


## Reply to “Comment on ‘Osmotic pressure of compressed lattice knots’”

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The free energy of a model of uniformly weighted lattice knots of length  $n$  and knot type  $K$  confined to a lattice cube of side length  $L-1$  is given by  $F_L(\phi) = -\frac{1}{V} \log p_{n,L}(K)$ , where  $V = L^3$  and where  $\phi = n/V$  is the concentration of monomers of the lattice knot in the confining cube. The limiting free energy of the model is  $F_\infty(\phi) = \lim_{L \rightarrow \infty} F_L(\phi)$  and the limiting osmotic pressure of monomers leaving the lattice knot to become solvent molecules is defined by  $\Pi_\infty(\phi) = \phi^2 \frac{d}{d\phi} [F_\infty(\phi)/\phi]$ . I show that, under very mild assumptions, the functions  $P_L(\phi) = \phi^2 \frac{d}{d\phi} [F_L(\phi)/\phi]|_n$  and  $\Pi_L(\phi) = \phi^2 \frac{d}{d\phi} [F_L(\phi)/\phi]|_L$  are finite-size approximations of  $\Pi_\infty(\phi)$ .

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The comment by A. Y. Grosberg contains useful information. However, some of this information is not relevant in context of the original manuscript, which appeared in Physical Review E [1]. The discrete nature of the lattice makes determining the osmotic pressure of monomers in a lattice knot confined to a cubical cavity or confining cube (see Fig. 2 in Ref. [1]) sufficiently complicated that other approaches must be followed (and in particular since it is not numerically feasible to work with lattices larger than  $15^3$ ).

Suppose the confining cube has side length  $L-1$  so that it contains  $V = L^3$  lattice sites ( $V$  is the *volume* of the cube). The length of the lattice knot is  $n$ , and if each vertex in the lattice knot is a monomer, then the monomer concentration is  $\phi = \frac{n}{V}$  in lattice units. The free energy per unit volume is defined for rational values of  $\phi$  by

$$F_L(\phi) = -\frac{1}{V} \log p_{n,L}(K), \quad (1)$$

where  $p_{n,L}(K)$  is the number of distinct lattice knots of type  $K$ , of length  $n$ , in a cube of volume  $V = L^3$ . This, in particular, is defined for rational values of  $\phi = \frac{n}{V}$ , and as  $L \rightarrow \infty$  the rational values of  $\phi$  becomes dense in  $[0,1]$  so that the limit

$$F_\infty(\phi) = \lim_{L \rightarrow \infty} F_L(\phi) \quad (2)$$

exists under very mild assumptions for every rational  $\phi$  on  $[0,1]$ . Thus,  $F_\infty(\phi)$  can be extended to a continuous function on  $[0,1]$ . While it seems difficult to prove, it is expected, and supported by numerical data, that  $F_\infty(\phi)$  is a convex function, and so is continuous and is differentiable almost everywhere in  $[0,1]$ . By interpolating the function  $F_L(\phi)$ , it can be extended to a continuous and differentiable function of  $\phi$  on  $[0,1]$  as well, in which case Eq. (2) still applies, but now for every  $\phi \in [0,1]$ .

Thus  $F_L(\phi)$  converges to  $F_\infty(\phi)$  and differs from it only by finite-size corrections. Notice that  $F_\infty(\phi)$  is *only* a function of  $\phi$ ; that is,

$$F_L(\phi) = F_\infty(\phi) + \epsilon(n, L), \quad (3)$$

where  $\epsilon(n, L)$  is a function of  $n$  and  $L$  (and so of  $\phi$ ) and  $\lim_{L \rightarrow \infty} \epsilon(n, L) = 0$  identically for any sequence of  $n$  [that is,  $\epsilon(n, L) = o(1)$ ].

The limiting osmotic pressure is defined by

$$\Pi_\infty(\phi) = -\lim_{V \rightarrow \infty} \frac{dF_{\text{tot}}}{dV} = \phi^2 \frac{d}{d\phi} \left[ \frac{1}{\phi} F_\infty(\phi) \right], \quad (4)$$

where  $F_{\text{tot}}$  is the total free energy of the model. Using a reasonable approximation to  $F_\infty(\phi)$ , e.g., a Flory-Huggins formula, shows that  $\Pi_\infty(\phi)$  is a non-negative function of  $\phi$  (as argued in the Comment by Grosberg).

For finite  $L$  the derivative at fixed  $n$ ,

$$P_L(\phi) = \phi^2 \frac{d}{d\phi} [F_L(\phi)/\phi]|_n, \quad (5)$$

is identified as the finite size osmotic pressure in the Comment by Grosberg (and the derivative to  $\phi$  is taken by varying  $L$  (or the volume  $V$ ) while fixing  $n$ . In particular, it is expected that

$$\Pi_\infty(\phi) = \lim_{L \rightarrow \infty} P_L(\phi). \quad (6)$$

Define, similarly to the above,

$$\Pi_L(\phi) = \phi^2 \frac{d}{d\phi} [F_L(\phi)/\phi]|_L. \quad (7)$$

This corresponds to  $\Pi_{\text{wrong}}$  in the Comment by Grosberg [see Eq. (3) therein]. Substitute Eq. (3) and simplify to see that

$$\Pi_L(\phi) - \Pi_\infty(\phi) = n^2 \frac{d}{dn} [\epsilon(n, L)/n]|_L. \quad (8)$$

Since  $\epsilon(n, L) \rightarrow 0$  as  $L \rightarrow \infty$ , it follows again, under mild assumptions [namely, that  $\epsilon(n, L) = o(1)$  and  $\epsilon'(n, L) = o(n^{-1})$ ], that the right-hand side vanishes as  $L$  approaches infinity (and so as  $n$  approaches infinity at fixed  $\phi$ ). This results in

$$\lim_{L \rightarrow \infty} \Pi_L(\phi) = \lim_{L \rightarrow \infty} P_L(\phi) = \Pi_\infty(\phi). \quad (9)$$

In other words, both  $\Pi_L(\phi)$  [Eq. (7)] and  $P_L(\phi)$  [Eq. (5)] are finite-size approximations to the limiting osmotic pressure  $\Pi_\infty(\phi)$ , as should be expected.

The function  $\Pi_L(\phi)$  is numerically accessible, and it is determined in the original paper [1].  $P_L(\phi)$  is not well defined in the lattice, in particular since a derivative to  $V$  (or to  $L$ ) is not easily defined or computed in the lattice. Using finite differences to  $L$  involves relatively large changes in volume which gives unreliable results or gives results with strong correction terms with parity effects. Thus, it is more prudent to compute  $\Pi_L(\phi)$  as a finite approximation to  $\Pi_\infty(\phi)$  using numerical derivatives on discrete data obtained by varying the length of the lattice knot while keeping  $L$  fixed.

The convergence of  $F_L(\phi)$  to  $F_\infty(\phi)$  is shown in Fig. 4 of Ref. [1], and these curves converge quickly to the limiting free energy  $F_\infty(\phi)$ . When  $L = 15$  the finite-size corrections are small as seen, for example, in the collapse of  $\Pi_L(\phi)$  to a limiting curve in Fig. 5 of Ref. [1]. A physical interpretation of  $\Pi_L(\phi)$  is given following Eq. (3) in Ref. [1]. The numerical results are plotted in Fig. 5 of that paper for unknots. Rescaling the data for unknots in Fig. 7 shows that there is a regime where the approximations are negative (this regime moves to smaller concentration  $\phi$  with increasing  $L$ , and vanishes, as expected, in the limit  $L \rightarrow \infty$ ). These negative values arise in finite-size corrections and is caused by entropic forces driving monomers into or out of the lattice knot (keeping its length near an equilibrium value). In the limit  $L \rightarrow \infty$  these results are consistent with  $\Pi_\infty(\phi) \geq 0$ . Similar results are seen for the trefoil and the figure eight knot.

The scaling of the negative interval uncovered in Figs. 7, 9, and 10 is predicted by a scaling analysis involving the metric exponent of lattice polygons in Ref. [1]. This supports the notion that  $\Pi_L(\phi)$  is a measure of the entropic forces that drive the exchange of monomers between the solvent and the lattice knot. Overall I am very confident in the prediction of stable equilibrium lengths for the lattice knots simulated in this study (for example, the lattice trefoil will have a stable average length approximately equal to  $3.94 L^{5/3}$  for values of  $L$  which are not too small).

One final observation: In a strict sense the lattice model is not athermal. The partition sum is  $p_{n,L}(K)$  [see Eq. (1) in Ref. [1]] so that the state space has a uniform distribution; that is, this model is at infinite temperature (since all states have equal weight). On the other hand, athermal conditions would hold if monomer-monomer interactions are energetically indistinguishable from monomer-solvent interactions. In this lattice model, the monomer-monomer interaction is a hard-core repulsion, and the monomer-solvent interaction is zero (that is, lattice sites are empty and do not interact with monomers). In an athermal system the Flory interaction parameter  $\chi = 0$ , and the numerical simulation in Ref. [2] shows emphatically (and unsurprisingly) that  $\chi > 0$  numerically for this model.

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[1] E. J. Janse van Rensburg, *Phys. Rev. E* **100**, 012501 (2019).

[2] E. J. Janse van Rensburg, *J. Phys. A* **53**, 015002 (2019).