

Comment on “Elasticity of flexible and semiflexible polymers with extensible bonds in the Gibbs and Helmholtz ensembles” [J. Chem. Phys. 136, 154906 (2012)]

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Citation: *J. Chem. Phys.* **138**, 157101 (2013); doi: 10.1063/1.4801655

View online: <http://dx.doi.org/10.1063/1.4801655>

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Comment on “Elasticity of flexible and semiflexible polymers with extensible bonds in the Gibbs and Helmholtz ensembles”

[J. Chem. Phys. 136, 154906 (2012)]

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(Received 15 November 2012; accepted 21 December 2012; published online 16 April 2013)

[<http://dx.doi.org/10.1063/1.4801655>]

The view that the Helmholtz (constant-displacement) and Gibbs (constant-force) ensembles for a single polymer chain yield equivalent results for their respective force-extension equations in the thermodynamic limit has been prevalent for more than half a century. Here, use of the term thermodynamic limit implies that the number of links (monomers) N is permitted to increase without limit ($N \rightarrow \infty$). In their recent article, Manca *et al.*¹ continue in this tradition. Their justification for this view in the general case is based primarily on their Eq. (24), which purports to show that the required condition for ensemble equivalence is fulfilled, namely, that the Helmholtz and Gibbs free energies, F and G , respectively, are related by a Legendre transform of F with respect to \mathbf{r} , i.e., $G = F - \mathbf{f} \cdot \mathbf{r}$, where \mathbf{f} is the vector force pulling on the chain and \mathbf{r} the displacement between the ends of the chain. In this Comment, which is based on previous work,^{2–4} we point out that not only is this condition not satisfied in the weak-stretching regime but assuming that it is satisfied, with the resulting identical force laws, can have serious repercussions.

Reference 1 uses the following equation, their Eq. (24), to describe the extent to which the expression for G fails to equal the Legendre transform of F ,

$$G = F - \mathbf{f} \cdot \mathbf{r} - k_B T \ln \Gamma, \quad (1)$$

where k_B is the Boltzmann constant and T the absolute temperature. The third term on the right-hand side of the equation vanishes if the Legendre relationship is valid, with Γ defined by

$$\Gamma = (2m\pi k_B T)^{3/2} \int d\mathbf{q} \exp[-(\mathbf{q} - \mathbf{r})(\partial^2 F / \partial \mathbf{r}^2)(\mathbf{q} - \mathbf{r}) / (2k_B T)]. \quad (2)$$

The authors state that “The quantities G , F , Γ , and $\mathbf{f} \cdot \mathbf{r}$ assume an extensive character (i.e., they are proportional to N) and therefore, the logarithmic term in Eq. (24) becomes negligible for large systems. Thus, for $N \rightarrow \infty$, the Legendre transformation is fulfilled.” A flaw in this argument is immediately apparent. Using the ideal freely jointed chain (FJC) model in the Gibbs mode and Gaussian approximation, one can see that the force-displacement scalar product is indeed proportional to N , $\langle \mathbf{f} \cdot \mathbf{r} \rangle \propto Nf^2$; however, it is also proportional to the square of the magnitude of the force; see the

Appendix. Thus, for any finite N , one can reduce f sufficiently to ensure that $\mathbf{f} \cdot \mathbf{r} \leq k_B T \ln \Gamma$. Here, we use the standard scalar, vector notation, i.e., $r = |\mathbf{r}|$ and $f = |\mathbf{f}|$. Because of symmetry considerations, certain functions of vectors can frequently be expressed in terms of scalars; e.g., $F(\mathbf{r}) = F(r)$.

It is instructive to examine the ensemble-equivalence problem from a different vantage point using the ideal FJC model in the weak-stretching regime. Here, the term weak-stretching will refer to that force regime where chains have a scalar end-to-end separation lying between the random-coil value and several times this distance. Within the FJC model, we compare the ensembles by determining whether the Legendre transformation of F is equivalent to G . The definition of the Legendre transform⁵ of F with respect to r , $F_{Lg}(r) = F(r) - r[\partial F(r)/\partial r]$, yields

$$F_{Lg}(r) = -k_B T b^2 r^2 \quad (3)$$

using the r -dependent part of the Helmholtz free energy, where $b^2 = 3/(2Na^2)$ and a is the link length. Please refer to the Appendix for details concerning the derivation of Eq. (3) through (5). The f -dependent part of the Gibbs free energy is found to be

$$G(f) = -k_B T v^2 / 4, \quad (4)$$

and the average of the squared end-separation distance is given by

$$\langle r^2 \rangle = (3/2 + v^2/4)/b^2, \quad (5)$$

where $v = f/(bk_B T)$. Solving Eq. (5) for v and substituting the result into Eq. (4), one obtains

$$G(\langle r^2 \rangle) = (3/2 - b^2 \langle r^2 \rangle) k_B T. \quad (6)$$

Comparing Eqs. (3) and (6) shows that a necessary condition for ensemble equivalence, $G(\langle r^2 \rangle) = F_{Lg}(r)$, is only satisfied when the degree of stretching is at least moderate; that is, when $b^2 \langle r^2 \rangle \gg 3/2$ or $\langle r^2 \rangle \gg \langle r^2 \rangle_0$. The zero subscript indicates the average mean-squared end separation in the absence of an external force, namely, the random-coil value Na^2 . Thus, in the weak-force regime the Legendre relationship between F and G is not valid, resulting in a *nonequivalence of ensembles*.

With the aid of the ideal FJC model and its accompanying force-extension expressions, several consequences of the equivalence-of-ensembles assumption in the weak-stretching

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regime can be explored. The following formulas (see the Appendix) derive from the constant-displacement (Helmholtz) and the constant-force (Gibbs) ensembles, respectively,

$$\langle f \rangle = 2k_B T b^2 \langle r \rangle, \quad (7)$$

$$f = 2k_B T b^2 \langle r \rangle. \quad (8)$$

A common interpretation of these two equations in the thermodynamic limit resulting from the equivalence-of-ensembles assumption¹ is that (i) the two equations are equivalent because the relative force and displacement fluctuations become negligible allowing the average $\langle \rangle$ notation to be dropped, and (ii) as a result of (i) the two can be expressed by the following single equation:

$$f = 2k_B T b^2 r, \quad [f = 2k_B T b^2 \mathbf{r}], \quad (9)$$

as in a macroscopic Hooke's law description of an ordinary spring. Unfortunately, these interpretations are valid only in the moderate stretching regime; for polymer-stretching experiments carried out at small fixed forces, Eq. (9) cannot be used to interpret the results. Because Eq. (9) describes an entropy spring of zero unstretched length, a conflict must necessarily arise in a constant-force experiment where $\langle r \rangle$ is measured,⁶⁻⁸ when the force decreases to zero and $\langle r \rangle$ approaches the random-coil value, $aN^{1/2}$, rather than zero. The conflict is, of course, readily resolved for extension-vs-force plots by recognizing that because large fluctuations are still present,² the averages must still be used with the understanding that $\langle r \rangle = \langle |\mathbf{r}| \rangle \neq |\langle \mathbf{r} \rangle|$. Thus in interpreting these experiments, the Gibbs ensemble result

$$\langle r \rangle = (\langle r \rangle_0 / 2) [\exp(-v^2/4) + (v + 2/v) \int_0^{v/2} dt \exp(-t^2)] \quad (10)$$

must be used, where $\langle r \rangle_0 = 2/(b\pi^{1/2})$. At moderate forces ($v \gg 1$), this expression becomes equivalent to Eq. (9), and Hooke's law is recovered.

Because $|\langle \mathbf{r} \rangle|$ in Eq. (8) is the magnitude of the average value of the projection of \mathbf{r} in the direction of the applied force, $\langle x \rangle$, the alleged agreement in the weak-stretching regime between the Helmholtz and Gibbs force laws with increasing N shown in Fig. 5 of Ref. 1 is a consequence of the fortuitous formal similarity between Eqs. (7) and (8) when N is sufficiently large so as to approximate Gaussian statistics – a similarity that belies the difference in configuration between the Helmholtz and Gibbs chains. This difference particularly manifests near zero force where Eq. (7) describes a loop-like structure whereas Eq. (8) describes a random coil. Rewriting Eq. (8) as

$$\langle x \rangle = f/(2k_B T b^2), \quad (11)$$

one can discern what is actually occurring at small forces; as the stretching force increases from zero, the x -component of the end-to-end displacement increases from zero in a linear fashion, while the actual end-to-end length $\langle r \rangle$ remains in the vicinity of its approximate unstretched length $\langle r \rangle_0$, as expressed by Eq. (10). The polymer chain as a whole responds to the external force by “rotating” analogous to an electric dipole in an electric field; this analogy is explained in detail in Ref. 3. The reason why Eq. (11) has the same formal structure

as Eq. (7) lies in the fact that the underlying end-to-end distribution function $P(r)$ is Gaussian. Were $P(r)$ to have a different form, Eq. (8) would in general be different from Eq. (7), and the confusion between the two most likely would not occur. Thus, we see that the differing Gibbs and Helmholtz ensembles do indeed give rise to differing force laws in the weak-stretching regime despite their formal similarity. The plots in Fig. 5 of Ref. 1 would be radically different in the weak-force region had the correct Gibbs extension, $\langle r \rangle$, been used instead of $|\langle \mathbf{r} \rangle|$. Finally, Manca *et al.*¹ do not discuss the role of relative fluctuation in the extension, $(\langle r^2 \rangle - \langle r \rangle^2)^{1/2}/\langle r \rangle$, which remains large in this force region even in the thermodynamic limit² thereby providing additional evidence against an equivalence of ensembles.

We have (i) demonstrated that the conclusion of Manca *et al.*¹ that the Helmholtz and Gibbs ensembles give rise to the same constitutive equation in the thermodynamic limit is not justified by showing the Legendre transform of the Helmholtz free energy is not equal to the Gibbs free energy in the weak-stretching regime and (ii) shown that this conclusion can have unfortunate consequences when used to interpret the results of polymer-stretching experiments in the weak-force regime.

We thank Mehmet Szen for helpful correspondence concerning the equivalence of ensembles problem.

APPENDIX: THE FREE ENERGIES DEFINED

The following derivations and discussion can be found in Refs. 2, 3, and 9. The momentum component of the partition functions does not enter into the relevant part of the calculation; therefore, only the configurational part is included here. The normalized, field-free, end-to-end distribution function for the ideal freely jointed chain in the Gaussian approximation is given by $P(\mathbf{r}) = P(r) = b^3 \pi^{-3/2} \exp(-b^2 r^2)$ for $r \ll Na$. In the Helmholtz ensemble, one has $F(\mathbf{r}, T) = -k_B T \{C(N) + \ln[P(\mathbf{r})]\}$, and $\langle f \rangle = \partial F(\mathbf{r}, T)/\partial \mathbf{r}$, where $C(N)$ is a constant proportional to N . In the Gibbs ensemble, one has $G(f, T) = -k_B T \ln[Z(f, T)]$, where

$$Z(f, T) = \exp[C(N)] \int d\mathbf{r} P(\mathbf{r}) \exp[\mathbf{f} \cdot \mathbf{r}/(k_B T)]. \quad (A1)$$

In the Gibbs ensemble, the average of an \mathbf{r} -dependent quantity $Q(\mathbf{r})$ is given by

$$\langle Q(\mathbf{r}) \rangle = Z(f, T)^{-1} \exp[C(N)] \times \int d\mathbf{r} Q(\mathbf{r}) P(\mathbf{r}) \exp[\mathbf{f} \cdot \mathbf{r}/(k_B T)]. \quad (A2)$$

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