_z\}
\]

where the differential volume element \(dr\) is equivalent to the product of \(dr_x\), \(dr_y\) and \(dr_z\). Furthermore, the product of three Gaussian distribution functions on the right side of the previous equation yields a Gaussian distribution for \(P(r; n)\). For each random flight conformation, the sum of the square of each net displacement along the positive \(x\)-, \(y\)-, and \(z\)-directions yields the square of the end-to-end chain length \(r^2\). In other words;
\[ r^2 = r_x^2 + r_y^2 + r_z^2 \]

When the previous equation is averaged with respect to the distribution of chain lengths, one obtains the following relation between all of the mean-square displacements mentioned above;

\[ \langle r^2 \rangle = n \lambda^2 = \langle r_x^2 \rangle + \langle r_y^2 \rangle + \langle r_z^2 \rangle = n \left( \lambda_x^2 + \lambda_y^2 + \lambda_z^2 \right) \]

Since the three-dimensional random flight problem is applicable for isotropic media, chain segments are not oriented preferentially along any coordinate direction. In fact;

\[ \langle r_x^2 \rangle = \langle r_y^2 \rangle = \langle r_z^2 \rangle = \frac{1}{3} \langle r^2 \rangle \]

The final expression for the Gaussian distribution of chain lengths \( r \) in three-dimensional space is;

\[
P(r;n) = \frac{1}{\sqrt{2\pi \langle r^2 \rangle}} \exp \left\{ -\frac{r^2}{2\langle r^2 \rangle} \right\}
\]

\[ = \left( \frac{3}{2\pi \langle r^2 \rangle} \right)^{3/2} \exp \left\{ -\frac{3}{2} \left( \frac{r_x^2 + r_y^2 + r_z^2}{\langle r^2 \rangle} \right) \right\} = \left( \frac{3}{2\pi \langle r^2 \rangle} \right)^{3/2} \exp \left\{ -\frac{3r^2}{2\langle r^2 \rangle} \right\}
\]

which is very similar to the Maxwell-Boltzmann distribution of molecular velocities for an ideal gas that exhibits three-dimensional motion. The three-dimensional Gaussian distribution function for end-to-end chain length \( r \) is asymptotically exact for a large number \( n \) of segments when \( r \) is significantly less than the contour length \( n\lambda \). It is not physically possible for \( P(r;n) \) to yield a nonzero probability when the end-to-end chain dimensions are greater than the contour length, but the Gaussian distribution does not vanish unless \( r \) tends toward infinity. This discrepancy, however small, between realistic predictions and the Gaussian expression for \( P(r;n) \) has been corrected by invoking the “Langevin” distribution via restricted Lagrange multiplier optimization, as discussed in Chapter 6 when the molecular optical anisotropy of random coils and rigid rod-like polymers was presented.
Properties of three-dimensional Gaussian distributions and their moments generating function. One of the primary objectives of this section is to demonstrate that the Laplace transform of the Gaussian distribution function \( P(r;n) \) contains information about the moments \( \langle r^n \rangle \), where the \( n \)th moment of \( P(r;n) \) is defined as follows:

\[
\langle r^n \rangle = \int_{-\infty}^{\infty} r^n P(r;n) dr = 4\pi \int_0^{\infty} r^n P(r;n) r^2 dr
\]

Now, in terms of the Laplace vector \( \mathbf{s} \) which is oriented along the \( z \)-direction of a rectangular Cartesian coordinate system such that end-to-end chain vector \( r \) makes an angle \( \Theta \) (i.e., polar angle \( \Theta \) in spherical coordinates) with respect to \( \mathbf{s} \), the Laplace transform of \( P(r;n) \) is:

\[
L(\mathbf{s};n) = \int_{-\infty}^{\infty} P(r;n) \exp(-r \cdot \mathbf{s}) dr = \int_0^{2\pi} d\varphi \int_0^{\infty} P(r;n) r^2 dr \int_0^{\pi} \exp(-rs \cos \Theta) \sin \Theta d\Theta
\]

In the previous expression, integration with respect to polar angle \( \Theta \) yields a hyperbolic sine function that can be expanded in a Taylor series in which only the odd terms survive. For example, if one makes the following substitution, \( u = \cos \Theta \) and \( du = -\sin \Theta d\Theta \), then:

\[
\int_0^{\pi} \exp(-rs \cos \Theta) \sin \Theta d\Theta = -\int_1^{-1} \exp(-rsu) du = \frac{1}{rs} \left\{ \exp(rs) - \exp(-rs) \right\} = \frac{2}{rs} \sinh(rs) = 2 \left\{ (rs) + \frac{1}{3!}(rs)^3 + \frac{1}{5!}(rs)^5 + \frac{1}{7!}(rs)^7 + \ldots \right\}
\]

Substitution of the previous result into the Laplace transform of \( P(r;n) \) and identification of various moments of the Gaussian distribution yields:

\[
L(\mathbf{s};n) = \int_{-\infty}^{\infty} P(r;n) \exp(-r \cdot \mathbf{s}) dr = 4\pi \int_0^{\infty} \left\{ 1 + \frac{1}{3!}(rs)^2 + \frac{1}{5!}(rs)^4 + \frac{1}{7!}(rs)^6 + \ldots \right\} P(r;n) r^2 dr = 1 + \frac{1}{3!} \langle r^2 \rangle s^2 + \frac{1}{5!} \langle r^4 \rangle s^4 + \frac{1}{7!} \langle r^6 \rangle s^6 + \ldots
\]

Hence, the Laplace transform \( L(\mathbf{s};n) \) of the Gaussian distribution function contains information about the even moments of \( P(r;n) \), which are identified on the far right side of the previous equation by \( \langle r^{2n} \rangle \), with \( n=0,1,2,\ldots \). It is reasonable to describe \( L(\mathbf{s};n) \) as the moments generating function of \( P(r;n) \). Since \( P(r;n) \) is an even function of the magnitude of the end-to-end chain vector because the Gaussian distribution was constructed to be...
orientation-insensitive, all odd moments of \( P(r; n) \) are zero. Furthermore, the moments generating function of the Gaussian distribution is an even function of the magnitude of the Laplace vector \( s \), as illustrated by the final result below;

\[
L(s; n) = \int_{-\infty}^{+\infty} P(r; n) \exp(-r \cdot s) dr = \exp\left\{ \frac{1}{6} \langle r^2 \rangle s^2 \right\}
\]

Justification for the previous functional form of \( L(s; n) \) is obtained by re-expressing the integrand of the moments generating function as a product of three integrals in rectangular Cartesian coordinates (i.e., \( dr = dr_x dr_y dr_z \)) that are almost identical;

\[
L(s; n) = \int_{-\infty}^{+\infty} P(r; n) \exp(-r \cdot s) dr = \left\{ \frac{3}{2\pi \langle r^2 \rangle} \right\}^{3/2} \int_{-\infty}^{+\infty} \exp\left\{ \frac{-3r_x^2}{2\langle r^2 \rangle} \right\} \exp(-r_x s_x) dr_x \int_{-\infty}^{+\infty} \exp\left\{ \frac{-3r_y^2}{2\langle r^2 \rangle} \right\} \exp(-r_y s_y) dr_y \int_{-\infty}^{+\infty} \exp\left\{ \frac{-3r_z^2}{2\langle r^2 \rangle} \right\} \exp(-r_z s_z) dr_z
\]

Focus on integration with respect to the x-component of the end-to-end chain vector (i.e., \( dr_x \)) and expand the exponential function that contains the x-component of the Laplace vector (i.e., \( s_x \)) in a Taylor series about \( r_x s_x = 0 \). All odd functions in the integrand do not contribute to the final result. Furthermore, integration limits for the even functions can be changed from \(-\infty \Rightarrow +\infty \) to \( 0 \Rightarrow +\infty \), if all results are multiplied by 2;

\[
\int_{-\infty}^{+\infty} \exp\left\{ \frac{-3r_x^2}{2\langle r^2 \rangle} \right\} \exp(-r_x s_x) dr_x = \int_{-\infty}^{+\infty} \left[ 1 - r_x s_x + \frac{1}{2!} (r_x s_x)^2 - \frac{1}{3!} (r_x s_x)^3 + \cdots + \frac{(-1)^j}{j!} (r_x s_x)^j + \cdots \right] \exp\left\{ \frac{-3r_x^2}{2\langle r^2 \rangle} \right\} dr_x
\]

\[
2 \sum_{m=0}^{\infty} \frac{s_x^{2m}}{(2m)!} \int_0^{+\infty} r_x^{2m} \exp\left\{ \frac{-3r_x^2}{2\langle r^2 \rangle} \right\} dr_x = \sum_{m=0}^{\infty} \frac{s_x^{2m}}{(2m)!} (-1)^m \frac{m!}{m} \sqrt{\frac{\pi}{a}} = \sqrt{\frac{\pi}{a}} \exp\left( \frac{s_x^2}{4a} \right)
\]

\[
a = \frac{3}{2\langle r^2 \rangle}
\]

Assistance was obtained from the helpful hints in problem 1 at the end of this chapter to evaluate the integrals in the summation above. It is necessary to evaluate several terms in the summation on the far right side of the previous equation to identify the Taylor series of an exponential function [i.e., \( \exp(s_x^2/4a) \)]. Finally one evaluates three similar products to calculate the moments generating function for Gaussian distributions;
\[
L(s; n) = \left[ \frac{3}{2\pi (r^2)} \right]^{3/2} \int_{-\infty}^{+\infty} \exp \left\{ -\frac{3r^2}{2(r^2)} \right\} \exp(-r \cdot s) \, dr \int_{-\infty}^{+\infty} \exp \left\{ -\frac{3r^2}{2(r^2)} \right\} \exp(-r \cdot s) \, dr \\
= \frac{3}{2\pi (r^2)} \left\{ \sqrt{\frac{2}{3}} \pi \langle r^2 \rangle \exp \left( \frac{1}{6} \langle r^2 \rangle s^2 \right) \right\}^2 \left\{ \sqrt{\frac{2}{3}} \pi \langle r^2 \rangle \exp \left( \frac{1}{6} \langle r^2 \rangle s^2 \right) \right\}^n = \exp \left( \frac{1}{6} \langle r^2 \rangle s^2 \right)
\]

If one expands the exponential function in the previous equation for \( L(s; n) \) in a Taylor series and compares both infinite series expressions for the moments generating function for Gaussian distributions;

\[
L(s; n) = \int_{-\infty}^{+\infty} P(r; n) \exp(-r \cdot s) \, dr = 1 + \frac{1}{3!} \langle r^2 \rangle s^2 + \frac{1}{5!} \langle r^4 \rangle s^4 + \frac{1}{7!} \langle r^6 \rangle s^6 + ... \\
= \exp \left( \frac{1}{6} \langle r^2 \rangle s^2 \right) = 1 + \frac{1}{6} \langle r^2 \rangle s^2 + \frac{1}{2!} \left( \frac{1}{6} \langle r^2 \rangle s^2 \right)^2 + \frac{1}{3!} \left( \frac{1}{6} \langle r^2 \rangle s^2 \right)^3 + \frac{1}{4!} \left( \frac{1}{6} \langle r^2 \rangle s^2 \right)^4 + ...
\]

then any even moment of \( P(r; n) \), \( \langle r^{2n} \rangle \), can be expressed in terms of the \( n^{th} \) power of the mean-square end-to-end chain length, \( \langle r^2 \rangle \). The result is;

\[
\langle r^{2n} \rangle = \frac{(2n + 1)!}{n!} \left( \frac{1}{6} \langle r^2 \rangle \right)^n
\]

**Mean-square radius of gyration of freely jointed chains.** The mean-square end-to-end chain distance is difficult to visualize when large molecules contain loops, rings, branches, or multi-arm star-like segments. For these types of structures, the radius of gyration provides a better description of molecular size. The mean-square end-to-end distance and the mean-square radius of gyration enjoy a very simple relation for ideal straight-chain molecules that obey the freely jointed assumptions, where the former is 6-fold larger than the latter. If all chain segments or repeat units of a macromolecule have the same mass (i.e., \( m_i = m \)), then the center of mass is defined by the following equation for large molecules that contain \( n+1 \) point masses (i.e., \( 0 < i < n \)) connected by \( n \) segments;

\[
\sum_{i=0}^{n} m_i r_{i,CM} = m \sum_{i=0}^{n} r_{i,CM} = 0
\]

where \( m_i \) is the mass of the \( i^{th} \) repeat unit, assumed to be concentrated at point \( i \), and \( r_{i,CM} \) represents a vector from the center of mass of the chain to the \( i^{th} \) point mass. The zeroth
point identifies the beginning of the chain and the n\textsuperscript{th} point corresponds to the chain end with end-to-end chain vector \( \mathbf{r} \). The mean-square radius of gyration is defined by summing \( \mathbf{r}_{i,CM} \cdot \mathbf{r}_{i,CM} \) over all n+1 mass points, dividing by the total number of mass points, and averaging (i.e., \( < > \)) the result with respect to the distribution of chain segments. Hence;

\[
\langle s^2 \rangle = \frac{1}{n+1} \sum_{i=0}^{n} \langle \mathbf{r}_{i,CM} \cdot \mathbf{r}_{i,CM} \rangle
\]

Now, rewrite \( \mathbf{r}_{i,CM} \) in terms of the vector from the center of mass to the beginning of the chain, \( \mathbf{r}_{0,CM} \), and the vector from the beginning of the chain to the \( i \)\textsuperscript{th} mass point, \( \mathbf{r}_{i0} \) via vector addition. The definition of the center of mass yields;

\[
\sum_{i=0}^{n} \mathbf{r}_{i,CM} = \sum_{i=0}^{n} \{ \mathbf{r}_{0,CM} + \mathbf{r}_{i0} \} = (n+1)\mathbf{r}_{0,CM} + \sum_{i=0}^{n} \mathbf{r}_{i0} = 0
\]

\[
\mathbf{r}_{0,CM} = -\frac{1}{n+1} \sum_{i=0}^{n} \mathbf{r}_{i0} = -\frac{1}{n+1} \sum_{j=0}^{n} \mathbf{r}_{j0}
\]

Next, one calculates the square of the magnitude of the vector from the center of mass to the \( i \)\textsuperscript{th} mass point;

\[
\mathbf{r}_{i,CM} \cdot \mathbf{r}_{i,CM} = \{ \mathbf{r}_{0,CM} + \mathbf{r}_{i0} \} \cdot \{ \mathbf{r}_{0,CM} + \mathbf{r}_{i0} \} = r_{0,CM}^2 + 2\mathbf{r}_{0,CM} \cdot \mathbf{r}_{i0} + r_{i0}^2
\]

The previous two results are employed to sum the magnitudes of the vectors from the center of mass to each of the n+1 mass points;

\[
\sum_{i=0}^{n} (\mathbf{r}_{i,CM} \cdot \mathbf{r}_{i,CM}) = (n+1)r_{0,CM}^2 + 2\sum_{i=0}^{n} \mathbf{r}_{i0} \cdot \sum_{i=0}^{n} r_{i0}^2
\]

\[
= \sum_{i=0}^{n} r_{i0}^2 + \frac{1}{n+1} \left( \sum_{i=0}^{n} \mathbf{r}_{i0} \right) \cdot \left( \sum_{j=0}^{n} \mathbf{r}_{j0} \right) - \frac{2}{n+1} \left( \sum_{j=0}^{n} \mathbf{r}_{j0} \right) \cdot \left( \sum_{i=0}^{n} \mathbf{r}_{i0} \right)
\]

\[
= \sum_{i=0}^{n} r_{i0}^2 - \frac{1}{n+1} \left( \sum_{i=0}^{n} \mathbf{r}_{i0} \right) \cdot \left( \sum_{j=0}^{n} \mathbf{r}_{j0} \right)
\]
Define segment vector $\mathbf{r}_{ij}$ from the $i^{th}$ mass point to the $j^{th}$ mass point in the chain in terms of the difference between vectors from the beginning of the chain to the $j^{th}$ point relative to the $i^{th}$ point:

$$
\mathbf{r}_{ji} = \mathbf{r}_{j0} - \mathbf{r}_{i0}
$$

$$
\mathbf{r}_{ji} \cdot \mathbf{r}_{ji} = r_{j0}^2 + r_{i0}^2 - 2 \mathbf{r}_{i0} \cdot \mathbf{r}_{j0}
$$

$$
\mathbf{r}_{i0} \cdot \mathbf{r}_{j0} = \frac{1}{2} \left\{ r_{j0}^2 + r_{i0}^2 - \mathbf{r}_{ji} \cdot \mathbf{r}_{ji} \right\}
$$

This relation between various segment vectors allows one to evaluate the double summation on the far right side of the expression for the sum the magnitudes of the vectors from the center of mass to each of the $n+1$ mass points. For example:

$$
\sum_{i=0}^{n} (\mathbf{r}_{i,CM} \cdot \mathbf{r}_{i,CM}) = \sum_{i=0}^{n} r_{i0}^2 - \frac{1}{n+1} \left\{ \sum_{i=0}^{n} r_{i0} \right\} \cdot \left\{ \sum_{j=0}^{n} r_{j0} \right\}
$$

$$
= \sum_{i=0}^{n} r_{i0}^2 - \frac{1}{n+1} \sum_{i=0}^{n} \sum_{j=0}^{n} \frac{1}{2} \left\{ r_{j0}^2 + r_{i0}^2 - \mathbf{r}_{ji} \cdot \mathbf{r}_{ji} \right\}
$$

$$
= \frac{1}{2(n+1)} \sum_{i=0}^{n} \sum_{j=0}^{n} \mathbf{r}_{ji} \cdot \mathbf{r}_{ji}
$$

Dividing the previous result by the total number of mass points (i.e., $n+1$) and averaging (i.e., $\langle \rangle$) with respect to the distribution of chain segments yields the mean-square radius of gyration for chains of arbitrary shape and conformational model;

$$
\langle s^2 \rangle = \frac{1}{n+1} \sum_{i=0}^{n} \langle \mathbf{r}_{i,CM} \cdot \mathbf{r}_{i,CM} \rangle = \frac{1}{2(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{n} \langle \mathbf{r}_{ji} \cdot \mathbf{r}_{ji} \rangle
$$

This result is not restricted to freely jointed chains. However, the remainder of this analysis focuses on segment vectors from the $i^{th}$ mass point to the $j^{th}$ mass point in freely jointed chains. Similar to the random coil results on pages 3-5 of this chapter for the mean-square end-to-end chain distance, in which individual segment vectors $\mathbf{h}_i$ from the $(i-1)^{st}$ mass point
to the $i^{th}$ mass point are uncorrelated for different values of $i$, one obtains the following ensemble average with respect to any orientation-insensitive distribution of chain vectors;

$$\langle r_{ji} \cdot r_{ji} \rangle = \lambda^2 |j - i|$$

when the length of each segment vector between adjacent mass points in the chain is $\lambda$. Obviously, when $i=0$ and $j=n$, the previous equation yields the mean-square end-to-end distance of the entire chain, as developed earlier in this chapter. It is not necessary to invoke Gaussian statistics for $r_{ji}$ when the $i^{th}$ and $j^{th}$ mass points in the chain are rather close such that the number of random steps between them is not too large. Simple vector analysis yields the previous equation for any value of the magnitude of the difference between $i$ and $j$ if the distribution function for freely jointed segments is independent of the orientation of each random step. Now, the mean-square radius of gyration for $n$ random steps in a freely jointed chain reduces to;

$$\langle s^2 \rangle = \frac{1}{n+1} \sum_{i=0}^{n} \langle r_{i,CM} \cdot r_{i,CM} \rangle = \frac{1}{2(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{n} \langle r_{ji} \cdot r_{ji} \rangle = \frac{\lambda^2}{2(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{n} |j - i|$$

Consider an $n+1$ by $n+1$ square matrix in which the value of $i$ in each cell increases from top to bottom and $j$ increases from left to right. Each of the $(n+1)^2$ cells in this square matrix is characterized by a unique set of values for $i$ and $j$. Differences between $i$ and $j$ vanish in each of the $n+1$ cells along the main diagonal from upper left to lower right. Hence, it is possible to evaluate the absolute magnitude of the difference between $i$ and $j$ in each cell of the square matrix by focusing only on the diagonals that are above the main diagonal and multiplying the sum by 2. For example, there are $n$ cells on the diagonal that is just above the main diagonal from upper left to lower right, and the difference between $i$ and $j$ in each of these $n$ cells is 1. Then, there are $n-1$ cells on the second diagonal above the main one from upper left to lower right, and the difference between $i$ and $j$ in each of these $n-1$ cells is 2. Finally, the diagonal in the upper right corner of the square matrix contains 1 cell in which $i=0$ and $j=n$; hence the difference between $i$ and $j$ is $n$. The double summation on the far right side of the previous equation is evaluated in detail when $n=6$. The numbers below represent $ij$-pairs in all 49 cells of the $7 \times 7$ matrix;
There are 7 cells on the main diagonal, upper left to lower right; \( j - i = 0 \) in each case.

(2) There are 6 cells on the diagonal just above the main one; \( j - i = 1 \), in each case.

(3) There are 5 cells on the diagonal just above the previous one; \( j - i = 2 \), in each case.

(4) There are 4 cells on the diagonal just above the previous one; \( j - i = 3 \), in each case.

(5) There are 3 cells on the diagonal just above the previous one; \( j - i = 4 \), in each case.

(6) There are 2 cells on the diagonal just above the previous one; \( j - i = 5 \), in each case.

(7) There is 1 cell on the diagonal just above the previous one; \( j - i = 6 \), in each case.

Since \( n=6 \) in this example, there are \( n+1-k \) cells on a given diagonal in which \( j - i = k \), and the index \( k \) ranges from 0 to \( n \). After multiplication by 2 to account for all cells on diagonals below the main diagonal from upper left to lower right, it is possible to evaluate the required summation as follows:

\[
\sum_{i=0}^{n} \sum_{j=0}^{n} |j - i| = 2 \sum_{k=0}^{n} k(n+1-k) = 2(n+1)\sum_{k=1}^{n} k - 2\sum_{k=1}^{n} k^2 \\
\sum_{k=1}^{n} k = \frac{n}{2}(n+1) \\
\sum_{k=1}^{n} k^2 = \frac{n}{6}(n+1)(2n+1)
\]

Finite sums for \( k \) and \( k^2 \), \( 1 \leq k \leq n \), can be found in the following reference; IS Gradshteyn & IM Ryzhik, *Tables of integrals, series, and products; corrected and enlarged edition*, Academic Press (1980), p. 1. Whereas the former sum of \( k \), \( 1 \leq k \leq n \), is rather trivial, the sum of \( k^2 \), \( 1 \leq k \leq n \), requires the use of factorial polynomials, calculation of the anti-difference of the factorial polynomial representation of \( k^2 \), and evaluation of this anti-difference at argument \( n+1 \) relative to an argument of 1. The mean-square radius of gyration of a freely jointed chain consisting of \( n \) random steps, each of length \( \lambda \), is given by the following expression when the number of steps is large;
Mean-square end-to-end distance of freely rotating chains. As a general rule, chain dimensions are larger when the backbone bond angles (i.e., C-C-C, C-O-C, C-N-C, etc.) are restricted, relative to the size of freely jointed chains that can “collapse upon themselves” with no excluded volume. The following vector analysis for semi-realistic chains with fixed bond angle $\pi-\Theta$ and free rotation about the valence cone yields the Eyring-Sadron equation for the mean-square end-to-end chain distance. Essentially a continuum of rotational isomeric states is allowed, corresponding to no preference for the Ramachandran backbone bond rotation angles $\phi$ and $\psi$ that correspond to trans ($\phi=180^0$), gauche + ($\phi=60^0$), and gauche – ($\phi=300^0$). There is no energy barrier between any of these chain conformations in this analysis. Even the cis or “eclipsed” conformation at $\phi=0^0$, which is highly unfavourable for real chains, is allowed (hence, the term “semi-realistic” is used to describe these chains). As discussed very early in this chapter, the following expression must be evaluated and averaged with respect to the normalized distribution of end-to-end chain vectors $P(r;n)$ to calculate the mean-square end-to-end chain distance;

$$\langle s^2 \rangle = \frac{\lambda^2}{2(n+1)^2} \sum_{i=0}^{n} \sum_{j=0}^{n} |j-i| = \frac{\lambda^2}{2(n+1)^2} \left\{ n(n+1) - \frac{n}{3}(n+1)(2n+1) \right\}$$

$$= \frac{\lambda^2}{2(n+1)^2} n(n+1) \left\{ n+1 - \frac{1}{3}(2n+1) \right\}$$

$$= \frac{1}{6} n \lambda^2 \left\{ \frac{n+2}{n+1} \right\} \approx \frac{1}{6} n \lambda^2$$

where $\mathbf{h}_i$ represents a segment vector of length $\lambda$ from the $(i-1)^{st}$ mass point to the $i^{th}$ mass point in the chain. Without invoking the Gaussian distribution of end-to-end chain vectors that is only appropriate for freely jointed chains, one evaluates the following scalar “dot” products of segment vectors;
\[ h_i \cdot h_{i+1} = \lambda^2 \cos \Theta \]
\[ h_i \cdot h_{i+3} = \lambda^2 \{ \cos \Theta \}^3 \]
\[ h_i \cdot h_k = \lambda^2 \{ \cos \Theta \}^{k-i} \]

where \( \Theta \) is the supplement of the actual backbone bond angle, given by \( \pi - \Theta \). For example, \( \Theta = 70.5^\circ \) and \( \pi - \Theta = 109.5^\circ \) when the chain backbone consists exclusively of carbon-carbon single bonds. Since the normalized distribution function of end-to-end chain vectors for semi-realistic chains exhibits no preference for any Ramachandran backbone bond rotation angle on the valence cone, the ensemble average of \( \cos \Theta \) is, simply, \( \cos \Theta = 1/3 \) for tetrahedral bond angles. The mean-square end-to-end distance of an \( n \)-segment chain, where the length of each segment is \( \lambda \), can be calculated from the following expression;

\[ \langle r^2 \rangle = \langle r \cdot r \rangle = \lambda^2 \left\{ n + \sum_{i,k=1,i \neq k}^n \{ \cos \Theta \}^{k-i} \right\} = \lambda^2 \left\{ n + \sum_{i,k=1,i \neq k}^n x^{k-i} \right\} \]

where \( x = \cos \Theta < 1 \) in the analysis below. The magnitude of the difference between \( k \) and \( i \), or \( j \) and \( i \), in an \( n \) by \( n \), or \( n+1 \) by \( n+1 \), square matrix was considered in the previous section for the mean-square radius of gyration. In summary, there are \( (n-p) \) terms in which the magnitude of the differences between \( k \) and \( i \) equals \( p \), where \( p \) ranges from 0 to \( n-1 \), and the entire sum must be multiplied by 2. Furthermore, all terms in which \( i \) and \( k \) are the same have already been removed from the double summation (i.e., \( n \lambda^2 \)), so one must neglect all contributions when \( p = 0 \). In the previous example, the summations ranged from 0 to \( n \) and the magnitude of the differences between \( j \) and \( i \) ranged from 0 to \( n \). Now, the summations range from 1 to \( n \), or 0 to \( n-1 \), so the magnitude of the differences between \( j \) and \( i \) ranges from 0 to \( (n-1) \). In the previous example, failure to remove all contributions where \( i \) and \( j \) are the same did not affect the summation because the magnitude of the differences between \( i \) and \( j \) was simply added. Now, contributions to the power series are not negligible when the exponent is zero. Consider the double summation on the far right side of the previous equation for the mean-square end-to-end chain distance;

\[ \sum_{i,k=1,i \neq k}^n x^{k-i} = 2 \sum_{p=1}^{n-1} (n - p) x^p = 2n \sum_{p=1}^{n-1} x^p - 2 \sum_{p=1}^{n-1} p x^p \]

The following techniques are employed to evaluate each finite sum on the far right side of the previous equation.
(1) The infinite power series of $x^p$, where $p$ ranges from 1 to $\infty$ and $x < 1$, can be evaluated by subtracting the power series of $x^{p+1}$ from the original power series. Since there are an infinite number of terms in each series, all terms cancel except the initial term in the series of $x^p$ when $p = 1$. For example;

$$
\sum_{p=1}^{\infty} x^p = x + x^2 + x^3 + x^4 + x^5 + \ldots
$$

$$
x \sum_{p=1}^{\infty} x^p = \sum_{p=1}^{\infty} x^{p+1} = x^2 + x^3 + x^4 + x^5 + \ldots
$$

$$(1 - x) \sum_{p=1}^{\infty} x^p = x
$$

(2) An infinite series can be split into a finite series and another infinite series via continuity of the index $p$. Then, the finite power series of $x^p$ can be written as the difference between two infinite series, both of which have been evaluated in step (1);

$$
\sum_{p=1}^{\infty} x^p = \frac{x}{1 - x} = \sum_{p=1}^{n-1} x^p + \sum_{p=n}^{\infty} x^p = \sum_{p=1}^{n-1} x^p + x^{n-1} \sum_{p=1}^{\infty} x^p = \sum_{p=1}^{n-1} x^p + \frac{x^n}{1 - x}
$$

$$
\sum_{p=1}^{n-1} x^p = \frac{x - x^n}{1 - x}
$$

(3) The finite power series of $px^p$, where $p$ ranges from 1 to $n-1$, can be evaluated by differentiating the final result from step (2) with respect to $x$, and then multiplying by $x$. Hence;

$$
\sum_{p=1}^{n-1} px^p = x \frac{d}{dx} \left\{ \sum_{p=1}^{n-1} x^p \right\} = x \frac{d}{dx} \left( \frac{x - x^n}{1 - x} \right)
$$

$$
= x \left[ \frac{(1-x)(1-nx^{n-1}) - (x-x^n)(-1)}{(1-x)^2} \right] = x \left[ \frac{(1-x^n)}{(1-x)^2} - \frac{nx^n}{1-x} \right]
$$

The Eyring-Sadron equation for the mean-square end-to-end chain distance of freely rotating chains is exact for any number $n$ of segments, where the length of each segment is $\lambda$.
\[ \langle r^2 \rangle = \lambda^2 \left\{ n + 2n \sum_{p=1}^{n-1} x^p - 2 \sum_{p=1}^{n-1} px^p \right\} = \lambda^2 \left\{ n + 2n \left( \frac{x - x^n}{1 - x} \right) - 2 \left[ \frac{x(1-x^n)}{(1-x)^2} - nx^n \right] \right\} \\
= n\lambda^2 \left\{ \frac{1 + x}{1 - x} - \frac{2x(1-x^n)}{n(1-x)^2} \right\} ; x = \cos \Theta 
\]

One obtains the following relation for freely rotating chains that contain a large number of segments (i.e., \( n \gg 1 \)) with tetrahedral backbone bond angles (i.e., \( \pi - \Theta = 109.5^\circ \), \( \Theta = 70.5^\circ \), \( x = \cos \Theta = 1/3 \));

\[ \langle r^2 \rangle \Rightarrow n\lambda^2 \left\{ \frac{1 + x}{1 - x} \right\} \Rightarrow 2n\lambda^2 \]

**Characteristic ratios, persistence length, and statistical segment length.** Several parameters have been defined to measure the deviation of realistic chain dimensions from either freely jointed or freely rotating chains in a theta solvent where polymer-solvent interactions are non-existent. Flory’s characteristic ratio \( C_n \) accounts for deviations of real chains in theta solvents from freely jointed chain dimensions. Based on results from the previous section for freely rotating chains, \( C_n \) depends on the number of segments in the chain, as illustrated below;

\[ C_n = \frac{\langle r^2 \rangle_{\text{solvent unperturbed}}}{n\lambda^2_{\text{freely rotating chains}}} = \frac{1 + \cos \Theta}{1 - \cos \Theta} - \frac{2 \cos \Theta \left( 1 - \cos^n \Theta \right)}{n \left( 1 - \cos \Theta \right)^2} \Rightarrow \frac{1 + \cos \Theta}{1 - \cos \Theta} \Rightarrow 2 \]

However, the characteristic ratio asymptotically approaches a constant when the number of chain segments is infinitely large. The Stockmayer-Kurata ratio \( \sigma_{SK} \) measures deviations of real chains in theta solvents from freely rotating dimensions. Hence, \( \sigma_{SK} \) reflects preferences for particular rotational isomeric states.

**Excluded volume and the expansion factor \( \alpha \) for real chains in “good” solvents; athermal solutions.** All previous discussion in this chapter focuses on ideal chains, with or without bond-angle restrictions. By definition, there is no excluded volume associated with ideal chains. When excluded volume is an important consideration, polymers prevent segments within the same chain, as well as neighboring molecules, from occupying overlapping regions of space. Consequently, the root-mean-square end-to-end distance of
ideal chains must be multiplied by the expansion factor $\alpha$, which is greater than unity, to obtain the actual dimensions of real chains. There are a total of $\upsilon$ chains, and $\upsilon_i$ represents the number of chains that have the same end-to-end chain distance $r_i$ in the expanded state. Hence, $\Sigma \upsilon_i = \upsilon$. It is important to emphasize that all $\upsilon_i$ chains with the same end-to-end distance do not necessarily have the same rotational state for each backbone bond. Conformations that exhibit different end-to-end chain distances are not equally probable, as described by the Gaussian distribution function $P_i(r_i)$ in the unperturbed state. For example, the exponentially decreasing probability density distribution function, $A \exp(-\beta^2 r_i \cdot r_i)$, for freely-jointed chains predicts that conformations with a larger end-to-end vector are less favourable. The answer to problem #1(a) at the end of this chapter reveals that the most probable length of ideal chains with no restrictions on bond angle or orientation is obtained by maximizing $4\pi Ar^2 \exp(-\beta^2 r \cdot r)$, which includes the volume element of a spherical shell of radius $r$ about the origin where one chain end is anchored, such that $r_{MostProbable} = 1/\beta$. Unperturbed chain conformations follow a Gaussian distribution in the ideal state, but polymer-solvent interactions cause chain expansion and produce non-Gaussian conformations. Analogous to elongation ratios for stretched networks, discussed later in this chapter and in the next chapter, the expansion factor $\alpha$ provides a connection between freely-jointed Gaussian chains in theta solvents and expanded real chains in good solvents. If $\omega_i$ represents the total number of conformations that are available to a single chain with end-to-end distance $r_i$, then the multiplicity of states $\Omega$ considers groups of conformations with different $r_i$, instead of counting each conformation separately. Hence, the same normalized Gaussian probability density distribution appears as a factor $\upsilon_i$ times in the multiplicity function because there are $\upsilon_i$ chains with the same end-to-end distance in the expanded state. One constructs the following expression for $\Omega$;

$$\Omega = \upsilon! \prod_{\text{groups of Conformations with different } r_i} \frac{\omega_i^{\upsilon_i}}{\upsilon_i!} \prod_{\text{groups of Conformations with different } r_i} \left\{\frac{\omega_0 P_i \varphi_i}{\upsilon_i!}\right\}^{\upsilon_i}$$

where $\omega_0$ is the total number of conformations that are available to a single chain, regardless of the end-to-end vector, $P_i$ identifies a subset of $\omega_0$ with end-to-end chain distance $r_i$ in the absence of excluded volume (i.e., Gaussian distribution function), and $\varphi_i$ reduces the total number of conformations with end-to-end chain distance $r_i$ as a consequence of excluded volume. These excluded volume factors (i.e., $\varphi_i$) are assumed to be the same for all $r_i$, which simplifies the analysis. If all chain conformations are equally probable and excluded volume is not an important consideration, then one sets each factor of $\omega_0 P_i \varphi_i$ to unity in the
multiplicity of states $\Omega$. Upon taking the logarithm of the previous equation and employing a simplified version of Sterling’s approximation (i.e., $\ln x! \approx x\ln x - x$), one obtains;

$$
\ln \Omega = \ln \nu! + \sum_{\text{groups of Conformations}} \sum_{\text{w/different } r_i} v_i \ln \left\{ \omega_0 P_i \varphi_i \right\} - \sum_{\text{groups of Conformations}} \sum_{\text{w/different } r_i} \ln v_i!
$$

$$
\ln \nu! \approx \nu \ln \nu - \nu = \ln \nu \sum_i v_i - \nu
$$

$$
\ln \Omega_0 = \nu \ln \omega_0
$$

$$
\ln \left\{ \frac{\Omega}{\Omega_0} \right\} \approx \sum_{\text{groups of Conformations}} \sum_{\text{w/different } r_i} v_i \ln \varphi_i + \sum_{\text{groups of Conformations}} \sum_{\text{w/different } r_i} \ln \left\{ \frac{vP_i}{v_i} \right\} \varphi_i \rightarrow \varphi
$$

$\Omega_0$ represents the total number of conformations available to an ensemble of $\nu$ chains with unconstrained end-to-end vectors. The corresponding entropy is $S_0 = k \ln \Omega_0$. The strategy is to employ Gaussian statistics for (i) freely-jointed chains and (ii) the radius of gyration distribution for segments about the center of mass, together with a lattice model description of excluded volume, to evaluate both terms on the far right side of the previous equation for $\ln \{\Omega/\Omega_0\}$. Boltzmann’s entropy equation (i.e., $S = k \ln \Omega$) provides a route to calculate equilibrium thermodynamic properties from this conformational study, and the expansion factor is chosen to minimize the Helmholtz free energy of the system of $\nu$ chains at constant temperature $T$ and total system volume $V$. Chain expansion does not increase the volume of dilute solutions, it only increases the probability for polymer-solvent interactions at the expense of segment-segment interactions within the same chain or between different chains. The discussion below is applicable to athermal solutions.

**Excluded volume parameter $\varphi$ via probability analysis on a cubic lattice and the radius of gyration distribution function.** Polymer chains contain $N$ segments, each of length $\lambda$. These segments are placed on a cubic lattice where each cell contains one chain segment. The volume of each cell is approximately $\lambda^3$. Consider a spherical shell of radius $r_k$ and thickness $dr_k$ about the center of mass of a single chain with uniform segment density. The segment distribution about the center of mass, or the radius of gyration distribution, is assumed to follow Gaussian statistics. Comparisons between the exact expression and the Gaussian approximation for the radius of gyration distribution function can be found in *Modern Theory of Polymer Solutions*, by H Yamakawa, Wiley (1971), Chapter#2, pp. 26-35. Differences between the exact and approximate distributions are negligible for all radii of...
gyration. Within volume element \( dV_k = 4\pi(r_k)^2dr_k \) about the center of mass, there are \( z_k \) lattice cells and \( N_k \) chain segments. Hence, \( z_k = dV_k/\lambda^3 \). Evaluate the probability that each of the \( N_k \) chain segments finds an empty lattice cell to occupy. Initially, this calculation is performed for all \( N_k \) segments within volume element \( dV_k \). Then, this analysis is extended to other regions of space that are described by spherical shells with all possible radii of gyration about the center of mass. For volume element \( dV_k \), there is unit probability that the first chain segment finds an empty lattice cell. All of the other \( N_k-1 \) segments experience decreasing probability of finding empty lattice cells in the same volume element \( dV_k \) as a consequence of excluded volume. For example, the probability that the second chain segment finds an empty lattice cell after the first segment is placed in this region is given by \( 1 - (1/z_k) \), which is equivalent to the difference between the total volume of this spherical shell at radius \( r_k \) and one lattice site (i.e., \( dV_k - \lambda^3 \)) relative to \( dV_k \). For \( 1 \leq x \leq N_k \), the probability that the \( x^{th} \) chain segment finds an empty lattice cell in region \( k \) is \( 1 - (x-1)/z_k \).

The excluded volume parameter \( \phi_k \) of interest in volume element \( dV_k \) is evaluated by considering all \( N_k \) chain segments in this region of space and multiplying all sequential probabilities that correspond to segments finding empty lattice cells. The result is:

\[
\ln \phi_k = \sum_{x=1}^{N_k} \ln \left( 1 - \frac{x-1}{z_k} \right) = -\sum_{x=1}^{N_k} \frac{x-1}{z_k} = \sum_{x=0}^{N_k-1} \frac{x}{z_k}
\]

For sufficiently dilute solutions, the total number \( N_k \) of chain segments in this region will be small relative to the total number \( z_k \) of lattice cells. Hence, one expands \( \ln(1-y) \approx -y - y^2/2 - y^3/3 - ... \) and truncates the Taylor series after the linear term [i.e., \( y = (x-1)/z_k \)]. Next, one replaces the summation by an integral to obtain the following result for \( \ln \phi_k \):

\[
\ln \phi_k \approx -\sum_{x=0}^{N_k-1} \frac{x}{z_k} \approx -\int_0^{N_k-1} \frac{x}{z_k} dx = -\frac{(N_k - 1)^2}{2z_k} \approx -\frac{N_k^2}{2z_k}
\]

This calculation of \( \phi_k \) represents an estimate of the fractional decrease in the number of conformations that are available to polymer chains in volume element \( dV_k \) due to excluded volume considerations. For freely-jointed polymer chains that contain \( N \) segments, each of length \( \lambda \), one estimates \( N_k \) within \( dV_k \) by invoking a Gaussian distribution of segments about the center of mass. The radius of gyration distribution \( P(s) \) for freely-jointed chain segments within a spherical shell of radius \( r_k \) about the center of mass is required, where \( s = r_k \) and the mean-square radius of gyration is \( \langle s^2 \rangle = \alpha^2 N \lambda^2 / 6 \). Implicitly, one assumes that
\(<s^2>\) is 6-fold smaller than \(<r^2>\) in \(\Theta\)-solvents and good solvents, which is accurate for the smoothed-density model where one cannot distinguish any differences between the expansion factors for \(<s^2>\) and \(<r^2>\) [see Modern Theory of Polymer Solutions, by H Yamakawa, Wiley (1971), Chapter 3, pp. 70-75]. Hence, \(N_k = Np(s=r_k)dV_k\), such that:

\[
N_k = 4\pi N r_k^2 \left\{ \frac{3}{2\pi \langle s^2 \rangle} \right\}^{3/2} \exp \left[ -\frac{3r_k^2}{2\langle s^2 \rangle} \right] dr_k
\]

\[
\langle s^2 \rangle = \frac{1}{6} \langle r^2 \rangle; \langle r^2 \rangle = \alpha^2 N\lambda^2
\]

Now, one extends this single-chain excluded volume analysis to other regions of space that are characterized by spherical shells with radius of gyration \(0 \leq s < \infty\) about the center of mass of the same chain, such that the mean-square end-to-end vector is \(<r^2> = \alpha^2 N\lambda^2\) and the mean-square radius of gyration is \(<s^2> = <r^2>/6\). Essentially, one (i) squares the Gaussian expression for \(N_k\), (ii) evaluates \(q_k\) in region \(k\) with volume element \(dV_k\) where the spherical shell has radius of gyration \(r_k\) about the center of mass of a single chain, (iii) calculates the excluded volume parameter for a single chain with prescribed end-to-end distance, and (iv) employs this result for chains of all sizes, which is consistent with an assumption in the previous subsection. Since products of \(q_k\)'s translate to sums of \(\ln q_k\)'s, and sums of \(\ln q_k\)'s over all regions of space can be replaced by integration with respect to \(r_k\), the excluded volume parameter of interest (i.e., \(\varphi\)) is obtained with assistance from the third integration formulae in Problem#1 at the end of this chapter;

\[
\ln \varphi = \sum_{k=1}^{\infty} \ln q_k = -\frac{1}{2} \sum_{k=1}^{\infty} N_k^2 z_k = -\frac{1}{2} \sum_{k=1}^{\infty} \frac{\lambda^3}{4\pi r_k^2 dr_k} N^2 (4\pi r_k^2 dr_k) \left\{ \frac{9}{\alpha^2 N\lambda^2} \right\}^3 \exp \left[ -\frac{18r_k^2}{\alpha^2 N\lambda^2} \right]
\]

\[
= -\sum_{k=1}^{\infty} 2\pi \lambda^3 N^2 r_k^2 dr_k \left\{ \frac{9}{\pi\alpha^2 N\lambda^2} \right\}^3 \exp \left[ -\frac{18r_k^2}{\alpha^2 N\lambda^2} \right]
\]

\[
\Rightarrow -2\pi \lambda^3 N^2 \left\{ \frac{9}{\pi\alpha^2 N\lambda^2} \right\}^3 \int_0^{\infty} r_k^2 \exp \left[ -\frac{18r_k^2}{\alpha^2 N\lambda^2} \right] dr_k = -\frac{27}{2^{5/2} \pi^{3/2}} N^{1/2} \alpha^{-3} = -0.86 N^{1/2} \alpha^{-3}
\]

Since the number of segments \(N\) in each polymer chain scales linearly with molecular weight MW (i.e., \(MW \approx N\)), this analysis of the excluded volume parameter \(\varphi\) yields the following molecular-weight scaling law;
\[ \varphi \approx \exp\left\{-MW^{1/2} \alpha^{-3}\right\} \]

Conformational entropic contribution to the multiplicity of states for real chains in “good” solvents. The previous expression for the excluded volume parameter must be considered in the following expression for complete evaluation of the multiplicity function \( \Omega \) and the associated conformational entropy of the system via \( k_B \ln \Omega \). Recall that \( P_i \) represents the fraction of chains with end-to-end distance \( r_i \) in the expanded state when excluded volume effects are absent. The excluded volume parameter \( \varphi \) reduces this fraction of chains described by \( P_i \). The previous equation reveals that there is a larger reduction in the fraction of chains with given dimensions when the molecular weight is larger and the expansion factor \( \alpha \) decreases toward unity. Since there are \( N \) segments per chain, and \( \lambda \) represents the length of each segment, the following equations provide an appropriate representation of the actual situation;

\[
\ln \left\{ \frac{\Omega}{\Omega_0} \right\} \approx v \ln \varphi + \sum_{\text{groups of Conformations w/different } r_i} v_i \ln \left\{ \frac{vP_i}{v_i} \right\}
\]

\[
P_i = 4\pi r_i^2 \left\{ \frac{3}{2\pi N^2 \lambda^2} \right\}^{3/2} \exp \left[ -\frac{3r_i^2}{2N\lambda^2} \right]
\]

There are \( v_i \) chains in the expanded state with end-to-end distance \( r_i \) and mean-square end-to-end vector \( \langle r^2 \rangle = \alpha^2 N \lambda^2 \) when excluded volume is considered and Gaussian statistics are not applicable to describe the distribution of \( r_i \), even though a Gaussian distribution of segments about the center of mass was invoked in the previous subsection for the radius of gyration distribution function in the expanded state. It must be emphasized, however, that these real chains with end-to-end distance \( r_i \) had unperturbed dimensions given by \( r_i/\alpha \) prior to expansion, as described by the Gaussian distribution function. Hence, within a spherical shell of radius \( r_i/\alpha \) about the origin where one end of the ideal chain is anchored, the orientation-independent distribution of freely-jointed ideal chain ends with end-to-end distance \( r_i/\alpha \) is;

\[
\frac{v_i}{v} = 4\pi B \frac{r_i^2}{\alpha^2} \exp \left\{ -\kappa^2 \frac{r_i^2}{\alpha^2} \right\}
\]

It is important to emphasize that the fraction of unperturbed chains with end-to-end distance \( r_i/\alpha \) in a spherical shell of radius \( r_i/\alpha \) about the origin is the same as the fraction of
real chains that experience expansion due to polymer-solvent interactions with end-to-end
distance $r_i$ in a spherical shell of radius $r_i$ about the same origin. Ideal chains follow a
Gaussian distribution with mean-square end-to-end distance given by $\langle r^2 \rangle_{\text{unperturbed}} = N\lambda^2$, whereas the dimensions of the real chains are $\langle r^2 \rangle_{\text{expanded}} = \alpha^2 N\lambda^2$. Constants $B$ and $\kappa$ in the
previous equation are determined from normalization and a freely-jointed second moment
given by $\langle r^2 \rangle_{\text{expanded}} = \alpha^2 N\lambda^2$, with excluded volume in the expanded state. The second
moment of $\nu_i/\nu$ is evaluated in the expanded state so that the results are representative of
real chains. In summary, the fraction of real chains with end-to-end distance $r_i$ that have
been expanded by a factor $\alpha$ relative to unperturbed ideal chains is obtained from a Gaussian
distribution that was constructed from the dimensions of the corresponding unperturbed
chains. The coefficient $\beta^2$ in the exponential of $P_i$ yields an ideal second moment given by
$\langle r^2 \rangle_{\text{unperturbed}}$, whereas the coefficient $\kappa^2$ in the exponential of $\nu_i/\nu$ yields a real second
moment of $\langle r^2 \rangle_{\text{expanded}}$. Both coefficients (i.e., $\beta^2$ and $\kappa^2$) are equivalent because the
expansion factor $\alpha$ is included in the exponential function for $\nu_i/\nu$. With assistance from
integration formula in Problem#1 at the end of this chapter, the appropriate equations to
calculate $B$ and $\kappa$ are;

$$\int_0^\infty \frac{\nu_i}{\nu} dr_i = \frac{4\pi B}{\alpha^2} \int_0^\infty r_i^2 \exp\left\{-\frac{\kappa^2 r_i^2}{\alpha^2}\right\}dr_i = \frac{4\pi B}{\alpha^2} \left[\frac{\pi^{1/2}\alpha^3}{4\kappa^3}\right] = 1$$

$$\int_0^\infty r_i^2 \frac{\nu_i}{\nu} dr_i = \frac{4\pi B}{\alpha^2} \int_0^\infty r_i^4 \exp\left\{-\frac{\kappa^2 r_i^2}{\alpha^2}\right\}dr_i = \frac{4\pi B}{\alpha^2} \left[\frac{3\pi^{1/2}\alpha^5}{8\kappa^5}\right] = \alpha^2 N\lambda^2$$

$$B = \frac{\kappa^3}{\pi^{3/2}\alpha}; \kappa^2 = \frac{3}{2N\lambda^2}$$

Finally, the fraction of chains with end-to-end distance $r_i$ in the expanded state, within a
spherical shell of radius $r_i$ about the origin where one chain end is anchored, is given by;

$$\frac{\nu_i}{\nu} = 4\pi r_i^2 \left[\frac{3}{2\pi\alpha^2 N\lambda^2}\right]^{3/2} \exp\left\{-\frac{3}{2N\lambda^2} \frac{r_i^2}{\alpha^2}\right\}$$

Now, all of the information is available to evaluate the summation of terms on the right side
of $\ln\{\Omega/\Omega_0\}$ after replacing the summation by integration over all possible chain lengths. The
calculation proceeds as follows;
\[
v_i \ln \left\{ \frac{vP_i}{v_i} \right\} = v 4 \pi r_i^2 \left[ \frac{3}{2 \pi \alpha^2 N \lambda^2} \right]^{3/2} \exp \left\{ -\frac{3}{2 N \lambda^2} \frac{r_i^2}{\alpha^2} \right\} \ln \left\{ \frac{4 \pi r_i^2 \left[ \frac{3}{2 \pi N \lambda^2} \right]^{3/2} \exp \left\{ -\frac{3 r_i^2}{2 N \lambda^2} \alpha^2 \right\}}{4 \pi r_i^2 \left[ \frac{3}{2 \pi \alpha^2 N \lambda^2} \right]^{3/2} \exp \left\{ -\frac{3 r_i^2}{2 N \lambda^2} \alpha^2 \right\}} \right\}
\]

Upon replacing the summation over all chain conformations with different \( r_i \) in the expanded state by integration with respect to \( r_i \), integration formula in Problem #1 at the end of this chapter yield the following result;

\[
\sum_{\text{groups of Conformations}} v_i \ln \left\{ \frac{vP_i}{v_i} \right\} \Rightarrow \int_0^\infty v_i \ln \left\{ \frac{vP_i}{v_i} \right\} dr_i
\]

\[
= 4 \pi v \left[ \frac{3}{2 \pi \alpha^2 N \lambda^2} \right]^{3/2} \ln \alpha^3 \int_0^\infty r_i^2 \exp \left\{ -\frac{3}{2 N \lambda^2} \frac{r_i^2}{\alpha^2} \right\} dr_i - \frac{3}{2 N \lambda^2} \int_0^\infty r_i^4 \exp \left\{ -\frac{3 r_i^2}{2 N \lambda^2} \alpha^2 \right\} dr_i
\]

\[
= 4 \pi v \left[ \frac{3}{2 \pi \alpha^2 N \lambda^2} \right]^{3/2} \left[ \frac{\pi^{1/2}}{4} \left( \frac{2}{3} \alpha^2 N \lambda^2 \right)^{3/2} \ln \alpha^3 - \frac{3}{2 N \lambda^2} \left( 1 - \frac{1}{\alpha^2} \right) \frac{3 \pi^{1/2}}{8} \left( \frac{2}{3} \alpha^2 N \lambda^2 \right)^{5/2} \right]
\]

\[
= v \ln \alpha^3 - \frac{3}{2} (\alpha^2 - 1) = 3v \ln \alpha - \frac{3}{2} (\alpha^2 - 1)
\]

Helmholtz free energy minimization yields the equilibrium chain expansion factor in athermal solutions. The conformational entropy change is always negative when an ensemble of \( v \) chains with unperturbed dimensions (i.e., \( \alpha = 1 \)) expand in good solvents such that \( \alpha > 1 \) and excluded volume is prevalent. As prescribed by Boltzmann’s equation;

\[
S - S_0 = k_{\text{Boltzmann}} \ln \left\{ \frac{\Omega}{\Omega_0} \right\} = k_{\text{Boltzmann}} v \left[ -0.86 N^{1/2} \alpha^{-3} + 3 \ln \alpha - \frac{3}{2} (\alpha^2 - 1) \right]
\]

If the internal energy of the system does not depend on the chain expansion factor \( \alpha \), then maximization of the previous entropy expression with respect to \( \alpha \), corresponding to the Gaussian chain statistics.
minimum reduction in entropy associated with excluded volume, yields a minimum in the Helmholtz free energy at equilibrium. This methodology allows one to predict equilibrium chain dimensions in dilute solution that depend on the total number \( N \) of segments per chain, the length \( \lambda \) of each segment, and the equilibrium expansion factor \( \alpha_{equilibrium} \) that is molecular-weight dependent but not segment-length dependent. In the expanded state, the root-mean-square end-to-end chain length is given by \( \langle r^2 \rangle^{1/2} = \alpha_{equilibrium} N^{1/2} \lambda \), which scales as molecular weight, or \( N \), to a power greater than one-half. When the total number of polymer chains \( \nu \) under consideration and the molecular weight of each chain (i.e., \( MW \approx N \)) are constant, the graph below illustrates how the dimensionless entropy change per chain [i.e., \((S - S_0) / \nu k_{Boltzmann}\)] depends on molecular weight and the expansion factor \( \alpha \).

**Effect of MW on Equilibrium Chain Expansion**

The equilibrium expansion factor \( \alpha_{equilibrium} \), which maximizes entropy and minimizes Helmholtz free energy, represents the solution to the following equation:

\[
\left\{ \frac{\partial}{\partial \alpha} (S - S_0) \right\}_{N,T,V \text{ or } N,T,\nu} = k_{Boltzmann} \nu \left[ (3)0.86N^{1/2} \alpha_{equilibrium}^{-4} + \frac{3}{\alpha_{equilibrium}^3} - 3\alpha_{equilibrium} \right] = 0
\]

\[
\alpha_{equilibrium}^5 - \frac{\alpha_{equilibrium}^3}{3} = 0.86N^{1/2}
\]

Gaussian chain statistics
revealing that $\alpha_{\text{equilibrium}}$ increases for higher-molecular-weight chains. In fact, for large expansion of high-molecular-weight chains in very good solvents where $\alpha_{\text{equilibrium}}$ is much greater than unity, the cubic term can be neglected in the previous equation relative to the 5th-power of $\alpha_{\text{equilibrium}}$, which predicts that the equilibrium chain expansion factor scales as the one-tenth power of molecular weight (i.e., $\alpha_{\text{equilibrium}} \approx N^{0.1}$). Under these conditions (i.e., high-molecular-weight chains in very good solvents), the root-mean-square end-to-end chain length scales as the six-tenths power of molecular weight, $<r^2>^{1/2} \approx N^{0.6}$.

**deGennes scaling analysis of Flory’s law for real chains in “good” solvents.** As mentioned at the end of the previous section, this development yields a universal scaling exponent, $\nu = 0.6$, for the molecular-weight dependence of the root-mean-square end-to-end length of three-dimensional chains when polymer-solvent interactions cause considerable chain expansion with respect to unperturbed dimensions. There are at least two factors that contribute to the overall free energy of real chains; monomer-monomer repulsive interactions favour chain expansion and entropy elasticity favours recoil. Equilibrium chain conformations are determined by free energy minimization. If chains contain N monomer segments and $<r^2>^{1/2} \approx N^\nu$, then the monomer molar density $c_{\text{monomer}}$ scales as $c_{\text{monomer}} \approx N/<r^2>^{3/2} \approx N^{1-3\nu}$. The unfavourable contribution of monomer-monomer repulsion to the overall free energy density [i.e., $k_{\text{Boltzmann}} TV_{\text{excluded}}\{c_{\text{monomer}}\}^2$, where $v_{\text{excluded}}$ represents the excluded volume for each segment] is integrated over the volume of a single chain, yielding the following scaling law for repulsive interactions that cause chain expansion;

$$F_{\text{repulsive}} \approx k_{\text{Boltzmann}} TV_{\text{excluded}}c_{\text{monomer}}^2 \langle r^2 \rangle^{3/2} \approx N^{2(1-3\nu)+3\nu} \approx N^{2-3\nu}$$

The competitive effect is due to entropy elasticity, which favours smaller end-to-end chain distances. The probability density distribution function $P(r)$ may not be Gaussian for real chain with excluded volume, but the connection between entropy and multiplicity of states via the Boltzmann relation, and the entropic contribution to elastic free energy are constructed to mimic ideal chains where $P(r) \approx \exp(-r \cdot r)$. Hence;

$$F_{\text{elastic}} \approx k_{\text{Boltzmann}} T \frac{\langle r \cdot r \rangle}{Na^2} \approx N^{2\nu-1}$$

where $Na^2$ is the mean-square end-to-end distance of unperturbed chains that contain N segments, each of length a. Equilibrium chain dimensions, $<r^2>^{1/2} \approx N^\nu$, correspond to minimization of the overall free energy (i.e., $F_{\text{repulsive}} + F_{\text{elastic}}$) with respect to the mean-square end-to-end vector $<r^2>$. Evaluation of the universal scaling exponent $\nu$ for real chains proceeds as follows;

31 Gaussian chain statistics
\[
\left\{ \frac{\partial}{\partial \langle r^2 \rangle} (F_{\text{repulsive}} + F_{\text{elastic}}) \right\}_T \approx k_{\text{Boltzmann}} T \left\{ \frac{\partial}{\partial \langle r^2 \rangle} \left( v_{\text{excluded}} c_{\text{monomer}}^2 \langle r^2 \rangle^{3/2} + \frac{\langle r^2 \rangle}{Na^2} \right) \right\}_T
\]

\[
\approx k_{\text{Boltzmann}} T \left\{ \frac{\partial}{\partial \langle r^2 \rangle} \left( v_{\text{excluded}} N^2 \langle r^2 \rangle^{-3/2} + \frac{\langle r^2 \rangle}{Na^2} \right) \right\}_T = 0
\]

\[
-\frac{3}{2} v_{\text{excluded}} N^2 \langle r^2 \rangle^{-5/2} + \frac{1}{Na^2} = 0
\]

\[
\langle r^2 \rangle^{5/2} \approx v_{\text{excluded}} N^3 a^2
\]

\[
\langle r^2 \rangle^{1/2} \approx N^{3/5}
\]

Notice that both contributions to the overall free energy (i.e., \( F_{\text{repulsive}} \approx N^{2-3\nu} \); \( F_{\text{elastic}} \approx N^{2\nu-1} \)) scale as \( N^{1/5} \) when \( \nu = 0.6 \) for three-dimensional chains in good solvents.

**Intrinsic viscosity of dilute polymer solutions and universal calibration curves for gel permeation chromatography.** The objective of this section is to illustrate how chain dimensions, based on Gaussian statistics, and the hydrodynamic size of a single macromolecule allow one to predict the molecular weight dependence of the intrinsic viscosity of dilute polymer solutions. Furthermore, these predictions suggest how one should construct a universal calibration curve for molecular weight determination from gel permeation chromatography, when the separation device is employed to measure the molecular weight distribution of polymer B based on calibrated residence times using known monodisperse fractions of polymer A.

**Einstein's theory for the viscosity of a dilute suspension of spherical particles in a Newtonian solvent.** A crude model for a dilute suspension of spherical particles is based on a single solid sphere of radius \( R \) surrounded by a Newtonian solvent with viscosity \( \eta_{\text{solvent}} \). The outer boundary of the solvent is identified by radius \( R_0 \). This allows one to represent the volume fraction of solid particles \( \phi \) in the true suspension by \( (R/R_0)^3 \) in the model, where dilute suspensions correspond to \( \phi \ll 1 \). The following assumptions are invoked to solve the hydrodynamic problem:

(a) Fluid flow is ideal far from the particle. This corresponds to the potential flow regime where viscous forces are negligible. Hence, there is a balance between convective forces, pressure forces and gravity forces far from the particle.
(b) In the vicinity of the particle, viscous forces are important, and they are balanced by pressure and gravity forces in the creeping flow regime. This corresponds to very slow flow in the momentum boundary layer adjacent to the solid particle, where convective forces that scale as \( <v>^2 \) are negligible (i.e., \( <v> \) is the average fluid velocity for flow past the particle).

The first method of solution equates the volume-averaged viscous stress tensor in the true suspension and the crude hydrodynamic model. For the true suspension, Newton’s law of viscosity for an incompressible fluid yields:

\[
\langle \tau \rangle_{\text{volume-averaged}} = -\eta_{\text{suspension}} \langle \dot{\gamma} \rangle_{\text{volume-averaged}}
\]

where the volume-averaged rate-of-strain tensor on the right side of the previous equation contains linear combinations of velocity gradients. The hydrodynamic model provides a crude estimate of the volume-averaged viscous stress tensor;

\[
\langle \tau \rangle_{\text{volume-averaged}} = -\eta_{\text{solute}} \left\{ 1 + \frac{5}{2} \left( \frac{\phi}{1 - \phi} \right) \right\} \langle \dot{\gamma} \rangle_{\text{volume-averaged}}
\]

Comparison of the previous two equations yields an expression for the viscosity of a dilute suspension when the volume fraction of solid particles \( \phi \) is much less than one, which implies that second and higher order terms in the solid particle volume fraction can be neglected;

\[
\eta_{\text{suspension}} = \eta_{\text{solute}} \left\{ 1 + \frac{5}{2} \left( \frac{\phi}{1 - \phi} \right) \right\} = \eta_{\text{solute}} \left\{ 1 + \frac{5}{2} \phi [1 + \phi + \phi^2 + \phi^3 + \ldots] \right\} \approx \eta_{\text{solute}} \left( 1 + \frac{5}{2} \phi \right)
\]

The second method of predicting the viscosity of a dilute suspension of spherical particles in a Newtonian solvent equates the average rate of kinetic energy dissipation in the true suspension and the crude hydrodynamic model. The irreversible degradation of mechanical energy to thermal energy, given by the following integration over system volume \( V \);

\[
-\int_V (\tau : \nabla \dot{\gamma}) dV
\]

is always positive for Newtonian fluids and contributes to entropy generation in non-equilibrium systems. The suspension viscosity based on this approach is;
\[ n_{\text{suspension}} = n_{\text{solvent}} \left\{ \frac{1 + \frac{1}{2} \phi}{(1 - \phi)^2} \right\} = n_{\text{solvent}} \left[ 1 + 2 \phi + 3 \phi^2 + 4 \phi^3 + \ldots \right] \approx n_{\text{solvent}} \left( 1 + \frac{5}{2} \phi \right) \]

Both strategies yield the same expression for the suspension viscosity when truncation occurs after the terms that are linear in the solid particle volume fraction. The second-order terms (i.e., \(2.5\phi^2\) vs. \(4\phi^2\)) are different in the two formulations summarized above. For a dilute suspension of spherical liquid droplets, with Newtonian viscosity \(n_{\text{droplet}}\), in a Newtonian solvent with viscosity \(n_{\text{solvent}}\), the effective viscosity of the suspension is;

\[ n_{\text{suspension}} = n_{\text{solvent}} \left\{ 1 + \frac{n_{\text{solvent}} + \frac{5}{2} n_{\text{droplet}}}{n_{\text{solvent}} + n_{\text{droplet}}} \phi + \ldots \right\} \]

when the series is truncated after the term that is linear in the liquid droplet volume fraction \(\phi\). This result is consistent with the two previous expressions for the viscosity of a dilute suspension of solid spherical particles when \(n_{\text{droplet}} >> n_{\text{solvent}}\).

**Intrinsic viscosity of dilute polymer solutions.** A hydrodynamic shell whose radius matches the root-mean-square end-to-end distance of a freely jointed chain surrounds a polymer molecule in a Newtonian solvent. Einstein’s theory for the viscosity of a dilute suspension of solid spherical particles is employed to evaluate the viscosity of the suspension. Then, one constructs the dimensionless relative viscosity \(n_{\text{relative}}\) as follows;

\[ n_{\text{relative}} = \frac{n_{\text{suspension}} - n_{\text{solvent}}}{n_{\text{solvent}}} = \frac{5}{2} \phi_{\text{Polymer}} \]

The volume fraction of polymer in solution is directly related to its concentration, which can be reported in grams per \(\text{cm}^3\) or grams per 100 \(\text{cm}^3\) (i.e., g/dL). If \(C_{\text{Polymer}}\) represents the polymer concentration with units of grams per dL, then the polymer volume fraction is calculated as follows, where each chain is modeled as a spherical coil with an effective hydrodynamic radius given by the root-mean-square end-to-end distance of a freely jointed chain;

\[ \phi_{\text{Polymer}} = \frac{1}{100} C_{\text{Polymer}} \frac{N_{\text{Avogadro}}}{M_{\text{Polymer}}} \left\{ \frac{4}{3} \pi \left( r^2 \right)^{3/2} \right\} \]
where Avogadro’s number and the molecular weight of the chain are required in the previous expression. The intrinsic viscosity $[\eta]$, with units of dL/g, is the intercept on a graph of $n_{\text{relative}}/C_{\text{Polymer}}$ vs. polymer concentration (i.e., $C_{\text{Polymer}}$). It can also be evaluated by the following limit:

$$\left[\eta\right] = \lim_{C_{\text{Polymer}} \to 0} \left\{ \frac{n_{\text{relative}}}{C_{\text{Polymer}}} \right\} \approx \frac{5}{2} \lim_{C_{\text{Polymer}} \to 0} \left\{ \frac{\phi_{\text{Polymer}}}{C_{\text{Polymer}}} \right\} = \frac{\pi}{30} \frac{N_{\text{Avogadro}}}{MW_{\text{Polymer}}} \langle r^2 \rangle^{3/2}$$

This analysis, based on Einstein’s theory for the viscosity of a dilute suspension of spherical particles, reveals that the product of intrinsic viscosity and polymer molecular weight scales as the 1.5 power of the mean-square end-to-end distance of a freely jointed chain, where $<r^2>^{0.5}$ is a measure of the hydrodynamical size of the chain in dilute solution. Gel permeation chromatography is a separation technique that distinguishes different molecular weight fractions of a polymer by hydrodynamic size. It seems reasonable that hydrodynamic size scales as the square-root of molecular weight for freely jointed chains in a $\Theta$-solvent because the second moment of the Gaussian distribution reveals that $<r^2> \approx n\lambda^2$, where the number of random steps $n$ is proportional to the degree of polymerization. The universal calibration curve for a specific column correlates residence time, retention time, or elution volume of a known molecular weight fraction of polystyrene, for example, with its hydrodynamic size. If the column is calibrated using known monodisperse fractions of polymer A, then residence time is correlated with molecular weight for polymer A. When the chromatographic column is used to identify a molecular weight fraction of polymer B that differs in chemical structure from polymer A, one measures the residence time of polymer B and locates the molecular weight of polymer A that corresponds to the same residence time. Since polymer A with known molecular weight and polymer B with unknown molecular weight exhibit the same residence time, they have identical hydrodynamic size. Hence, one equates the product of intrinsic viscosity and molecular weight for both polymers and calculates the corresponding molecular weight of polymer B. The intrinsic viscosity for a particular polymer depends on the solvent, temperature, and molecular weight, as described in the following section via the Mark-Houwink equation.

**Scaling laws for intrinsic viscosity and the Mark-Houwink equation.** Intrinsic viscosity calculations based on Einstein’s theory for the viscosity of a dilute suspension of solid spheres yields the following result:

$$\left[\eta\right] = 6.3 \times 10^{22} \frac{\langle r^2 \rangle^{3/2}}{MW_{\text{Polymer}}}$$
Since intrinsic viscosities can be calculated by extrapolating solution viscometry measurements to infinite dilution, and mean-square end-to-end chain dimensions are related to radii of gyration which can be calculated from light scattering data, the constant in the previous equation should be changed from the predicted value of $6.3 \times 10^{22}$ to the experimental value of $2.0 \pm 0.6 \times 10^{21}$ for many polymers. The unperturbed dimensions of a freely jointed polymer chain under $\Theta$-solvent conditions are characterized by the mean-square end-to-end distance $<r^2>$, which scales linearly with molecular weight because the number of random steps $n$ is proportional to the degree of polymerization. Hence, intrinsic viscosity scales as the 0.5 power of molecular weight in a $\Theta$-solvent. This result represents a subset of the following scaling law for intrinsic viscosity, which is known classically as the Mark-Houwink equation;

$$\left[\eta\right] = K\left\{\left\langle MW_{\text{Polymer}}\right\rangle_v\right\}^\alpha \
\Rightarrow K\left(MW_{\text{Polymer}}\right)^\alpha$$

The temperature-dependent Mark-Houwink parameters $K$ and $\alpha$ are unique to each polymer-solvent pair. For polydisperse polymers, the viscosity-average molecular weight should be used in the previous equation. Under $\Theta$-solvent conditions, the exponent $\alpha$ is 0.5, as discussed above. Classic examples of $\Theta$-solvent conditions that can be used to study unperturbed chain dimensions in the absence of polymer-solvent interactions are;

(a) Poly(isobutylene) in benzene at 24°C
(b) Natural rubber in $n$-propyl ketone at 14.5°C
(c) Poly(vinyl acetate) in ethyl $n$-butyl ketone at 29°C

Tabulated Mark-Houwink exponents $\alpha$ can be used to determine the molecular weight dependence of mean-square end-to-end chain dimensions above the $\Theta$-point. For example;

$$\left\langle r^2\right\rangle \approx \left\{\left[\eta\right]MW_{\text{Polymer}}\right\}^{2/3} \approx \left\{\left(MW_{\text{Polymer}}\right)^{\alpha+1}\right\}^{2/3} \approx \left(MW_{\text{Polymer}}\right)^{2/3(\alpha+1)}$$

**Intrinsic viscosities of polystyrene and poly(ethylene oxide).** Consider an atactic vinyl polymer, like polystyrene, with a number-average molecular weight of $10^5$ daltons in tetrahydrofuran at the $\Theta$-temperature. Since the repeat unit [i.e., $\text{CH}_2\text{CH(C}_6\text{H}_5)$] molecular weight is approximately $10^2$ daltons, there are $10^3$ monomer segments in the chain. Within the context of freely jointed chains in a $\Theta$-solvent that contain $n$ random steps of length $\lambda$, $n$ corresponds to the degree of polymerization (i.e., $\approx 10^3$) and $\lambda$ represents the linear dimension of a repeat unit that is modeled as a straight segment. The repeat unit
consists of 2 carbon-carbon single bonds with a C-C bond length of 1.54Å and a C-C-C bond angle of 109.5°. Hence, \( \lambda \) is calculated as follows:

\[
\lambda = 2\left\{1.54 \times 10^{-8} \text{ cm}\right\} \sin \left(\frac{109.5^\circ}{2}\right) = 2.51 \times 10^{-8} \text{ cm}
\]

The root-mean-square end-to-end chain distance is 80Å, whereas the contour length of the macromolecule, evaluated by traversing two carbon-carbon single bonds per repeat unit, is 3080Å. Based on freely jointed chain dimensions, the intrinsic viscosity is 0.32 dL/g using the Einstein constant of \( 6.3 \times 10^{22} \) and 0.010 dL/g using the experimental constant of \( 2 \times 10^{21} \) for a broad range of polymers. As a second example of intrinsic viscosity calculations, a \( 9 \times 10^5 \) molecular-weight sample of poly(ethylene oxide), with repeat unit chemical structure of \( \text{CH}_2\text{CH}_2\text{O} \), is dissolved in water at the \( \Theta \)-temperature. The carbon-carbon single bond length is 1.54Å, the carbon-oxygen single bond length is 1.43Å, and both the C-C-O and C-O-C bond angles are 109.5°. The effective length of a random step \( \lambda \) is obtained by modeling a repeat unit as a “straight segment” with one C-C bond and 2 C-O bonds. Hence;

\[
\lambda = \left\{1.54 \times 10^{-8} \text{ cm}\right\} \sin \left(\frac{109.5^\circ}{2}\right) + 2\left\{1.43 \times 10^{-8} \text{ cm}\right\} \sin \left(\frac{109.5^\circ}{2}\right) = 3.6 \times 10^{-8} \text{ cm}
\]

Furthermore, the PEO chains are freely rotating with restricted bond angles of 109.5°, which increases the mean-square end-to-end chain distance by a factor of 2. The intrinsic viscosity at the \( \Theta \)-temperature is;

\[
[\eta] = \frac{2.0 \times 10^{21} \left\{2 \frac{MW_{\text{Polymer}}}{MW_{\text{repeat}}} \lambda^2\right\}^{3/2}}{MW_{\text{Polymer}}} = 0.85 \frac{dL}{g}
\]

These examples provide typical ranges for the intrinsic viscosity of common polymers with reasonable molecular weights.

**Effect of pH during dilute-aqueous-solution preparation of solid films on the glass transition.** A few examples are summarized below to illustrate this effect, where the \( pH \) of aqueous polyelectrolyte solutions, which can be manipulated via NaOH, affects the glass transition temperature of the solid residue that is recovered after evaporation of the solvent. When an aqueous solution that contains 1% poly(acrylic acid) is
prepared at \( pH = 2.7 \) (without NaOH), the solid residue exhibits a glass transition temperature of \( 135^\circ C \). Addition of concentrated NaOH during solution preparation yields \( pHs \) of 5 and 7, with corresponding glass transition temperatures of \( 165^\circ C \) and \( 225^\circ C \) for the solid residues. Capillary viscometry measurements of these 1% aqueous solutions yield dimensionless relative viscosities (i.e., \( \eta_{relative} \));

\[
\eta_{relative} = \frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}}
\]

that are summarized in the following table;

**Viscosities of dilute (i.e., 1 wt.% ) aqueous solutions of poly(acrylic acid) and the corresponding glass transition temperatures of the solid residue after solvent evaporation**

<table>
<thead>
<tr>
<th>Solution pH via NaOH</th>
<th>Relative viscosity</th>
<th>( T_g ) of solid residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7 (no NaOH)</td>
<td>4</td>
<td>( 135^\circ C )</td>
</tr>
<tr>
<td>5</td>
<td>55</td>
<td>( 165^\circ C )</td>
</tr>
<tr>
<td>7</td>
<td>92</td>
<td>( 225^\circ C )</td>
</tr>
</tbody>
</table>

The actual viscosities of the solvent (i.e., \( H_2O \)) and the solution are given by \( \eta_{solvent} \) and \( \eta_{solution} \), respectively, in the previous equation. These viscosities are calculated from efflux times \( t_{efflux} \) required to drain the bulb above a tilted capillary tube (see analysis in the *Appendix* of this chapter; \( \mu/\rho = bt_{efflux} \) where \( \mu \) is the Newtonian equivalent of \( \eta \)). The increase in relative viscosity can be explained by more coulombic repulsion and chain expansion at higher NaOH concentrations and higher \( pH \), because the *degree of dissociation* of acidic sidegroups is larger, and \( H^+ \) in the weakly dissociated COOH sidegroup of poly(acrylic acid) is scavenged by \( OH^- \) counterions in the added base (i.e., NaOH). There is not much discussion in the research literature of the effect of \( pH \) during solution preparation on the \( T_g \) of solid films that are recovered after solvent evaporation. There are at least two possible reasons why glass transition temperatures increase significantly when solid films are prepared at higher \( pH \). As mentioned above, chain conformation in the solid state, which mimics coulombic repulsion at higher \( pH \) in solution, should produce more extended chains that exhibit larger hydrodynamic size. The discussion of intrinsic viscosity reveals that chain expansion and hydrodynamic size directly affect solution viscosity, as illustrated in the Table above. The most important factors that affect the glass transition temperature of solid films are ion pairing and \( Na^+ \) cation clustering (i.e., the *ionomer effect*). In solution, some counterions (i.e., \( H^+, Na^+ \), etc.) will be loosely associated with the polyanion, whereas some
counterions will be strongly associated (condensed counterions). There will also be specific binding effects. Ion-specific electrodes can be employed to measure the chemical potential of various counterions. The interpretation of free vs. bound counterions that are separated from or attached to the polyanion (i.e., polymer chain with anionically charged sidegroups) depends on the physics of the measurement system employed to characterize polyelectrolytes.

**Figure**
Effect of metal cation concentration on pH in aqueous solutions of poly(acrylic acid). pH decreases at higher metal cation concentrations.

*deGennes scaling analysis of the threshold overlap molar density $c^*$ in concentrated polymer solutions, and the concept of “blobs”.* This section focuses on 3-dimensional chains in good solvents (i.e., $<r^2>^{1/2} \approx aN^\nu$) when coil overlap occurs in the intermediate regime between dilute solutions and solids. The threshold monomer concentration $c^*$ is comparable to the local monomer concentration within a single chain. Hence;

$$c^* \approx c_{\text{monomer}} \approx \frac{N}{\langle r^2 \rangle^{3/2}} \approx a^{-3} N^{1-3\nu} \Rightarrow a^{-3} N^{-4/5}$$

where $a$ corresponds to the monomer segment length. If $a^3$ represents monomer volume on a cubic lattice and $c^*$ describes the threshold number of monomers per volume of lattice required for coil overlap, then the critical polymer volume fraction $\varphi^*$ scales as;
In semi-dilute solutions, one concludes that critical polymer concentrations and critical polymer volume fractions decrease for higher molecular-weight chains according to the previous two scaling laws. Polymer chains contact each other, and they are on the verge of interpenetration, in semi-dilute solutions when solute volume fractions $\varphi \approx \varphi^*$. One envisions a single chain in semi-dilute solution as a succession of interconnected (but independent) “blobs”, where Flory’s law of real chains describes the conformation of $g$ monomer segments within each blob. In simple terms, a blob with mesh size $\xi$ describes a region of space in solution with volume $(4/3)\pi \xi^3$ that contains $g$ monomers which do not interact with other chains. The total number of interconnected blobs per chain is $N/g$. An important consideration, here, is that the root-mean-square end-to-end length of 3-dimensional chains that contain $N$ monomer segments with excluded volume is comparable to the blob radius $\xi$ when $\varphi \approx \varphi^*$, because interpenetration has not begun and $g \approx N$. At higher solute volume fractions, $\varphi > \varphi^*$, chain dimensions are significantly larger than blob radius $\xi$ and $g < N$, so $\xi$ is a decreasing function of $\varphi$ and independent of the total number of segments $N$ per chain. It is necessary to require that $\xi$ must decrease at larger polymer volume fractions (i.e., $\varphi > \varphi^*$) because segments within one blob do not interact with other chains, and this region of space in solution becomes smaller at higher solute concentrations. Application of Flory’s law of real chains within each blob, together with the restrictions mentioned immediately above, yields the following scaling law for the polymer volume fraction dependence of mesh size $\xi$:

$$
\xi(\varphi) \Rightarrow a^\nu g^v \approx \left(\varphi^* / \varphi\right)^k = a N^v \left(N^{1-3\nu} / \varphi\right)^k \neq f(N)
$$

Hence, $\xi \approx \varphi^{-\kappa}$ and $v + \kappa(1 - 3\nu) = 0$ to eliminate any dependence of $\xi$ on the total number of chain segments $N$ when the polymer volume fraction is greater than its critical value, such that coil overlap and interpenetration occur, and chain dimensions are much larger than the mesh size of an individual blob. Dependence of mesh size $\xi$ and the number of monomers $g$ per blob on polymer volume fraction $\varphi$ is summarized below for 3-dimensional chains with excluded volume;

$$
\kappa = \frac{v}{3\nu - 1} \Rightarrow \frac{3}{4}
$$

$$
\xi(\varphi) \approx \varphi^{-\kappa} \Rightarrow \varphi^{-3/4}
$$

$$
g(\varphi) \approx \varphi^{-\kappa/v} \Rightarrow \varphi^{-5/4}
$$
Entropically elastic retractive forces in rubberlike solids via statistical thermodynamics of Gaussian chains. This is a classic example of the use of Gaussian chain statistics and macroscopic thermodynamics in the presence of an external force field to predict the stress-strain behaviour of rubberlike solids that experience affine deformation. The principle of affine deformation states that the individual network strands and crosslink junctions deform in the same way that macroscopic dimensions of the sample deform. One invokes the principle of affine deformation because Gaussian statistics are used to describe the conformation of individual network strands between crosslink junctions, whereas stress-strain analysis is based on deformation of macroscopic sample dimensions.

Characteristic mechanical response of elastomers. High-molecular-weight polymers that exhibit rubberlike elasticity are known as elastomers. These materials respond almost instantaneously to an external force field with negligible viscous dissipation. Elastomers recover their original dimensions rather quickly when the external force field is removed. Hence, the creep recovery process occurs quickly. Chemically crosslinked elastomers exhibit complete recovery of original dimensions, whereas thermoplastic elastomers do not recover completely because there is significant stress-strain hysteresis due to chain-chain slippage when covalent chemical crosslinks are absent. The following structural properties of polymeric materials are required for elastomeric response.

(i) high molecular weight
(ii) low glass transition temperatures, such that the material is used above its $T_g$
(iii) flexible chain structure with rapid interconversion among rotational isomers
(iv) weak intermolecular attractive forces
(v) minimum degree of order and high segmental mobility prior to stretching
(vi) permanent crosslinks for rapid retraction with no irrecoverable deformation

The connection between entropy and probability density distribution functions. For ideal networks with random chemical crosslinks, Gaussian chain statistics describe the conformational characteristics of network strands between crosslink junctions. The statistical problem begins by invoking Boltzmann’s relation between entropy $S$ and the multiplicity of states $\Omega$. Since energy differences among all of the conformations for a particular network strand are not considered, analogous to the microcanonical ensemble in statistical thermodynamics, $\Omega$ scales linearly with the probability that a given conformation exists. Hence, the “counting problem” reduces to $S = k \ln \Omega$, which appears on Boltzmann’s tombstone at the Zentralfriedhof (central cemetery) in the district of Simmering in Vienna, Austria. This is the largest and most famous of Vienna’s 50 cemeteries, that opened in 1874, spanning 2.4 square kilometers, and containing 3.3 million interred.
Analogous to the three-dimensional probability density distribution function $P(r; n)$, $\Omega$ depends on the magnitude of the end-to-end chain vector $r$. If the total number of possible chain conformations available to the network strands is given by the acronym TNPC, and $\Delta V$ represents a volume element which contains a sufficient number of strands such that statistics are applicable, then the total number (i.e., multiplicity) of conformations with end-to-end chain vector $r$ is given by:

$$\Omega(|r|) = (TNPC)\Delta V\left(\frac{3}{2\pi\langle r^2 \rangle}\right)^{3/2} \exp \left\{-\frac{3r^2}{2\langle r^2 \rangle}\right\}$$

Hence, on a “per-network-strand basis”, one calculates the entropy for freely jointed chains with end-to-end chain vector $r$, realizing that $S$, similar to $P(r, n)$ and $\Omega$, depends on the magnitude of $r$. Furthermore, $S$ scales as $r^2$ such that tensile deformation induces larger chain dimensions and a reduction in entropy;

$$S(|r|) = k \ln(TNPC) + k \ln(\Delta V) + \frac{3}{2} k \ln\left(\frac{3}{2\pi\langle r^2 \rangle}\right) - \frac{3kr^2}{2\langle r^2 \rangle}$$
where the mean-square end-to-end chain distance of network strands \(<r^2>\) is given by \(n\lambda^2\) in the absence of crosslink junctions. A distribution in the number of random steps \(n\) is required to account properly for a distribution in the molecular weight of individual network strands between crosslink junctions. The fact that all network strands are connected to each other via an intricate web of permanent junction points when the crosslink density surpasses the percolation threshold is considered in the development below via the effect of affine deformation on the square of the end-to-end chain vector, \(r^2\). For example, \(r^2\) is expressed in terms of the sum of squared displacements along three mutually orthogonal directions of a rectangular Cartesian coordinate system;

\[
r^2 = x^2 + y^2 + z^2
\]

Next, one introduces relative elongations \(\delta_x, \delta_y, \text{ and } \delta_z\) in the \(x\)-, \(y\)-, and \(z\)-directions, respectively, such that \(\delta_i\) represents the instantaneous displacement in the \(i\)th coordinate direction divided by the initial dimension in the same direction prior to deformation. Hence;

\[
\delta_x = \frac{x}{x_{\text{initial}}}, \delta_y = \frac{y}{y_{\text{initial}}}, \delta_z = \frac{z}{z_{\text{initial}}}
\]

The principle of affine deformation allows one to re-express the \(x\)-, \(y\)-, and \(z\)-projections of the square of the end-to-end chain vector for the deformed sample in terms of relative elongations, which correspond to normal components of the engineering strain tensor +1. Let the initial dimensions of the undeformed crosslinked sample resemble a cube, such that \(x_{\text{initial}} = y_{\text{initial}} = z_{\text{initial}}\) at both the macroscopic and microscopic levels of description. Now, the square of the end-to-end chain vector in the undeformed crosslinked state is;

\[
r_{\text{ undeformed \ w/crosslinks}}^2 = x_{\text{initial}}^2 + y_{\text{initial}}^2 + z_{\text{initial}}^2 = 3x_{\text{initial}}^2
\]

This is consistent with an isotropic crosslinked material in the undeformed state. The effect of deformation on the entropy \(S\) per network strand is expressed in terms of relative elongations;

\[
S = const \tan t - \frac{3}{2}k \left\{ \frac{x^2 + y^2 + z^2}{\langle r^2 \rangle_{\text{WithoutCrosslinks}}} \right\} = const \tan t - \frac{1}{2}k \left\{ \frac{r_{\text{ undeformed \ w/crosslinks}}^2}{\langle r^2 \rangle_{\text{WithoutCrosslinks}}} \right\} \left( \delta_x^2 + \delta_y^2 + \delta_z^2 \right)
\]
Two important concepts about rubberlike materials are invoked to re-express elongations $\delta_y$ and $\delta_z$, transverse to the stretch direction, in terms of $\delta_x$ for uniaxial stretching in the x-direction. Since Poisson’s ratio is 0.5 for incompressible liquids and crosslinked solid materials that exhibit no volume change upon deformation in tension, compression, or shear, one equates initial volume to the instantaneous volume at any level of deformation, assuming that the constant-volume assumption is valid for all reasonable values of $\delta_x$ that are not too large;

$$Volume_{\text{initial}} = x_{\text{initial}}y_{\text{initial}}z_{\text{initial}} = Volume_{\text{instantaneous}} = xyz$$

The mismatch between prediction and experiment for the stress-strain response of crosslink rubberlike solids at large deformation can be traced, in part, to the fact that the constant-volume assumption is not valid beyond approximately 100% strain (i.e., $\delta_x \approx 2$). In other words, Poisson’s ratio decreases below the value of 0.5, indicating that transverse contraction of the material does not offset the volume increase due to uniaxial extension at large strain. The second important concept for isotropic materials that are subjected to uniaxial deformation is that lateral contraction is the same in both transverse directions, which implies that $\delta_y = \delta_z = (\delta_x)^{0.5}$. The effect of uniaxial deformation in the x-direction on the entropy per network strand of an incompressible solid with isotropic lateral contraction is;

$$S = \text{constant} \times \frac{1}{2} k \left\{ \frac{r_{\text{undeformed}}^2}{\left\langle r^2 \right\rangle_{\text{WithoutCrosslinks}}} \right\} \left( \delta_x^2 + \frac{2}{\delta_x} \right)$$

Multiply the previous expression by Avogadro’s number $N_{\text{Avogadro}}$, which represents the number of network strands per mole, where a mole is defined by the number of repeat units $n$ in the chain between crosslink junctions, and evaluate the entropy for a mole of network strands before (i.e., $\delta_x=1$) and after stretching (i.e., $\delta_x>1$). One obtains the following expression for this entropy change at elongation $\delta_x$;

$$\Delta S = S(\delta_x) - S(\delta_x = 1) = -\frac{1}{2} R \left\{ \frac{r_{\text{undeformed}}^2}{\left\langle r^2 \right\rangle_{\text{WithoutCrosslinks}}} \right\} \left( \delta_x^2 + \frac{2}{\delta_x} - 3 \right)$$

It should be obvious that the entropy change is always negative, except in the undeformed state, because elongation $\delta_x \geq 1$. The quantity in brackets {} in the previous equation is
known classically as the “front factor” $g$, and it provides molecular information about the
dimensions of undeformed network strands in the presence of crosslink junctions relative to
the unperturbed size of “equivalent” network strands in the “free” state when crosslinks are
absent. Neutron scattering experiments on isotopically labeled (i.e., deuterated) networks
shed light on the magnitude of the $g$ factor, which is greater than unity.

Classical thermodynamics in the presence of external force fields. Without focusing
on molecular structure or chain conformations between crosslink junctions, the differential
expression of the first law for an ideal rubberlike material that deforms at constant volume
allows one to evaluate equilibrium retractive forces in terms of entropy gradients. If $dq$ and
dw represent inexact differentials for the heat absorbed and work done by the system,
respectively, then;

$$dU = dq - dw$$

where $dq = TdS$ at temperature $T$ and extensive entropy $S$. The system is the crosslinked
elastomer, and in the presence of external vector force $f$ that deforms the system by
differential displacement $dr$, the work done by the system is;

$$dw = pdV - f \cdot dr$$

at pressure $p$, and extensive system volume $V$. The negative sign in the previous expression
for $dw$ suggests that the external field performs work on the system as it is deformed. The
first law in differential form reduces to;

$$dU = TdS - pdV + f \cdot dr$$

Differentiation of the first law with respect to displacement vector $r$ at constant $T$ yields an
expression for the external vector force $f$;

$$\left( \frac{\partial U}{\partial r} \right)_T = T \left( \frac{\partial S}{\partial r} \right)_T - p \left( \frac{\partial V}{\partial r} \right)_T + f$$

For ideal rubber-like materials that deform at constant volume when Poisson’s ratio is 0.5,
the volume derivative on the right side of the previous equation vanishes. Furthermore,
there is no energy barrier to deformation for freely jointed and freely rotating Gaussian
chains, in response to bending backbone bond angles or rotation about the valence cone. In
other words, the internal energy derivative in the previous equation also vanishes because all
conformations exhibit the same energy for ideal elastomers. In agreement with these
assumptions, one calculates the external vector force in terms of the entropy gradient as follows;

\[ f = -T \left( \frac{\partial S}{\partial \mathbf{r}} \right)_T = -T (\nabla_T S) = -T \left( \frac{\partial S}{\partial \mathbf{r}} \right)_T \delta_r \]

where \( \delta_r \) is a unit vector in the direction of the macroscopic displacement. For materials that obey the principle of affine deformation, \( \delta_r \) is also a unit vector in the direction of the end-to-end chain vector. At equilibrium, \( f \) also represents the retractive force that is established within the crosslinked system.

**Hooke’s law of elasticity for ideal rubber-like materials.** The equilibrium retractive force in a crosslinked elastomer is a manifestation of “entropy elasticity”, because the presence of permanent crosslink junctions and the conformational description of network strands via Gaussian statistics correspond to entropy reduction upon deformation. Equilibrium states of a system are characterized by energy minimization and entropy maximization. The former criterion is appropriate for metal-like materials in which Hooke’s law is a consequence of “energy elasticity”. Energy increases, and it is stored reversibly, when metals are subjected to tensile deformation or compression. When entropy is the major contributor to macroscopic mechanical properties, and the multiplicity of conformational states is linked directly to the Gaussian probability density distribution function for individual network strands, the systems strives for smaller dimensions and larger entropy in the presence of an external tensile force field. Information from the previous two subsections allows one to evaluate the system’s retractive force for 1 mole of network strands at constant temperature when the mean-square end-to-end distance of an ensemble of network strands is independent of the state of deformation;

\[ f = -TN_{\text{Avogadro}} \frac{\partial}{\partial \mathbf{r}} \left[ k \ln(TNPC) + k \ln(\Delta V) + \frac{3}{2} k \ln \left( \frac{3}{2\pi \langle r^2 \rangle} \right) - \frac{3kr^2}{2\langle r^2 \rangle_{\text{WithoutCrosslinks}}} \right] = \frac{3RT \mathbf{r}}{\langle r^2 \rangle_{\text{WithoutCrosslinks}}} \]

Hence, the retractive force is co-linear with the end-to-end chain vector \( \mathbf{r} \), and the previous macroscopic force-displacement constitutive equation is analogous to Hooke’s law of elasticity with spring force constant, or modulus of elasticity \( E \), given by;

\[ E = \frac{3RT}{\langle r^2 \rangle_{\text{WithoutCrosslinks}}} \]
This modulus has dimensions of force per length, instead of force per area, because force has not been converted to stress and displacement has not been re-expressed in terms of strain or elongation in the constitutive equation. Most importantly, elastic moduli increase at higher temperatures when retractive forces are “entropy-driven” for crosslinked elastomers, whereas the deformation of metals in which retractive forces are “energy-driven” exhibits elastic moduli that decrease at higher temperature. An interesting consequence of this result can be demonstrated by attaching weights separately to a metal wire and a rubber band in a well-controlled temperature chamber. It might be necessary to attach a much heavier weight to the wire such that observable elongations are obtained. However, weights should be chosen to induce small displacements that are within the regime where Hooke’s law is applicable (i.e., the linear elastic regime). After equilibrium is achieved and displacements are measured, one increases the temperature and re-evaluates the equilibrium displacements. The product of elastic modulus and displacement must be the same at both temperatures for the rubber band because the force has not changed, and the same statement is true for the wire. The increase in elastic modulus of the rubber band induces a decrease in displacement at higher temperature, whereas the reverse applies to the wire. Hence, the weight attached to the rubber band rises to higher elevations when the temperature increases, but the weight attached to the wire descends to lower elevations. This is an example of the macroscopic differences between entropy elasticity and energy elasticity.

*Constitutive relation between stress and elongation for ideal rubber-like materials.* Let’s return to the effect of uniaxial deformation in the x-direction on the entropy per network strand of an incompressible solid with isotropic lateral contraction;

\[
S = \text{constant} - \frac{1}{2} k \left( \frac{r^2_{\text{undeformed w/crosslinks}}}{\langle r^2 \rangle_{\text{WithoutCrosslinks}}} \right) \left( \delta_x^2 + \frac{2}{\delta_x} \right)
\]

There are \(N_{\text{Avogadro}}\) network strands per mole and \(N\) moles of network strands, where MW represents the average molecular weight of chain segments between crosslink junction points. Hence, the extensive entropy of the elastomeric network is obtained via multiplication of the previous equation by both \(N_{\text{Avogadro}}\) and \(N\). The rubber-like material is subjected to uniaxial extension in the x-direction with displacement \(x = x_{\text{initial}} \delta_x\) that is co-linear with the retractive force. Consequently, the generalized “dot product” expression for the contribution from the external field in the differential form of the first law of thermodynamics (i.e., \(f \cdot dr\)) is replaced by \(f_x \, dx\) or, in terms of relative elongation in the x-direction, \(f_x \, x_{\text{initial}} \, d\delta_x\). For an ideal rubber-like solid that exhibits no volume change upon extension, the equilibrium retractive force in the x-direction is;
The engineering stress $\tau_{xx}$ (i.e., normal tensile stress) due to $f_x$ is obtained via division of the previous equation by the initial cross-sectional area (i.e., $y_{initial}z_{initial}$) perpendicular to the x-direction. One obtains;

$$
(\tau_{xx})_{Engineering} = \frac{f_x}{y_{initial}z_{initial}} = \frac{NRT}{Volume_{initial}} \left\{ \frac{r^2_{undeformed \ w/crosslinks}}{\langle r^2 \rangle_{WithoutCrosslinks}} \right\} \left( \delta_x - \frac{1}{\delta_x^2} \right) = \nu gRT \left( \delta_x - \frac{1}{\delta_x^2} \right)
$$

where $\nu$ is the molar crosslink density (i.e., moles of network strands per initial sample volume). The instantaneous “true” stress is larger than the engineering stress because one divides $f_x$ by the instantaneous cross-sectional area (i.e., $yz$) instead of the initial cross-sectional area, and $yz < y_{initial}z_{initial}$ due to lateral contraction of the sample upon extension. A negative value of Poisson’s ratio is required for materials to expand laterally upon uniaxial deformation [see RF Almgren, An isotropic three-dimensional structure with Poisson’s ratio = -1, Journal of Elasticity, 15, 427-430 (1985); R Lakes, Foam structures with a negative Poisson’s ratio, Science, 235, 1038-1040 (1987)]. Hence;

$$
(\tau_{xx})_{True} = \frac{f_x}{yz} = \frac{f_x}{y_{initial}z_{initial}} \left( \frac{y_{initial}}{y} \left( \frac{z_{initial}}{z} \right) \right) = \delta_y \delta_z = (\tau_{xx})_{Engineering} = \nu gRT \left( \delta_x^2 - \frac{1}{\delta_x} \right)
$$

If one calculates the equilibrium crosslink density $\rho_{crosslink}$ (i.e., grams of network strands per initial sample volume) by swelling the rubber-like material in various solvents and measuring the volume of imbibed solvent, then $\nu = \rho_{crosslink}/MW_c$.

Appendix---Capillary viscometry:
Transient analysis of draining an incompressible Newtonian fluid from a spherical bulb with a tilted capillary tube to simulate the performance of capillary viscometers for the determination of momentum diffusivities and fluid viscosities

This problem combines the unsteady state macroscopic mass balance and the Hagen-Poiseuille law for laminar tube flow, together with the volume of fluid in a partially filled sphere. The overall objectives are to (i) predict the capillary constant “b”, based solely on geometric parameters of the viscometer, and (ii) compare this prediction with experimental values obtained by calibrating a capillary viscometer using fluids with known viscosity and density. The system is defined as fluid within the bulb plus the capillary, and one seeks the time required to drain only the bulb above a capillary that is oriented at angle Θ with respect to gravity. Hence, this is an example of the unsteady state macroscopic mass balance where the fictitious inlet plane “floats” on the upper surface of liquid in the bulb such that the average velocities of the fluid and the surface are equal. Consequently, there is no contribution from convective mass transfer across the inlet plane. Fluid flow across the stationary outlet plane at the exit from the capillary is described by the Hagen-Poiseuille law for incompressible Newtonian fluids. The macroscopic mass balance for an incompressible fluid with time-varying system volume, no inlet contribution, and one stationary outlet plane reduces to;

\[ \rho \frac{dV_{\text{system}}}{dt} = -\rho Q_{HP} = -\rho \frac{\pi R_{\text{Tube}}^4 \Delta P}{8 \mu L} \]

where the capillary has radius \( R_{\text{Tube}} \) and length \( L \), and \( P \) represents dynamic pressure. Laminar flow occurs through a cylindrical capillary tube of length \( L \), regardless of whether the capillary is vertical or tilted at angle Θ with respect to gravity. The angle of tilt is considered in the dynamic pressure difference \( \Delta P \) from tube inlet to tube outlet. If \( h(t) \) describes the height of fluid within the spherical bulb above the capillary at any time \( t \), and the “zero of potential energy” is placed arbitrarily at the exit from the capillary, then fluid pressure at the capillary entrance is \( p_{\text{ambient}} + \rho gh(t) \), based on approximate hydrostatic conditions in the bulb, and dynamic pressure at the capillary entrance is given by the sum of fluid pressure and gravitational potential energy per unit volume of fluid. Since the capillary entrance is at higher elevation than the capillary exit, by a distance \( L \cos \Theta \), one evaluates dynamic pressure at the capillary inlet as follows;

\[ P_{\text{inlet}} = p_{\text{ambient}} + \rho gh(t) + \rho gL \cos \Theta \]
There is no contribution from gravitational potential energy to dynamic pressure at the capillary exit because it coincides with the potential energy reference plane. Ambient pressure exists on the upper surface of liquid in the bulb and at the capillary exit. Hence, the dynamic pressure difference $\Delta P = P_{\text{inlet}} - P_{\text{outlet}}$ is given by $\rho g \{ h + L \cos \Theta \}$. One must solve the following time-dependent ODE to relate momentum diffusivity to efflux time:

$$\frac{dV_{\text{system}}}{dt} = \frac{d}{dt} \left[ V_{\text{PartiallyFilledSphere}} + \pi R_{\text{Tube}}^2 L \right] = \frac{d}{dt} V_{\text{PartiallyFilledSphere}} = -\frac{\pi R_{\text{Tube}}^4}{8 (\mu / \rho) L} \{ h(t) + L \cos \Theta \}$$

Fluid volume within the capillary tube is constant during the analysis of efflux times because one measures the time required to drain the bulb, not the capillary. The next task is to evaluate the volume of fluid in a partially filled sphere of radius $R_{\text{Sphere}}$ when the fluid achieves height $h(t)$. This calculation is performed in cylindrical coordinates by stacking an infinite number of cylinders with infinitesimal thickness $dz$ and radius $\omega(z)$, such that $\omega(z)$ vanishes when $z = 0$ and $z = 2 R_{\text{Sphere}}$, but $\omega(z) = R_{\text{Sphere}}$ when the sphere is 50% filled. Let the spherical bulb sit on the origin of an $xyz$-coordinate system such that the center of the sphere is found at a distance $z = R_{\text{Sphere}}$ upward from the origin in the $z$-direction. If the sphere is filled with fluid to height $z$ that can be greater than or less than the sphere radius, then the liquid surface is circular and the following relation allows one to predict the radius $\omega(z)$ of the circular surface of liquid:

$$\left\{ \omega(z) \right\}^2 + \left( z - R_{\text{Sphere}} \right)^2 = R_{\text{Sphere}}^2$$

$$\left\{ \omega(z) \right\}^2 = 2 z R_{\text{Sphere}} - z^2$$

Now, calculate the volume of an infinite number of cylinders with radius $\omega(z)$ and thickness $dz$ stacked upon each other using a differential volume element in cylindrical coordinates. When fluid achieves height $h(t)$ in this partially filled sphere, one evaluates the following triple integral to obtain the liquid volume:

$$V_{\text{PartiallyFilledSphere}} = \iiint dV = \int_0^{2 \pi} d\Theta \int_0^{h(t)} dz \int_0^{h(t)} r dr = \pi \int_0^{h(t)} \left\{ \omega(z) \right\}^2 dz$$

$$= \pi \int_0^{h(t)} \left\{ 2 z R_{\text{Sphere}} - z^2 \right\} dz = \pi \left\{ R_{\text{Sphere}}^3 h^2(t) - \frac{1}{3} h^3(t) \right\}$$

As expected, the liquid volume vanishes when $h=0$, it achieves the normal volume of a sphere $[i.e., (4/3) \pi R_{\text{Sphere}}^3]$ when $h=2R_{\text{Sphere}}$, and it achieves 50% of the normal sphere volume
when \( h = R_{\text{Sphere}} \). The time-rate-of-change of system volume in the unsteady state mass balance is obtained via differentiation of the volume of this partially filled sphere with respect to time, because the fluid height \( h(t) \) is time-dependent as the sphere drains. One obtains the following result via separation of variables;

\[
\frac{d}{dt} V_{\text{PartiallyFilledSphere}} = \pi \left\{ 2R_{\text{sphere}} h(t) - h^2(t) \right\} \frac{dh}{dt} = -\frac{\pi R_{\text{Tube}}^4 g}{8(\mu / \rho) L} \left\{ h(t) + L \cos \Theta \right\}
\]

\[
\mu = \frac{g R_{\text{Tube}}^4}{8 L \int_0^{t_{\text{efflux}}} \frac{h(2R_{\text{sphere}} - h)}{(h + L \cos \Theta)} dh} = b t_{\text{efflux}}
\]

with the following integration limits; \( h = 2R_{\text{Sphere}} \) initially at \( t = 0 \), and \( h = 0 \) at the efflux time required to drain the bulb. The results of this analysis yield the functional dependence of the capillary constant “\( b \)”;

\[
b = \frac{2R_{\text{Sphere}}}{8 L \int_0^{2R_{\text{Sphere}}} \frac{h(2R_{\text{Sphere}} - h)}{(h + L \cos \Theta)} dh}
\]

The capillary constant depends on the (i) dimensions of the capillary tube, (ii) orientation of the capillary with respect to gravity, (iii) volume (or radius) of the spherical bulb, and (iv) strength of the gravitational field. The capillary constant does not depend on temperature or the physical properties of the fluid, provided that the fluid is incompressible and Newtonian.

**Detailed evaluation of the capillary constant and comparison with experimental results.** The next task is to evaluate the complex integral expression in the previous equation for the capillary constant. Begin with the following substitution so that the denominator of the integrand can be rewritten in terms of only one variable \( \Psi \). Let \( \Psi = h + L \cos \Theta \). Integration proceeds as follows;

\[
\int_0^{2R_{\text{Sphere}}} \frac{h(2R_{\text{Sphere}} - h)}{(h + L \cos \Theta)} dh = \int_{L \cos \Theta}^{2R_{\text{Sphere}} + L \cos \Theta} \left( \frac{(\Psi - L \cos \Theta)(2R_{\text{Sphere}} - \Psi + L \cos \Theta)}{\Psi} \right) d\Psi
\]

The integrand reduces to a simple function of \( \Psi \) that can be integrated rather easily;
\[
\frac{(\Psi - L \cos \Theta)(2R_{\text{sphere}} - \Psi + L \cos \Theta)}{\Psi} = 2R_{\text{sphere}} - \Psi + 2L \cos \Theta - \frac{L \cos \Theta(2R_{\text{sphere}} + L \cos \Theta)}{\Psi}
\]

Integration from $L \cos \Theta$ to $2R_{\text{sphere}} + L \cos \Theta$ yields the following expression;

\[
\int_{L \cos \Theta}^{2R_{\text{sphere}} + L \cos \Theta} \left\{ 2(R_{\text{sphere}} + L \cos \Theta) - \Psi - \frac{L \cos \Theta(2R_{\text{sphere}} + L \cos \Theta)}{\Psi} \right\} d\Psi
\]

\[
= 2\left\{ R_{\text{sphere}} + L \cos \Theta \right\} \left\{ 2R_{\text{sphere}} + L \cos \Theta - L \cos \Theta \right\} - \frac{1}{2} \left\{ (2R_{\text{sphere}} + L \cos \Theta)^2 - (L \cos \Theta)^2 \right\}
\]

\[
- L \cos \Theta(2R_{\text{sphere}} + L \cos \Theta) \ln \frac{2R_{\text{sphere}} + L \cos \Theta}{L \cos \Theta}
\]

\[
= 2R_{\text{sphere}} \left( R_{\text{sphere}} + L \cos \Theta \right) - L \cos \Theta(2R_{\text{sphere}} + L \cos \Theta) \ln \left\{ 1 + \frac{2R_{\text{sphere}}}{L \cos \Theta} \right\}
\]

Finally, the capillary constant can be written in terms of the gravitational acceleration constant and several geometric parameters that characterize the spherical bulb and the tilted capillary tube;

\[
b = \frac{gR_{\text{Tube}}^4}{8L} \frac{2R_{\text{sphere}} \left( R_{\text{sphere}} + L \cos \Theta \right) - L \cos \Theta(2R_{\text{sphere}} + L \cos \Theta) \ln \left\{ 1 + \frac{2R_{\text{sphere}}}{L \cos \Theta} \right\}}{2R_{\text{sphere}} \left( R_{\text{sphere}} + L \cos \Theta \right) - L \cos \Theta(2R_{\text{sphere}} + L \cos \Theta) \ln \left\{ 1 + \frac{2R_{\text{sphere}}}{L \cos \Theta} \right\}}
\]

Geometric parameters and capillary constants are summarized below for two different Cannon-Fenske capillary viscometers. If longer efflux times are desirable to minimize errors associated with end effects and experimental reproducibility, then one should use a viscometer with a smaller capillary constant.

<table>
<thead>
<tr>
<th>Geometric Characteristics</th>
<th>Size#100</th>
<th>Size#150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulb volume, assumed to be spherical (mL)</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Bulb radius, $R_{\text{sphere}}$ (cm)</td>
<td>1.24</td>
<td>1.24</td>
</tr>
<tr>
<td>Capillary length, L (cm)</td>
<td>7.6</td>
<td>6.7</td>
</tr>
<tr>
<td>Capillary radius, $R_{\text{Tube}}$ (cm)</td>
<td>0.041</td>
<td>0.05</td>
</tr>
<tr>
<td>Capillary tilt angle with respect to gravity (degrees)</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Capillary constant, predicted (cm$^2$/sec$^2$)</td>
<td>1.53x10$^{-4}$</td>
<td>3.45x10$^{-4}$</td>
</tr>
<tr>
<td>Capillary constant, experimental (cm$^2$/sec$^2$)</td>
<td>1.5x10$^{-4}$</td>
<td>3.5x10$^{-4}$</td>
</tr>
</tbody>
</table>
Draining Power-law fluids from a right circular cylindrical tank via a tilted capillary tube; comparison of efflux and half-times

The capillary viscometer in the previous section is re-analyzed when an incompressible power-law fluid is drained from a cylindrical tank instead of a spherical bulb. The unsteady state mass balance with no inlet stream and one outlet is analogous to the previous development, except that it is necessary to (i) modify the time-varying system volume and (ii) use a generalized expression for the volumetric flowrate of non-Newtonian fluids through straight tubes with radius $R_{\text{Tube}}$ and length $L$ in the laminar regime. The dynamic pressure difference from capillary inlet to capillary outlet in the generalized Hagen-Poiseuille law for tilted tubes is identical to that in the previous section if $h(t)$ represents the variable height of fluid in a cylindrical tank. Hence, the starting point for this analysis, to drain the tank but not the capillary tube, is:

$$ \frac{dV_{\text{system}}}{dt} = \frac{d}{dt} \left[ V_{\text{PartiallyFilledTank}} + \pi R_{\text{Tube}}^2 L \right] = \pi R_{\text{Tank}}^2 \frac{dh}{dt} = -\frac{n}{1+3n} \pi R_{\text{Tube}}^{3+1/n} \left[ \frac{\rho g}{2mL} \{ h(t) + L \cos \Theta \} \right]^{1/n} $$

If the initial height of fluid in the tank is $H$ (i.e., $h=H$ at $t=0$), then one defines the half-time $t_{1/2}$ and the efflux time $t_{\text{efflux}}$ as $h=H/2$ at $t=t_{1/2}$ and $h=0$ at $t=t_{\text{efflux}}$, respectively. The remainder of this analysis compares half-times and efflux times for incompressible Newtonian fluids, when $n=1$ and $m=\mu$. The overall objective is to prove, unequivocally, that the efflux time is greater than twice the half-time for any set of initial conditions and viscometer geometries, including all orientations (i.e., angle $\Theta$) of the exit capillary with respect to gravity. For fluids that obey Newton’s law of viscosity, the previous expression reduces to:

$$ R_{\text{Tank}}^2 \frac{dh}{dt} = -\frac{gR_{\text{Tube}}^4}{8(\mu/\rho)L} \{ h(t) + L \cos \Theta \} $$

This unsteady state macroscopic mass balance for incompressible Newtonian fluids yields a much simpler result for the momentum diffusivity via the half-time or the efflux time, relative to the final expression for $\mu/\rho$ from the previous section when a spherical bulb is drained. From a practical viewpoint, there are two geometric parameters (i.e., $H$ and $R_{\text{Tank}}$) that must be related to the volume of the bulb above the capillary tube (i.e., $\text{Volume}_{\text{Bulb}} \approx \pi R_{\text{Tank}}^2 H$). In contrast, when the bulb volume is modeled as a sphere instead of a right circular cylinder, one identifies the sphere radius via $\text{Volume}_{\text{Bulb}} = (4/3)\pi R_{\text{Sphere}}^3$. Hence, even though two parameters (i.e., $H$ and $R_{\text{Tank}}$) are related by one equation (i.e., $\text{Volume}_{\text{Bulb}} \approx \pi R_{\text{Tank}}^2 H$), one predicts the momentum diffusivity for this “tank-draining” problem as follows;
Obviously, one can predict momentum diffusivities for incompressible Newtonian fluids via laboratory measurements of efflux times or half-times. The capillary constant based on efflux times is smaller than the capillary constant based on half-times, because the product of the appropriate capillary constant and either the half-time or the efflux time yields the momentum diffusivity which is insensitive to the time required to drain either one-half of the total volume of the tank (or bulb) or the total volume of fluid above the capillary tube. The rather simple relation between half-time and efflux time, based on the previous equation, is;

\[ \frac{t_{\text{efflux}}}{t_{1/2}} = \frac{\int_0^H \frac{dh}{h + L \cos \Theta}}{\int_{1/2}^H \frac{dh}{h + L \cos \Theta}} > 2 \]

Numerical substitutions for the (i) initial height \( H \) of fluid in the cylindrical tank, (ii) length \( L \) of the capillary tube, and (iii) angle of tilt \( \Theta \) with respect to gravity reveal that the ratio of \( t_{\text{efflux}} \) to \( t_{1/2} \) is always greater than 2. In fact, this ratio (i.e., \( t_{\text{efflux}}/t_{1/2} \)) becomes significantly greater than 2 when \( H \) is larger, \( L \) is smaller, and \( \Theta \) approaches \( \pi/2 \). When the capillary tube is horizontal (i.e., \( \Theta = \pi/2 \)), it is important to emphasize that the half-time is finite;

\[ t_{1/2} = \frac{8(\mu / \rho)LR_{\text{Tank}}^2}{gR_{\text{Tube}}^4} \ln \left\{ \frac{H + L \cos \Theta}{0 + L \cos \Theta} \right\} \Rightarrow \frac{8(\mu / \rho)LR_{\text{Tank}}^2}{gR_{\text{Tube}}^4} \ln \left\{ \frac{1}{2} H + L \cos \Theta \right\}_{\Theta=\pi/2} \]

but an infinite amount of time is required to drain the total volume of fluid in the tank. These trends can be rationalized in terms of a dynamic pressure difference from capillary inlet to capillary outlet that decreases at longer times because the hydrostatic pressure at the capillary inlet is directly proportional to the instantaneous height of fluid in the reservoir.

**Problem#1**
For a freely-jointed polymer chain with no bond-angle or valence-cone restrictions, the probability distribution function for finding an end-to-end chain length of \( r \) (i.e., scalar) after \( n \) random segmental steps, each of length \( \lambda \), is;
\[ P(r; n) = 4\pi Ar^2 \exp\{-\beta^2 r^2\} \]

\[ \beta^2 = \frac{3}{2\langle r^2 \rangle} = \frac{3}{2n\lambda^2} \]

\[ A = \frac{\beta^3}{\pi^{3/2}} = \left\{ \frac{3}{2\pi n\lambda^2} \right\}^{3/2} \]

(a) Obtain an expression for the most probable end-to-end chain length, regardless of orientation angles $\Theta$ and $\varphi$ in spherical coordinates. It should be emphasized that there is a vanishingly small volume at the origin of the coordinate system, where $r = 0$, such that it is not possible to accommodate any chains with end-to-end chain length $r = 0$.

*Answer:* $r_{\text{MostProbable}} = 1/\beta = \lambda\sqrt{(2n/3)} = 0.82\, \lambda\sqrt{n}$

(b) Obtain an expression for the average end-to-end chain length, $<r>$, which is analogous to the first moment of the distribution function $P(r; n)$.

*Answer:* $<r> = 2/\{\beta\sqrt{\pi}\} = \lambda\sqrt{(8n/3\pi)} = 0.92\, \lambda\sqrt{n}$

(c) Obtain an expression for the root-mean-square end-to-end chain length, $<r>^{1/2}$, which corresponds to the square root of the second moment of the distribution function $P(r; n)$.

*Answer:* $<r>^{1/2} = (1/\beta)^{\sqrt{3/2}} = \lambda\sqrt{n}$

The following integral expressions are helpful to solve this problem;
\[ \int_0^\infty \exp(-ax^2) \, dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \]

\[ \int_0^\infty x \exp(-ax^2) \, dx = \frac{1}{2a} \]

\[ \int_0^\infty x^2 \exp(-ax^2) \, dx = -\frac{d}{da} \left\{ \int_0^\infty \exp(-ax^2) \, dx \right\} \]

\[ \int_0^\infty x^3 \exp(-ax^2) \, dx = -\frac{d}{da} \left\{ \int_0^\infty x \exp(-ax^2) \, dx \right\} \]

\[ \int_0^\infty x^4 \exp(-ax^2) \, dx = \frac{d^2}{da^2} \left\{ \int_0^\infty \exp(-ax^2) \, dx \right\} \]

**Problem #2**

(a) Determine the scaling law relation between intrinsic viscosity and molecular weight for real chains when the root-mean-square end-to-end vector is proportional to the 3/5th power of molecular weight (i.e., \( \langle r^2 \rangle^{1/2} \approx MW^{0.6} \)) in *good* solvents where \( T > \Theta \).

(b) Calculate the intrinsic viscosity of a 1,600,000-molecular-weight sample of poly(ethylene oxide) in water at the \( \Theta \)-temperature. The repeat unit structural formula of PEO is (\( \text{CH}_2\text{CH}_2\text{O} \) or \(-\text{C}-\text{C}-\text{O}-\)). Account for the fact that the chain is not "freely-jointed", but that the bond angles are restricted to be 109.5°. The carbon-carbon backbone bond length is 1.54 Å, and the carbon-oxygen backbone bond length is 1.43 Å.

**Problem #3**

(a) A polymer is analyzed for molecular weight determination by dissolving small amounts of it in tetrahydrofuran. The dilute solution is injected into a gel permeation chromatographic column and the output curve is recorded at 25°C and 65°C. Draw the output curve at both temperatures on one set of axes. Label the axes and describe briefly in words why the output curve changes as a function of temperature even though the molecular weight of the polymer is the same at both temperatures.

(b) The output curve from a gel permeation chromatographic experiment reveals that the molecular weight distribution is bimodal. The material that exits the column with shorter residence times has a narrow distribution of chain lengths. The material that exits the column with longer residence times has a broad distribution of chain lengths.
Draw the output curve with molecular weight as the independent variable on the horizontal axis.

**Problem #4**

A phenomenological treatment of rubber elasticity produces the following constitutive relation between engineering stress $\sigma$ and elongation $\delta = 1 + \varepsilon$, where $\varepsilon$ is the engineering strain. This phenomenological relation is known as the Mooney-Rivlin equation and provides agreement with experimental data up to elongations as large as $\delta = 4$, which is equivalent to engineering strains as large as 300% (i.e., $\varepsilon = 3$). The Mooney-Rivlin equation is written in terms of two undetermined constants, $C_1$ and $C_2$, which are evaluated empirically to obtain the best match with the actual stress-strain curve for a rubberlike material.

$$
\tau = 2 \left\{ \delta - \frac{1}{\delta^2} \right\} \left\{ C_1 + \frac{C_2}{\delta} \right\}
$$

(a) You are given a set of stress-strain data in the form $\tau$ vs. $\varepsilon$ for a lightly crosslinked elastomer. Describe the data manipulation procedure that is required to calculate the Mooney-Rivlin constants for this material based on a linear relationship (i.e., slope-intercept method).

(b) You know the crosslink density of this elastomer in units of grams per cubic centimeter because it is possible to swell the rubberlike material in various solvents and measure the volume uptake of each solvent. You also can estimate the front factor $g$ from neutron scattering experiments on isotopically labelled networks. Remember that the front factor provides molecular information about the dimensions of network strands in the presence of junction points relative to the unperturbed size of "equivalent" network strands in the "free" state without crosslinks. Use this information about the crosslink density $\rho$ and the front factor $g$, together with the Mooney-Rivlin constants $C_1$ and $C_2$ that have been calculated in part (a), to estimate the average molecular weight of network strands between crosslink junctions.

(c) Obtain a phenomenological constitutive equation for true stress based on the Mooney-Rivlin relation given above. Remember that the engineering stress $\tau$ is based on the initial cross sectional area of the sample ($y_0 z_0$), transverse to the direction of uniaxial extension (i.e., the x-direction). True stress is based on the instantaneous cross sectional area transverse to the stretch direction. When one considers either engineering stress or true stress, it is reasonable to assume that there is no volume change due to extension for a rubberlike material with a Poisson ratio of 1/2 (i.e.,
0.5). It is also reasonable to assume that the solid material is isotropic with respect to mechanical deformation.

(d) Sketch the dimensionless entropy change ($\Delta S/R$ with respect to the undeformed sample) per mole of network strands for a rubber band as a function of elongation $\delta$, where $\delta$ is a measure of the strained length of the sample in the direction of uniaxial extension. Remember that the crosslink junctions deform in the same way that the macroscopic dimensions of the sample deform for a rubberlike material that obeys the principle of "affine deformation".

Problem#5
In an all-carbon-backbone chain, the probability density distribution function, with dimensions of inverse volume, for end-to-end chain vector $\mathbf{r}$ after $n$ random steps, each of length $\lambda$, is given by the following non-Gaussian expression that illustrates how $P(\mathbf{r};n)$ depends only on the magnitude of the end-to-end vector $\mathbf{r}$;

$$P(\mathbf{r};n) = \zeta \exp \left\{ -\frac{r^3}{\gamma \langle r^2 \rangle^{3/2}} \right\}$$

where the constants $\zeta$ and $\gamma$ depend on $n$ and $\lambda$. The dimensions of $\zeta$ are inverse volume, and $\gamma$ is dimensionless. Since $P(\mathbf{r};n)$ is normalized, one writes;

$$\int_{-\infty}^{+\infty} P(\mathbf{r};n) d\mathbf{r} = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \Theta d\Theta \int_0^{\infty} r^2 P(\mathbf{r};n) dr = 4\pi \zeta \int_0^{\infty} r^2 \exp \left\{ -\frac{r^3}{\gamma \langle r^2 \rangle^{3/2}} \right\} dr = 1$$

For moderate elongations that are not too large, the mean-square end-to-end chain length $\langle r^2 \rangle$ depends on $n$ and $\lambda$, but not strain.

(a) Obtain an expression for the vector force generated by ideal non-Gaussian macromolecular chains upon extension that exhibit no energetic restrictions to conformational rearrangements. Then, identify the direction in which this vector force acts.

Answer:
If $N$ represents an exceedingly large number of conformations that are available to these polymer chains, then the multiplicity of states $\Omega$ for chains with end-to-end vector $\mathbf{r}$ is;
$$\Omega(r; n) = NP(r; n)$$

Now, one employs the Helmholtz free energy (i.e., \(A = U - TS\)) to calculate the isothermal retractive force when internal energy \(U\) is independent of strain, or end-to-end distance \(r\). This condition, \(U \neq f(r)\) and \(S = g(r)\), is described by *entropy elasticity*. The relevant thermodynamic expression for retractive force \(f\), together with Boltzmann’s equation that connects entropy \(S\) and the multiplicity of states \(\Omega\) is;

$$f = \nabla A = -T \nabla S = -kT \nabla \ln \Omega = -\delta_r kT \left\{ \frac{\partial \ln \Omega}{\partial r} \right\}_T = \delta_r \frac{3kTr^2}{\gamma \left\langle r^2 \right\rangle^{3/2}}$$

Since the probability density distribution function \(P(r; n)\), multiplicity \(\Omega\), entropy \(S\), and Helmholtz free energy \(A\) depend on the magnitude of the end-to-end chain vector \(r\), one concludes that the retractive force \(f\) acts exclusively in the \(r\)-direction in spherical coordinates, along a straight line that connects both ends of the chain, where one end is anchored at the origin.

(b) Why does the retractive force calculated in part (a) exhibit a stronger dependence on end-to-end chain distance \(r\) relative to Gaussian chains that represent the focus of this chapter?

*Answer:* For the non-Gaussian distribution function described in this problem, the conformational entropy decreases faster with chain extension relative to Gaussian chains. Hence, for any end-to-end chain distance \(r\) that is greater than the root-mean-square end-to-end distance, the non-Gaussian distribution predicts that there are fewer chains, smaller multiplicity, and lower entropy relative to Gaussian chains. These trends are all consistent with larger entropically elastic retractive forces for non-Gaussian chains that exhibit stronger entropy gradients upon extension. This particular non-Gaussian distribution creates a larger driving force for stretched chains to contract and increase their conformational freedom.