

Quiz 12 Polymer Physics April 17, 2020

J. Paturej, J.-U. Sommer, and T. Kreer *Universal Equation of State for Flexible Polymers Beyond the Semidilute Regime* PRL **122** 087801 (2019) propose an extension to the concentrated regime of the scaling theory of J. des Cloizeaux and G. Jannink for osmotic pressure in the semi-dilute regime.

- a) Paturej first discusses the des Cloizeaux theory mentioning equation 1,

$$\frac{P}{kT} = A_1 c^{3\nu/(3\nu-1)} \propto c^\beta, \quad (1)$$

Where p is the osmotic pressure, ν is $1/d_f$. Paturej gives $\nu = 0.588$ and $\beta = 2.309$.

Explain the origin of equation (1) and give the normal value for β given in the original paper by des Cloizeaux. Comment on the origin of the 0.588 value.

- b) Paturej indicates that equation (1) is valid above c^* but below c^+ . c^+ reflects the end of the semi-dilute regime and the beginning of the concentrated regime and has a value between 0.1 and 0.2 volume fraction.

-What is c^* and what is a typical value of c^* in volume fraction for a polymer of 100,000 grams/mole?

- c) Paturej uses the nomenclature that a concentration blob has a size ξ , with g Kuhn units in a blob so that $g \sim \xi^{5/3}$ in a self-avoiding walk. The concentration is given by $c \sim g/\xi^3$. This yields $\xi \sim c^{-\nu/(3\nu-1)} \sim c^{-\beta/3}$

Derive what Paturej calls des Cloizeaux's law:

$$p\xi^3 \propto kT. \quad (3)$$

- d) Derive that $R \sim c^{-1/8}$.

- e) Figure 1 shows that the des Cloizeaux power-law fails at about $c/c^* = 10$, top is the data of Noda et al and the bottom is simulations from this .

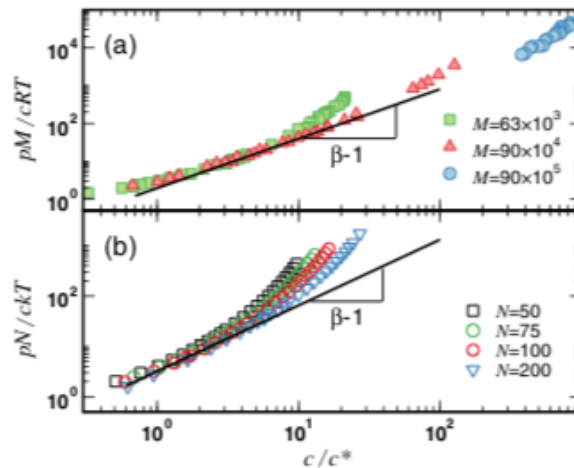
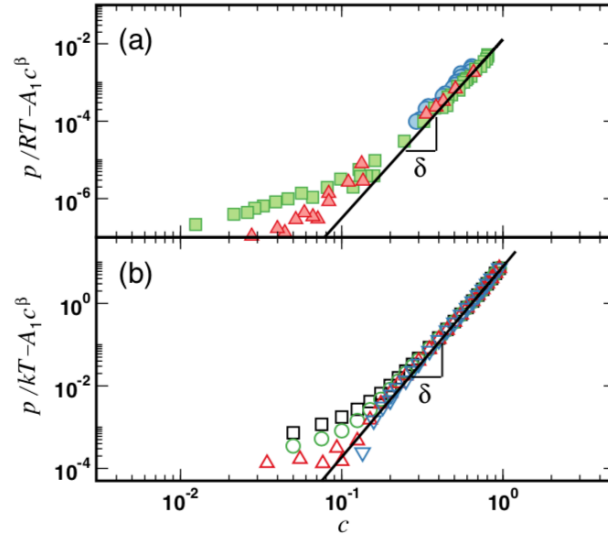


Figure 2 shows that the excess above the des Cloizeaux power-law, above $c/c^* = 10$, can be described by a simple power-law with a slope $\delta = 2\beta$.



Yielding:

$$\frac{p}{kT} = A_1 c^\beta + A_2 c^{2\beta}. \quad (5)$$

What is the meaning of A_2 in equation (5). Is this approach reasonable? How does it compare with the use of a term similar to A_2 (Grosberg's C) in the coil collapse theory of Grosberg? How can C lead to collapse for Grosberg but higher osmotic pressure for Paturej? Is this consistent?

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- a) Paturej first discusses the des Cloizeaux theory mentioning equation 1,

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Where p is the osmotic pressure, ν is $1/d_f$. Paturej gives $\nu = 0.588$ and $\beta = 2.309$.

Explain the origin of equation (1) and give the normal value for β given in the original paper by des Cloizeaux. Comment on the origin of the 0.588 value.

Osmotic pressure depends on $(1/N)(c/c^*)^P$ in the semi-dilute regime. c^* depends on $N^{-4/5}$ but p can't depend on N above c^* so $P = 5/4$ and p depends on $c^{9/4}$. $\beta = 2.25$. We found that $df = 1.67$ for a SAW by the Flory Krigbaum theory with some approximations. But if it is numerically integrated we obtained 1.72, $1/1.72 = 0.581$. We also found that $df = 1.70$ for simulations results yielding 0.588.

- b) Paturej indicates that equation (1) is valid above c^* but below c^+ which has a value between 0.1 and 0.2 volume fraction and reflects the end of the semi-dilute regime and the beginning of the concentrated regime. What is c^* and what is a typical value of volume fraction for a polymer of 100,000 grams/mole?

c^* is the overlap concentration, N/R^3 . It has a value of about 1% for a normal polymer chain.

- c) Paturej uses the nomenclature that a concentration blob has a size ξ , with g Kuhn units in a blob so that $g \sim \xi^{5/3}$ in a self-avoiding walk. The concentration is given by $c \sim g/\xi^3$. This yields $\xi \sim c^{-\nu/(3\nu-1)} \sim c^{-\beta/3}$

Derive what Paturej calls des Cloizeaux's law:

$$p\xi^3 \propto kT. \quad (3)$$

$kTc^\beta \sim p$ from equation (1). And from above, $1/c^\beta \sim \xi^3$, so $p\xi^3 \sim kT$.

- d) Derive that $R \sim c^{-1/8}$.

This is done in the notes and in the Paturej paper. $R = (N/g)^{1/2} \xi$, and $g \sim \xi^{5/3}$, so $R \sim N\xi^{1/6}$. $\xi \sim c^{-\beta/3} = c^{-5/12}$.

$$\begin{aligned} \xi &= b \left(\frac{N}{n_\xi} \right)^{3/5} \sim \left(\frac{c}{c^*} \right)^{-3/4} \\ n_\xi &\sim \left(\frac{c}{c^*} \right)^{(3/4)(5/3)} = \left(\frac{c}{c^*} \right)^{(5/4)} \\ R &= \xi n_\xi^{1/2} \sim \left(\frac{c}{c^*} \right)^{-3/4} \left(\frac{c}{c^*} \right)^{(5/8)} = \left(\frac{c}{c^*} \right)^{-1/8} \end{aligned}$$

e) Yielding:

$$\frac{p}{kT} = A_1 c^\beta + A_2 c^{2\beta}. \quad (5)$$

What is the meaning of A_2 in equation (5). Is this approach reasonable? How does it compare with the use of a term similar to A_2 (Grosberg's C) in the coil collapse theory of Grosberg? How can C lead to collapse for Grosberg but higher osmotic pressure for Paturej? Is this consistent?

A_2 in this equation is related to the third virial coefficient, since A_1 is related to the second virial coefficient. It isn't exactly the second virial coefficient since β isn't 2. Similarly, A_2 isn't exactly the third virial coefficient. For Grosberg C is the cause of coil collapse, B and C are of opposite sign. For this case A_1 and A_2 are of the same sign, both are positive. Higher osmotic pressure indicates more miscible so the second virial coefficient in this case favors dispersion. The approach seems reasonable and the plots seem to support what is proposed.

The main problem is that the figure published by Noda doesn't look totally like the figure in this paper. Noda's figure doesn't show deviation from the 9/4 power so the deviation that is shown in this paper is strictly due to Paturej's use of 0.588 rather than 0.6, $df = 1.70$ rather than 1.67. (The actual slope should probably be 0.581. It is difficult to tell if that would impact the results.) The story becomes a bit dicey when you realize that it is all based on the 0.588 (1.70) simulation result. This is well hidden in the paper.

