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ARTICLE *in* THE JOURNAL OF CHEMICAL PHYSICS · APRIL 2013

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Citation: J. Chem. Phys. 138, 157102 (2013); doi: 10.1063/1.4801656

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Response to “Comment on ‘Elasticity of flexible and semiflexible polymers with extensible bonds in the Gibbs and Helmholtz ensembles’” [J. Chem. Phys. 138, 157101 (2013)]

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(Received 10 January 2013; accepted 29 March 2013; published online 16 April 2013)

[<http://dx.doi.org/10.1063/1.4801656>]

In this Response to Comment¹ we address some criticisms concerning the equivalence of the force-extension curves measured with different statistical ensembles in the thermodynamic limit. We show that the results presented in our paper² are correct and, at the same time, we also prove that some “forms of inequivalence” introduced by Neumann^{3,4} are not in conflict with our achievements. In order to clearly explain these points we organize the present Response in two different statements hereafter referred to as Property A and Property B. The results of Ref. 2 (Sec. II E) can be formalized as follows.

Property A: We consider a polymer system with N monomers described by $F(\vec{r}) = -k_B T \log Z_{\vec{r}}(\vec{r}, T)$ with Helmholtz isometric conditions (\vec{r} constant) and by $G(\vec{f}) = -k_B T \log Z_{\vec{f}}(\vec{f}, T)$ with Gibbs isotensional conditions (\vec{f} constant). The definitions of the partition functions $Z_{\vec{r}}$ and $Z_{\vec{f}}$ can be found in Ref. 2 (see Eqs. (4) and (10)). The corresponding constitutive equations valid for any value of N are

$$\langle \vec{f} \rangle = \frac{\partial F(\vec{r})}{\partial \vec{r}} \triangleq \phi(\vec{r}) \quad (\text{Helmholtz}), \quad (1)$$

$$\langle \vec{r} \rangle = -\frac{\partial G(\vec{f})}{\partial \vec{f}} \triangleq \psi(\vec{f}) \quad (\text{Gibbs}). \quad (2)$$

Moreover, in the thermodynamic limit (i.e., $N \rightarrow \infty$):

- (i) we have that $\phi = \psi^{-1}$ or, equivalently, $\psi = \phi^{-1}$ (where ϕ and ψ are vector functions mapping \mathbb{R}^3 in \mathbb{R}^3);
- (ii) the following Legendre transforms are valid:

$$G(\phi(\vec{r})) = F(\vec{r}) - \phi(\vec{r}) \cdot \vec{r}, \quad (3)$$

$$F(\psi(\vec{f})) = G(\vec{f}) + \vec{f} \cdot \psi(\vec{f}). \quad (4)$$

The proof of this property sketched in Ref. 2 is correct. While the second point (ii) was verified through Eqs. (24) and (25) of Ref. 2, the equivalence between (i) and (ii) is a stan-

dard result in the theory of Legendre transforms.^{5,6} A formal and unequivocally proof of Property A for Gaussian polymers and for chains of rigid rods can be found in Ref. 7, which is a recent work of great importance to clarify this subject. We proved the equivalence for $N \rightarrow \infty$ between $\langle \vec{f} \rangle = \phi(\vec{r})$ and $\langle \vec{r} \rangle = \psi(\vec{f})$ (i.e., $\phi = \psi^{-1}$ for $N \rightarrow \infty$). It is true for a couple (\vec{r}, \vec{f}) of conjugated variables. Of course, other choices exhibit different behaviors.

Within our context, the argument presented in the Comment¹ is not valid in two main points:

- It is true that “for any finite N , one can reduce f sufficiently to ensure that $\vec{f} \cdot \vec{r} \leq k_B T \log \Gamma$,” as stated in the Comment; nevertheless, if $N \rightarrow \infty$ the logarithmic term is definitively negligible ($\frac{\log N}{N} \rightarrow 0$ if $N \rightarrow \infty$) for any applied force confirming the validity of the Legendre transform in the thermodynamic limit.
- In the Comment there is another attempt to prove that the Legendre transform given in Eq. (3) is not valid in the weak force regime (for a freely jointed chain in Gaussian approximation). The Legendre transform of $F(\vec{r})$ is given by $F_{Lg}(\vec{r}) - k_B T b^2 \vec{r} \cdot \vec{r}$ (see Eq. (3) of the Comment) and it should be compared with $G(\vec{f}) = -\vec{f} \cdot \vec{f} / (4k_B T b^2)$ (see Eq. (4) of the Comment). Here $b^2 = 3/(2Nl^2)$ where l is the bond length.⁸ To perform the comparison we must substitute $\vec{f} \rightarrow \phi(\vec{r})$ in $G(\vec{f})$, as stated in the above Eq. (3). Since $\phi(\vec{r}) = 2k_B T b^2 \vec{r}$ (see Eq. (7) of the Comment) the Legendre transform is perfectly verified. The author of the Comment instead of using the correct substitution $\vec{f} \rightarrow \phi(\vec{r})$ uses the average of the squared end-separation (Eq. (5) of the Comment) leading to non-correct conclusions. To corroborate this point we remark that the author of the Comment correctly obtains $\phi = \psi^{-1}$ (see Eqs. (7) and (8) of the Comment), a condition mathematically equivalent to the Legendre transforms between F and G .^{5,6} Because of the above arguments the Comment appears to be self-contradictory; the problem is now solved through the correct substitution of variables. Moreover, the

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validity of the Legendre transform for Gaussian polymers is rigorously proved in Ref. 7 (for any applied force).

To conclude the first part of this Response we remark that the Property A does not state that the density probability is the same for the Helmholtz and the Gibbs ensembles: rather, we proved that the mathematical form of the constitutive equations (Eqs. (1) and (2)), i.e., the physical response, is identical in the thermodynamic limit.

In spite of previous considerations, useful to place our result in the proper context, we wish to underline that a “form of inequivalence,” discovered by Neumann^{3,4} is correct, interesting, and, at the same time, not conflicting with Property A. We observe that the constitutive laws given in Eqs. (1) and (2) map different quantities: $\langle \vec{f} \rangle$ and \vec{r} for the Helmholtz ensemble and $\langle \vec{r} \rangle$ and \vec{f} for the Gibbs one. For example, in Fig. 5 of Ref. 2 we plotted on the same graph $|\vec{r}|$ versus $|\langle \vec{f} \rangle|$ for the Helmholtz results and $|\langle \vec{r} \rangle|$ versus $|\vec{f}|$ for the Gibbs ones (we adopted scalar dimensionless variable for convenience). For $N \rightarrow \infty$ the two ensembles converged to the same curve, because of the Property A. We also underline that numerical results are further confirmed by the fact that the expression of the asymptotic (N large) force-extension curve was analytically determined (see Eqs. (32) and (33) of Ref. 2). Following the works of Neumann we observe that different comparisons, based on different average values, can be useful and show some “inequivalences:” they can be summarized as follows.

Property B: For spherically symmetric systems we can consider these force-extension responses:

$$|\langle \vec{f} \rangle| = \alpha(|\vec{r}|), \quad (5)$$

$$|\langle \vec{r} \rangle| = \gamma(|\vec{f}|), \quad (6)$$

for the Helmholtz case and the following relations:

$$|\vec{r}| = \beta(|\vec{f}|), \quad (7)$$

$$|\vec{r}| = \delta(|\vec{f}|), \quad (8)$$

for the Gibbs one. The functions α and β are the scalar counterparts of ϕ and ψ defined in Property A. Hence, we have $\beta = \alpha^{-1}$ (or $\alpha = \beta^{-1}$) in the thermodynamic limit. On the contrary, one can prove that $\gamma^{-1} \neq \beta$, $\alpha^{-1} \neq \delta$, and $\gamma^{-1} \neq \delta$ for any polymer length N and, therefore, also for systems in the thermodynamic limit.

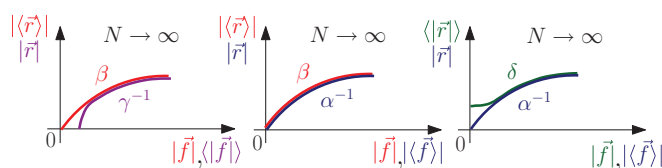


FIG. 1. Schematic representation of the relationships among the functions defined in Property B. The central panel corresponds to Fig. 5 of Ref. 2. The right panel corresponds to Fig. 4 or 5 of Ref. 9.

It is easy to verify that $\gamma(0) > 0$ and $\delta(0) > 0$ for any value of N by writing the expressions of the average values with the pertinent canonical probability densities. Since it is always true that $\alpha(0) = 0$ and $\beta(0) = 0$, it is not difficult to prove the Property B. The different behavior between γ and β or between α^{-1} and δ is not related to the length of the polymer but rather to the transformation of random variables introduced to determine the average value of the modulus (2-norm) of the vectors \vec{r} and \vec{f} (see Eqs. (6) and (8)). In Fig. 1 one can find three plots explaining the relations among the above functions. We observe that the differences between the curves γ^{-1} and β (or α^{-1} and δ) are observable in the regime of small forces or extensions, as predicted by Neumann.^{3,4} Indeed, the function δ has been analytically studied by Neumann^{3,4} in the Gaussian approximation and the results have been confirmed by Süzen *et al.*⁹ through molecular dynamics simulations (also with quite small N). The dual function γ is less tractable from the analytical point of view (because it describes the Helmholtz case) but it could be numerically investigated, e.g., with Monte Carlo techniques or molecular dynamics simulations.

To conclude, we agree with the Comment that these “forms of inequivalences” can be important for the interpretation of experiments, but they are coherent with the equivalence of the constitutive responses described in Property A.

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