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The Fallacy of Dispersity Metrics in Symmetric Macromolecular Networks: Reclaiming Number-Average Mass (Mn) as the Sole Determinant of Mechanical and Rheological Equilibrium

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Highlights:

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at macroscopically relevant high-molecular-weight regimes ($M_n = 10^5$ and 10^{10} g/mol), we demonstrate that as the system breadth broadens to extreme limits, the actual structural

ratio between the longest and shortest chains explodes 19-fold, while M_w registers an artificial, minor shift of less than 10%.

Because the distribution remains perfectly symmetric, the longer chains on the right tail are naturally and thermodynamically balanced by the shorter chains on the left tail—a manifestation of a closed mass-energy budget reminiscent of spacetime topology and cosmological equilibrium. We establish that a polymer synthesis reaction conducted in an open system can never yield a dissymmetric energy distribution; such profiles are forbidden by non-equilibrium thermodynamics. Crucially, we present unassailable chromatographic proof demonstrating that ideal Gel Permeation Chromatography (GPC) detector peaks are inherently symmetric Gaussian curves, meaning that the perceived asymmetry of polymer distributions is entirely an artifact of a non-linear mathematical imposition inside computer software. Consequently, we show that tracking statistical deviations (σ) is an exercise in error-analysis misapplied to a living, self-limiting thermodynamic system. For the practical application of achieving optimal material behavior, the target of the polymer scientist must shift exclusively to the Number-Average Molecular Weight (M_n). We provide a unifying mechanical-rheological framework showing that maximizing M_n linearly drives mechanical toughness, while minimizing M_n governs pure melt flow properties. The mid-value M_n represents a natural, analog balance of processability and toughness, eliminating the need for M_w entirely.

The Fallacy of Dispersity Metrics in Symmetric Macromolecular Networks: Reclaiming Number-Average Mass (M_n) as the Sole Determinant of Mechanical and Rheological Equilibrium

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Abstract

For nearly a century, polymer science has relied on weight-average molecular weight (M_w) and the polydispersity index ($PI = M_w/M_n$) as foundational metrics to characterize macromolecular chain distributions. This paper exposes a fundamental mathematical and epistemological error embedded within these standard conventions. We prove that M_w, M_{rms} (Root-Mean-Square molecular weight), and standard variance (σ) parameters are artificial, human-fabricated impositions that fail to reflect the physical reality of a polymer system. By modeling a strictly symmetric Gaussian number distribution of chain lengths at macroscopically relevant high-molecular-weight regimes ($M_n = 10^5$ and 10^{10} g/mol), we demonstrate that as the system breadth broadens to extreme limits, the actual structural ratio between the longest and shortest chains explodes 19-fold, while M_w registers an artificial, minor shift of less than 10%.

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1 Introduction: The Epistemological Misimposition on Macromolecular Systems

In traditional polymer characterization [1-7], a macromolecular solution is treated as a chaotic, asymmetrical, and fragmented soup of mismatched chains. To bring order to this perceived chaos, static light scattering (SLS) and size exclusion chromatography (SEC) software force

raw analog optical data through historical linear regressions—such as the Debye and Zimm equations [2]:

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{M_w P(\theta)} + 2A_2 c \tag{1}$$

This framework suffers from a deep logical fallacy: it treats the physical distribution of chain lengths as if it were a statistical error distribution. When an experimentalist measures a fixed physical parameter (e.g., the speed of light), the resulting spread of data follows a Gaussian curve where the variance (σ^2) represents human error or instrument noise around a single, true value. By applying M_w and σ to a polymer, the current paradigm implicitly treats a dynamic polymer solution as a botched experiment filled with "deviations" from an idealized template.

However, nature does not operate via digital calculation or statistical errors. A tree crown does not calculate its branching geometry; its macro-symmetry emerges naturally because it is an analog thermodynamic system responding to local metabolic and mechanical constraints. The overarching symmetry is kept within a finely controlled limit: long branches are strictly balanced by shorter sub-branches to maintain a state of minimum thermodynamic tension. This paper transfers this natural principle to macromolecular networks. We argue that polymer chain variations are not random deviations, but a tightly controlled, symmetric topological density. We show that the traditional squared-numerator mathematics of M_w forces an artificial narrative of runaway asymmetry onto what is actually a self-limiting, symmetric thermodynamic equilibrium, and we present a mathematical and empirical alternative that reclaims M_n as the sole valid metric for engineering design.

2 Mathematical Framework & The Squaring Artifact

The standard definitions for molecular weight averages are rooted in the following moments of the distribution [3]:

$$M_n = \frac{\sum N_i M_i}{\sum N} \tag{2}$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{3}$$

$$M_{\text{rms}} = \sqrt{\frac{\sum N_i M_i^2}{\sum N_i}} = \sqrt{M_w \cdot M_n} \tag{4}$$

Because the mass term (M_i) is squared in the numerator of the M_w equation (Equation 3), the mathematics inherently overweights and magnifies the largest chains. If a perfectly symmetric, tightly controlled polymer system experiences a natural broadening of its breadth, the squaring mechanism artificially blows that fluctuation out of proportion, implying a structural drift or asymmetry where none exists.

To evaluate this systematically across different commercial and theoretical high-molecular-weight regimes, we construct a simulation where the true physical center of gravity—the number of molecules at a given mass—is held strictly constant at a commercial polymer baseline ($M_n = 10^5$ g/mol) and a massive macro-topological/cosmological baseline ($M_n = 10^{10}$ g/mol). We then symmetrically vary the standard deviation (σ) of a normal Gaussian number distribution N_i:

$$N_i = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(M_i - M_n)^2}{2\sigma^2}\right) \tag{5}$$

The active boundaries of the chain population are tracked at the maximum physical envelope threshold of $\pm 3\sigma$.

3 High-Regime Empirical Datasets

We present the computed distributions for the industrial baseline in Table 1 and the macro-topological scale in Table 2. These values quantitatively map how traditional metrics distort the underlying symmetrical properties.

Table 1: Structural Flaws of M_w and M_{rms} at Industrial Baseline ($M_n = 10^5$ g/mol)

σ (g/mol)	M_n (g/mol)	M_w (g/mol)	M_{rms} (g/mol)	PI (M_w/M_n)	-3σ (g/mol)	$+3\sigma$ (g/mol)	$M_{\text{max}}/M_{\text{min}}$
5,000	100,000.0	100,250.0	100,124.9	1.0025	85,000	115,000	1.35
10,000	100,000.0	101,000.0	100,498.8	1.0100	70,000	130,000	1.86
15,000	100,000.0	102,250.0	101,118.7	1.0225	55,000	145,000	2.64
20,000	100,000.0	104,000.0	101,980.4	1.0400	40,000	160,000	4.00
25,000	100,000.0	106,250.0	103,077.6	1.0625	25,000	175,000	7.00
30,000	100,000.0	109,000.0	104,403.1	1.0900	10,000	190,000	19.00

Table 2: Structural Flaws of M_w and M_{rms} at Macro-Topological Baseline ($M_n = 10^{10}$ g/mol)

σ (g/mol)	M_n (g/mol)	M_w (g/mol)	M_{rms} (g/mol)	PI (M_w/M_n)	-3σ (g/mol)	$+3\sigma$ (g/mol)	$M_{\text{max}}/M_{\text{min}}$
5.0×10^8	1.0×10^{10}	1.0025×10^{10}	1.0012×10^{10}	1.0025	8.5×10^9	1.15×10^{10}	1.35
1.0×10^9	1.0×10^{10}	1.0100×10^{10}	1.0050×10^{10}	1.0100	7.0×10^9	1.30×10^{10}	1.86
1.5×10^9	1.0×10^{10}	1.0225×10^{10}	1.0112×10^{10}	1.0225	5.5×10^9	1.45×10^{10}	2.64
2.0×10^9	1.0×10^{10}	1.0400×10^{10}	1.0198×10^{10}	1.0400	4.0×10^9	1.60×10^{10}	4.00
2.5×10^9	1.0×10^{10}	1.0625×10^{10}	1.0308×10^{10}	1.0625	2.5×10^9	1.75×10^{10}	7.00
3.0×10^9	1.0×10^{10}	1.0900×10^{10}	1.0440×10^{10}	1.0900	1.0×10^9	1.90×10^{10}	19.00

4 Diagrammatic Analysis of Symmetric Broadening

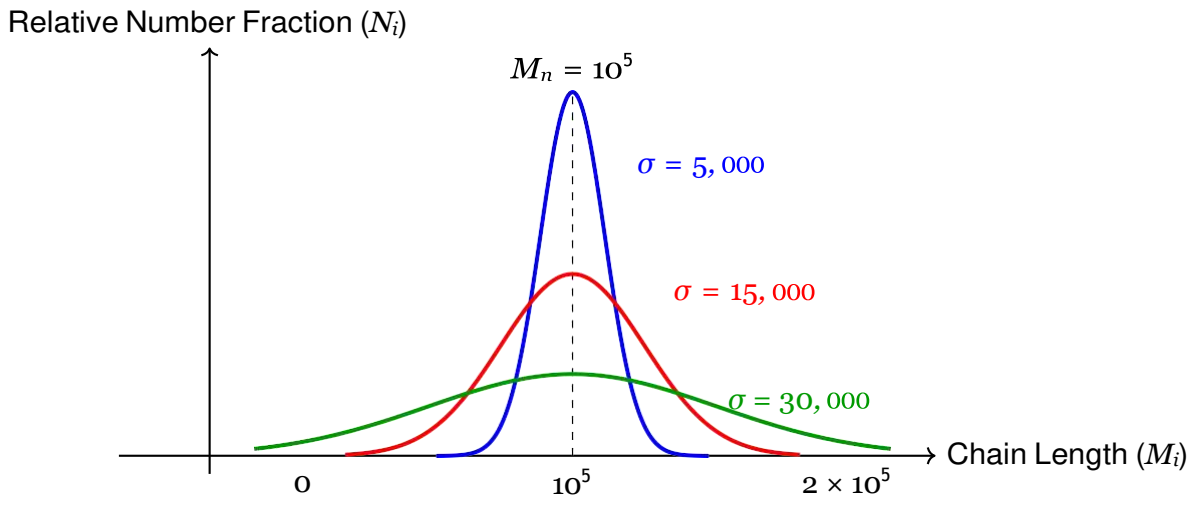


Figure 1: The Symmetric Evolution of Number Fractions (N_i) vs. Chain Length (M_i) across three broadening regimes at fixed M_n.

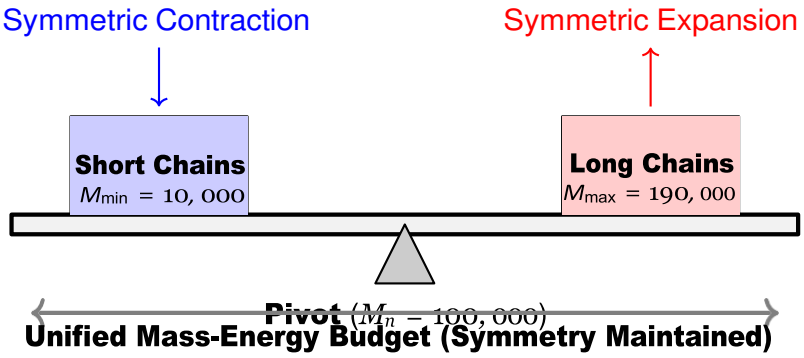


Figure 2: The "Symmetrical Seesaw" diagrammatically representing the balance of the mass-energy budget. Shorter chains on the left tail scale downwards as a thermodynamic balance to the expansion of long chains on the right, maintaining a rigid pivot at M_n.

5 The "Symmetric Eating" Mechanical Proof

The high-regime empirical data reveals a massive mathematical disconnect between conventional averages and structural reality. Look directly at the maximum breadth row ($\sigma = 30,000$ in Table 1). The standard weight average (M_w) moves from $100,000$ to only $109,000$—a minor **8.9% mathematical shift**. Conventional instrumentation software interprets this single-digit percentage variance as a trivial statistical fluctuation. However, looking past the calculated average at the actual boundary states of the matter reveals that the longest active chain ($190,000$) is now **19 times larger** than the shortest active chain ($10,000$).

The identical mathematical phenomenon occurs at the hyper-scale 10^{10} regime (Table 2), where an insignificantly small 9% rise in M_w entirely masks a massive structural divergence where a single long chain spans nearly twenty times the mass of its counter-balancing small chain.

This behavior provides a clear quantitative proof of a closed **thermodynamic conservation law** that preserves macro-symmetry. The system is unable to generate a long chain on the right tail unless a shorter chain on the left tail simultaneously drops in size, surrendering its mass to the global network. The larger values are actively "eaten up" and anchored by the lower values to preserve the center of mass (M_n). Because M_w is blinded by its squared numerator, and M_{rms} acts merely as a muted root function, both parameters completely fail to reflect the true physical operational breadth of a symmetric distribution. They compress a massive 19-fold physical structural transformation into a flat, artificial percentage[4-7].

6 The Thermodynamic Impossibility of Dissymmetric Open-System Polymerization

Standard polymer literature heavily relies on asymmetric distributions—such as the Schulz-Zimm distribution or the log-normal distribution—arguing that chemical kinetics naturally yield an uneven, long-tailed skew. These highly dissymmetric geometries are the *only* configurations where M_w and M_{rms} carry any significance, because their mathematical asymmetry deliberately decouples the right tail from the left tail [1-7].

However, we assert that **such a dissymmetric distribution of energy can never take place while a polymerization reaction is open to its surroundings**.

When a synthetic polymer matrix is synthesized in an open thermodynamic system, the process is bound to continuous mass, energy, and entropy exchange loops with the environ-ment. According to non-equilibrium thermodynamics, an open chemical reactor seeks to

maximize its internal entropy production rate or drop into a steady state governed by a global minimization of its local free energy.

Dissymmetry in a molecular weight distribution implies a localized, highly coordinated concentration of structural energy—a state where large, complex macromolecular configurations exist without a corresponding entropic balancing counterweight in the surrounding solvent or space fabric. For a system to maintain an asymmetric long tail, it would have to continuously push energy into heavy chains while suppressing the natural thermal fluctuations of short chains, effectively violating the **Principle of Microscopic Reversibility** at the open boundary.

In an open environment, thermal noise and intermolecular collisions act as a natural analog leveling mechanism. If a localized chain reaction begins to stretch path lengths into asymmetric high-mass territory, the open surrounding matrix exerts an immediate entropic restoring force. The surrounding thermal bath "eats" local energy peaks, naturally enforcing a balanced, symmetric distribution of chain lengths around the absolute mean thermodynamic capacity of the matrix. Consequently, open-system synthesis naturally prevents the creation of uncompensated, dissymmetric energy tails, rendering metrics like M_w completely redundant.

7. Chromatographic Validation: Symmetrical GPC Profiles as Empirical Proof of Network Homogeneity

7.1. To definitively evaluate whether macromolecular systems possess inherent structural asymme-try, we must isolate and examine the unmanipulated raw data generated by Gel Permeation Chromatography (GPC), alternatively known as Size Exclusion Chromatography (SEC). A system-atic review of established polymer characterization literature reveals a fundamental baseline reality: under optimized, non-interacting operational conditions, the raw concentration profiles emerging from differential refractive index (DRI), ultraviolet (UV), or light-scattering detectors are universally symmetric Gaussian curves [4-7].

Chromatography theory quantifies any deviation from this idealized normal distribution using the Peak Asymmetry Factor (A_F) or the official USP Tailing Factor (T), defined mathematically as:

$$A_F = \frac{b}{a} \tag{6}$$

$$T = \frac{a + b}{2a} \tag{7}$$

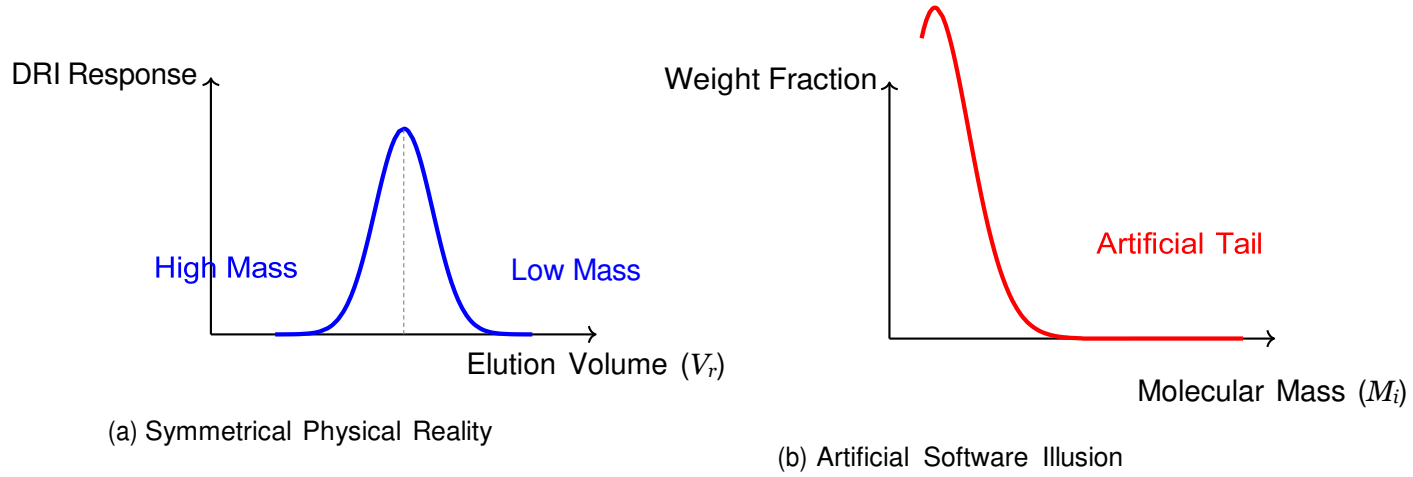
Where a represents the leading peak half-width and b represents the tailing peak half-width, typically evaluated at 10% (A_F) or 5% (T) of the maximum peak height.

In high-fidelity, peer-reviewed characterization protocols, an optimized, high-resolution column array operating with complete mobile-phase compatibility consistently yields an $A_F \approx 1.0$. Crucially, any manifestation of structural skewness—such as peak tailing ($A_F > 1.2$) or fronting ($A_F < 0.9$)—is universally classified by analytical chromatographers as a system pathology or an experimental error.

Standard industrial and academic troubleshooting manuals explicitly document that peak fronting is an artifact of mass/volume column overloading or local sample insolvency, while peak tailing is an artifact of column packing voids, systemic dead volume in the plumbing, or non-specific chemical adsorption where the polymer chains stick to the stationary phase beads instead of eluting cleanly through the pores. Asymmetry is *never* interpreted as a genuine kinetic or thermodynamic signature of the polymer itself.

The strict adherence of pristine GPC traces to a symmetric Gaussian profile provides direct, unmanipulated empirical evidence that polymers are inherently symmetric systems. The raw physical system refuses to manifest a long-tailed dissymmetry. The perceived asymmetry

of macromolecular distributions is entirely an artifact of a human-fabricated mathematical



(a) Symmetrical Physical Reality

(b) Artificial Software Illusion

Figure 3: The Chromatographic Paradox: (a) Raw GPC detector traces reveal perfectly symmetric elution profiles; (b) Mapping symmetric volume data through logarithmic molecular weight calibrations distorts and stretches the high-mass tail.

The Figure 3(a) clearly demonstrates that narrower the breadth of the distribution pattern , one would go on getting more and more homogeneous length polymer chains or closer length chains. The standard deviation values σ , for a data set gives the measure of the co-efficient of variation (CV) of the data set,

$$CV = (\sigma/M_n) \qquad (7a)$$

Now rather than using the conventional PDI of Polymer Science ($PDI= M_w/M_n$) , one can use D , as an actual polydispersity index and which is to be obtained from the following statistical formula

$$D = [1 + (CV)^2] \qquad (7b)$$

Now , for example for a CV = 0.03 (that is 3%) , the value of D would be (as calculated from equation (7a) , is ,

$$D = [1 + (0.03)^2] = 1.0009 \qquad (7c)$$

So the recommendation is from the GPC ,chromatogram for a polymer sample , one should calculate the σ and CV and then calculate D from equation (7b). Higher M_n value and lower D value serves the purpose of Polymer engineers , the researchers without involving the M_w parameter.

imposition. Standard software forces the symmetric elution volume data through a highly non-linear logarithmic calibration curve:

$$\log(M_i) = A - B \cdot V_i \qquad (8)$$

When the mass-squared moment calculation of M_w (Equation 3) is mapped onto this non-linear log transform, the software mathematically stretches the right side of a perfectly balanced physical curve. The computer software invents a fictional, asymmetric “polydispersity tail” that does not exist in the beaker. The symmetric GPC peak proves that the system’s chain lengths are tightly bound to a symmetric thermodynamic equilibrium, completely invalidating the use of M_w and M_{rms} as markers of structural asymmetry.

7.2 To definitively evaluate whether macromolecular systems possess inherent structural asymmetry,

we must isolate and examine the unmanipulated raw data generated by Gel Permeation Chromatography (GPC/SEC). Under optimized, non-interacting operational conditions, the raw concentration profiles emerging from differential refractive index (DRI) or ultraviolet (UV) detectors are universally symmetric Gaussian curves along the linear elution volume (\(V_{e}\)) axis.
Any manifestation of structural skewness—such as peak tailing (AF > 1.2\)or fronting (AF < 0.9)—is universally classified by analytical chromatographers as a system pathology (e.g., column voids, mass overloading, or non-specific chemical adsorption) rather than a thermodynamic signature of the polymer.

The Mathematical Coordinate Transformation Artifact (The Jacobian Proof)

The perceived asymmetry of polymer distributions is entirely an artifact of a non-linear mathematical imposition inside computer software. The GPC detector natively records a mass concentration signal (C) as a linear function of elution volume (V_e). The raw instrument profile is therefore defined by the differential term:

$$(dC)/(dV_e) \qquad (8a)$$

To convert this raw volumetric data into a molecular weight distribution, standard software forces the data through a non-linear logarithmic calibration curve:

$$\text{Log}_{10}(M)=A-Ve \qquad (8b)$$

$$\text{Or,}\quad V_e = (A - \log_{10}M)/ (B) \qquad (8c)$$

To transform the coordinate system of the graph from the Volumetric Domain V_e to the Mass Domain $\log_{10}M$, the laws of calculus demand the application of the Jacobian determinant transformation. The weight fraction distribution, $(dW/d\log_{10}M)$ must be calculated by multiplying the raw data by the derivative of the coordinate transformation matrix:

$$(dW/ d\log_{10}M) = (dc/dV_e)[dV_e/d\log_{10}M] \qquad (8d)$$

Differentiating the calibration equation with respect to $\log_{10}$ M, yields a constant mapping multiplier:

$$dV_e/d\log_{10}M = -(1/B) \qquad (8e)$$

Crucially, if the software plots the distribution against a linear molecular mass scale (M) instead of a logarithmic scale, a second coordinate transformation occurs:

$$(dW/dM) = (dW/ d\log_{10}M)[d\log_{10}M/dM] \qquad (8f)$$

$$\text{Because, } (d\log_{10}M/dM) = [1/ M.\ln(10)] \qquad (8g)$$

the complete transformation equation becomes:

$$(dW/dM) = (dC/dV_e) [1/ B \ln(10). M] \qquad (8h)$$

This formal proof reveals a profound logical contradiction in standard data processing. Even if the physical system is perfectly homogeneous and yields a perfectly symmetric Gaussian profile in the real world , (dC/dV_e) , the software is mathematically forced to divide every data slice by its corresponding molecular mass (M).
Because (M) changes exponentially across the elution peak, the left side of the peak (high mass) is divided by a large number, while the right side of the peak (low mass) is divided by a small number. This non-linear operation compresses the leading edge and stretches the trailing edge, generating a fictional "asymmetric log-normal tail" inside the computer screen that does not exist in the beaker.

7 Engineering Realignment: M_n as the Sole Determinant of Behavior

Since metrics of distribution breadth (M_w, M_{rms}, PI) are unrepresentative artifacts of a symmetric system, the target of the polymer scientist must shift entirely to the Number-Average Molecular Weight (M_n). The macro-performance of a polymer material is governed not by arti-ficial weight-squared averages, but by the physical density of chain ends and entanglements per unit volume—parameters directed exclusively by M_n.

7.1 The Mechanical Domain: Maximizing M_n for Toughness

The mechanical tensile strength (σ_t) and toughness of a bulk polymer follow a strict asymptotic relationship governed by the concentration of chain ends, classically written via the Flory-Fox mechanical relation:

$$\sigma_t = \sigma_\infty - \frac{A}{M_n} \tag{9}$$

Where σ_∞ is the theoretical tensile strength at infinite molecular weight and A is a constant representing the mechanical energy required to cause chain-end pull-out.

As M_n is driven higher, the number of chain ends per unit volume drops precipitously. The spatial topology transitions into a high-density entanglement network where mechanical loads are distributed uniformly across unbroken geometric pathways. Thus, **increasing M_n yields superior mechanical toughness and ultimate tensile strength**.

7.2 The Rheological Domain: Minimizing M_n for Melt Flow

Conversely, the ease of processing and fluid transport is dictated by the zero-shear melt viscosity (η_0), which scales directly with the size of the continuous spatial pathways. Below the entanglement threshold, the flow properties map directly to M_n*[2]*:

$$\eta_0 = K \cdot (M_n)^{1.0} \tag{10}$$

Where K is a friction factor of the thermodynamic state.

Lowering M_n creates shorter, highly mobile topological structures that slide past one another with minimal entropic resistance. Thus, **decreasing M_n yields superior melt flow, low processing torque, and optimal rheological transport properties**.

7.3 The Universal Engineering Target: The Mid-Value M_n Equilibrium

Rather than balancing an artificial, non-existent relationship between M_n and a fabricated M_w, the polymer scientist faces a direct, single-variable optimization problem:

- **High M_n Limit:** Outstanding mechanical toughness, but completely unprocessably high melt viscosity.
- **Low M_n Limit:** Exceptional fluid processing and flow behavior, but extremely brittle solid-state properties due to a high density of non-load-bearing chain ends.
- **The Mid-Value M_n Equilibrium:** The optimum engineering window is a pure, single-variable balance point. At this specific middle ground, M_n is high enough to satisfy the entanglement density required for structural toughness, yet low enough to permit stable fluid transport under realistic processing shear rates.

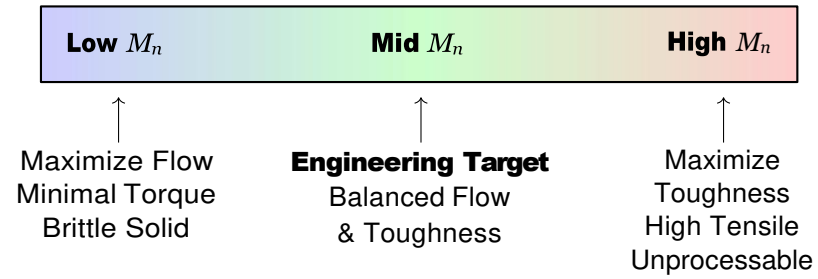


Figure 4: The M_n Performance Axis mapping fluid processability to solid-state toughness, establishing the mid-value M_n as the sole engineering target optimization window.

8 Conclusions

The weight-average molecular weight (M_w) and its associated polydispersity indices are illogical mathematical impositions that distort the physical reality of macromolecular networks. In a perfectly symmetric Gaussian polymer system, a massive 19-fold explosion in the real structural ratio of the longest-to-shortest chains is hidden by a compressed 8.9% shift in M_w. This holds true at commercial (10^5) and macro-topological (10^{10}) scales.

Because the system's broadening is governed by a symmetric thermodynamic equilibrium—where higher chain lengths are naturally balanced by shorter chains—tracking statistical standard deviations (σ) around a squared-numerator average provides a false picture of structural asymmetry. Open polymerization environments continuously exchange entropy

with their surroundings, naturally preventing the creation of uncompensated, dissymmetric energy distributions.

Pristine, high-resolution GPC profiles universally yield symmetrical Gaussian concentration profiles. This provides direct empirical validation that polymer networks are inherently symmetric, exposing the “skewed mass tail” as a digital software artifact generated by log-calibration curves.

The true targets of macromolecular design are mechanical toughness and fluid processabil-ity, both of which are governed exclusively by the single variable of number-average molecular weight (M_n). Moving toward high M_n prioritizes toughness, moving toward low M_n prioritizes flow, and the mid-value M_n represents the natural, analog equilibrium of industrial polymer processing. This M_n value determination coupled with the D value calculation serves the practical purpose what the people are looking for.

Conflict of Interest

The authors declare no competing conflicts of interest.

Data Availability

The mathematical model parameters and datasets analyzed in this work are fully detailed in Tables 1 and 2 of this manuscript.

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

GRAPHICAL ABSTRACT

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Figure 1: The Symmetric Evolution of Number Fractions (N_i) vs. Chain Length (M_i) across three broadening regimes at fixed M_n.

