Excluded-volume corrections to the single-chain static properties of a polymer melt: temperature, density and potential effects

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Abstract

Excluded volume effects on single-chain statics are introduced by analytic corrections to the Rouse results. The final expressions do not depend on free parameters. They are compared with numerical simulations of a polymer melt for different values of the temperature, the density and the interaction potential. Density and interactions control the Energy Landscape of the system whereas the temperature selects the accessible regions. The agreement between the theory and the Rouse modes **does not depend markedly on the temperature with some improvement for the first modes (large length scales)**. Differently, increasing the packing and the stiffness of the monomer-monomer interaction reduces the deviations for the first modes but it leaves the magnitude of the deviations for the high-indexes modes (short length scales) nearly unaffected **or with some tendency to increase**. The scaling properties of the corrections are briefly discussed.

Preprint submitted to Elsevier Science *29 March 2007*

Key words:

PACS: 61.25.Hq, 02.70.Ns

1 Introduction

The amorphous polymers have been often described by simplified single-chain effective-medium theories [1–3]. The success of the latter is mostly due to the universality of structural and dynamic properties on length scales greater than the statistical segment length, and time scales much larger than the typical local time scale of torsional transitions. The Rouse model [4] belongs to the above class of theories and is the simplest bead-spring model for flexible polymer chains [1–3]. It is expressed in terms of either continuous [2] or discrete [5–8] mode distributions and neglects the interactions between monomers which are distant along the chain, i.e. excluded volume, hydrodynamic and other solvent-mediated interactions, and chain entanglements are not considered. In addition to the usual application to non-entangled chains in concentrated solutions, the model also serves in the description of the entangled chains: the tube model analyzes the motion of the Rouse chain confined in a tube-like regime for calculating various kinds of dynamic properties [2].

In the Rouse model each chain is composed of $M_R - 1$ segments being modelled by M_R non-interacting beads, connected by entropic springs with force constant $\kappa = 3k_BT/a_R^2$, where a_R is the average size of the segment, i.e. the root mean square length of the spring, k_B is the Boltzmann constant, and

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T is the absolute temperature. No other interaction between the beads is present. In particular, this means that the chains are "phantoms", i.e. they can be crossed by themselves and other chains. The model considers a given chain and regards the surrounding ones as a uniform frictional medium. The surrounding chains are depicted to exert on each bead of the selected chain also a fast-fluctuating random force to ensure proper equilibrium properties via the fluctuation-dissipation theorem. The Rouse model has been tested by experiments [9–12] and numerical simulations [13–19].

The phantom Rouse chains have static properties which differ from the numerical results on more realistic polymer models with excluded volume [17]. From this respect, we recently derived simple analytic corrections leading to meaningful improvements [20]. Our approach works well with short, unentangled chains where the usual field-theory renormalization procedure [2,21] is expected to fail. Nonetheless, preliminary results for long chains were made available [20].

The present paper extends the results of ref.[20], where chain length was changed under isothermal and isobaric conditions, by investigating how the single-chain static properties of a melt of unentangled polymers are affected by the monomer-monomer interaction potential, the temperature and the density. It seems proper to put the present study in the context of the the multidimensional potential energy surface as a function of particle coordinates, the so called potential energy landscape (PEL) [22]. For a system with constant volume the landscape is fixed and its sampling as a function of temperature provides information on its dynamic behaviour. Differently, changing the density and the intermolecular potential (apart from the special case of molecular interactions being proportional to a common inverse-power of distances) is expected to affect the rugged character of the PEL, in particular the total number of basins, their spread in energy and the vibrational properties of individual energy. The changes of such features proved to affect the fragility of the system [23,24].

The paper is organized as follows. In Sec. 2 the theory is outlined. In Sec. 3 the numerical methods are presented. In Sec. 4 and Sec. 5 the theoretical results are compared with the simulations and then discussed.

2 Excluded-volume corrections

2.1 Static properties of the Rouse modes

The discrete [5,8] Rouse model [4] describes a single linear chain as a series of $M_R - 1$ segments being modelled by M_R non-interacting beads, connected by entropic springs in the presence of a highly damping gaussian environment. The solution, i.e. the position of the n-th bead $\mathbf{r}_n$, is conveniently expressed in terms of normal coordinates, the so-called Rouse modes $\mathbf{X}_p^R$ with $p = 0, \ldots, M_R - 1$, to be written as:

$$\mathbf{X}_p^R(t) = \frac{1}{M_R} \sum_{n=1}^{M_R} \mathbf{r}_n(t) \cos\left[\frac{(n-1/2)p\pi}{M_R}\right] \tag{1}$$

Henceforth, the mode with index $p = 0$, i.e. the chain center-of-mass, will be not considered. The static cross-correlations between the Rouse modes vanish. In particular, for $p, q > 0$

$$\langle \mathbf{X}_p^R \cdot \mathbf{X}_q^R \rangle = \delta_{pq} \frac{a_R^2}{8M_R \sin^2(p\pi/2M_R)} \tag{2}$$

The Rouse chain provides a coarse-grained picture of flexible linear polymers with bond length b_0 and M monomers, the $m-$th one being located at the position $\mathbf{R}_m$, $1 \leq m \leq M$ (see Fig. 1 a). The segment and the bond lengths are related via the characteristic ratio C_∞ by $a_R = \sqrt{C_\infty} b_0$ [2]. The rationale is that the presence of excluded volume results in a homogeneous dilation of the chain at the largest length scales [21]. For fully flexible chains, $\sqrt{C_\infty} \sim 1$ [17,25] and the identification $M_R = M$ is safe. In that case the actual route to calculate the modes in numerical simulations starts by defining ($1 \leq p \leq M-1$):

$$\mathbf{X}_p(t) = b_0 \sum_{n=1}^{M-1} d_{p\,n} \, \mathbf{b}_n(t) \tag{3}$$

where $\mathbf{b}_m$ is the unit vector along the m-th bond of the chain:

$$\mathbf{b}_m = \frac{1}{b_0}(\mathbf{R}_{m+1} - \mathbf{R}_m) \tag{4}$$

and

$$d_{p\,n} = -\frac{1}{2M} \sin\left[\frac{pn\pi}{M}\right] \csc\left[\frac{p\pi}{2M}\right] \tag{5}$$

The static cross correlations between the modes read:

$$\langle \mathbf{X}_p \cdot \mathbf{X}_q \rangle = \delta_{pq} \frac{b_0^2}{8M \sin^2(p\pi/2M)} + b_0^2 \sum_{i=1}^{M-2} D_{p\,q\,i} \tag{6}$$

with

$$D_{p\,q\,i} = \sum_{k=1}^{M-1-i} (d_{p\,i} d_{q\,i+k} + d_{q\,i} d_{p\,i+k}) \langle \mathbf{b}_i \cdot \mathbf{b}_{i+k} \rangle \tag{7}$$

The first term on the rhs of Eq. 6 coincides with Eq. 2 having replaced the mean square length of the Rouse segment a_R^2 with the square length of the bond b_0^2

and the number of Rouse segments with the number of bonds. The second term of Eq. 6 provides the corrections due to the non-vanishing static correlations between different bonds. If the chain is a phantom $\langle \mathbf{b}_m \cdot \mathbf{b}_{m+k} \rangle = \delta_{k\,0}$ and the corrections vanish, i.e. $D_{p\,q\,i} = 0$.

2.2 Bond-bond static correlations

Eqs. 6 and 7 show that the static properties of the Rouse modes with $p > 0$ depend on the bond-bond static correlation $\langle \mathbf{b}_m \cdot \mathbf{b}_{m+k} \rangle$, i.e. the average cosine of the angle between the m-th and $(m+k)$-th bonds. Explicit expressions of the latter quantity are known since long time for the case of linear chains with *fixed* bond (or valence) angle $\gamma_m = \gamma$, between the m-th and $(m+1)$-th bonds (see Fig. 1 b) both in the absence [26] and the presence [27] of a torsional potential $U(\phi_m)$, ϕ_m being the dihedral angle, hindering the rotation of the chain around the m-th bond. That results were reviewed by Flory [28] and, more recently, by others [2,29]. Here, we are interested in a variant of the above well-known results which was first discussed in ref.[20], i.e. the possibility that the valence angle γ_m is *not* fixed and spans a finite range being limited by the excluded volume effects between the $m-$th and the $(m+2)-$th beads. Analogously to the classical treatments of the case with fixed valence angle [2,28,29], the statistics of both the valence and the dihedral angles are taken as independent of each other and also independent of the bond position m along the chain. For the present purposes torsional potentials are neglected, i.e. the dihedral angle ϕ covers the range $0 \leq \phi \leq 2\pi$ with equal probability. Under the above hypothesis one proves that [20]:

$$\langle \mathbf{b}_m \cdot \mathbf{b}_{m+k} \rangle = \langle \cos\gamma \rangle^{|k|} \tag{8}$$

With the aim of including the excluded-volume effects one adopts suitable expressions for the average quantity $\langle \cos\gamma \rangle$. A number of different possibilities were presented in ref.[20]. It was found that the most effective one is the SM3 model yielding :

$$\langle \cos\gamma \rangle^{(\mathrm{SM3})} = \frac{\int_0^{2b_0} \left(\frac{r^2}{2b_0^2} - 1 \right) e^{-\beta U_T(r)} dr}{\int_0^{2b_0} e^{-\beta U_T(r)} dr} \tag{9}$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant and :

$$U_T(r) = [U(r) + \epsilon] H(r_{min} - r) \tag{10}$$

where $H(x)$ is the Heaviside step function. $U_T(r)$ vanishes in the minimum at $r = r_{min}$ of the interaction potential between non-bonded monomers $U(r)$ ($U(r_{min}) = \epsilon$). That shift ensures that the potential is continuous.

Two features of the SM3 model must be pointed out: 1) the model assumes that the static properties are dominated by the repulsive part of the potential. This is in the same spirit of the Weeks-Chandler-Andersen reference-potential theory (WCA) for monoatomic liquids [30] and its PRISM extension to polymers [31]; 2) the model depends on an ansatz (the insertion of an effective r^{-1} weight in the integrals of Eq.9) which overweights the configurations with close monomers (small r values).

2.3 Scaling properties

Given a Rouse chain with M_R beads, a decimated chain with $M'_R = M_R/\alpha$ ($\alpha > 1$) is a Rouse chain itself [2]. One may wonder if that feature is also present in our extension for fully flexible chains. For the latter the bond-bond correlations $\langle \mathbf{b}_m \cdot \mathbf{b}_{m+k} \rangle$, Eq.8, vanish virtually for $k > 2$ and reasonable values of the average $\langle \cos\gamma \rangle$ [20]. It may be proven that for the decimated chain

$$\langle \mathbf{b}'_{m'} \cdot \mathbf{b}'_{m'+k} \rangle = f(\alpha, \langle \cos\gamma \rangle) \, \langle \cos\gamma \rangle^{(|k|-1)\alpha}, \qquad k \geq 1 \tag{11}$$

where f is a decreasing function of α. If $\alpha > 2$ the static properties of the Rouse modes of the decimated chain with excluded-volume corrections reduce to the ones of the usual Rouse model, i.e. $\langle \mathbf{b}'_{m'} \cdot \mathbf{b}'_{m'+k} \rangle$ is negligible for $k \geq 1$.

3 Numerical methods

We investigate systems of $N = 200$ fully flexible linear chains with $M = 10$ monomers by molecular-dynamics methods (MD) [32]. The interaction between non-bonded monomers occurs via the parametric potential [33,24]:

$$V(r; l, s) = \frac{\epsilon}{s-l} \left[l \left(\frac{r_{min}}{r} \right)^s - s \left(\frac{r_{min}}{r} \right)^l \right]. \tag{12}$$

For different (l, s) pairs the steepness of the repulsive and the attractive wings is changed while leaving unchanged both the position $r_{min} = \sqrt[6]{2}\,\sigma$ and the depth of the global minimum ϵ (Fig.2). For $l = 6, s = 12$ the usual Lennard-Jones potential is recovered. Actually, the potential is cut off at $r_{\rm cut} = 2.5\sigma$ and properly shifted so as to vanish at that point and to make it continuous everywhere. The interaction of bonded monomers is set by summing the Lennard-Jones potential $V(r; 6, 12)$ to the Finitely Extensible Nonlinear Elastic potential (FENE) with characteristic parameters $K = 30\epsilon\sigma^{-2}$ and $R_0 = 1.5\sigma$ [19] leading to the average bond length $b_0 = 0.97\sigma$. From now on we set $\sigma = 1, \epsilon = 1$ and $k_B = 1$. The samples are equilibrated at a given temperature and density. Data are collected during production runs in microcanonical conditions. The system is studied at densities $\rho = 0.7, 0.8, 0.9, 1.0$ and temperatures $T = 1.2, 1.8, 3.0$. The results have been averaged over five independent runs at least. Note that decamers ($M = 10$) are shorter than the entanglement length of the present model $N_{\mathrm{e}} \sim 32$ [19].

4 Results

The Rouse modes $\mathbf{X}_p$ are found to be fairly orthogonal. In fact, the quantity $\langle \mathbf{X}_p \cdot \mathbf{X}_q \rangle$ with $p \neq q$ is two-three orders of magnitude less than the moduli of the involved modes (data not shown) in agreement with other studies [15,17].

Figs. 3,4,5 compare the MD results concerning the moduli of the Rouse modes $\mathbf{X}_p$ with the predictions of the SM3 model via Eqs. 6,7,8,9,10 with no adjustable parameter.

Fig. 3 plots the relative errors for different temperatures. **Decreasing the temperature, the deviations for the Rouse mode with $p = 1, 2$, i.e. the ones accounting for the chain conformations on the longest length scales [2], decrease. Differently, for $p > 2$ the deviations increase. Fig. 3 (insert) shows that the average of the moduli of the relative errors over all the Rouse modes is nearly temperature independent.**

Fig. 4 shows that, on increasing the density, the deviations for the Rouse mode with $p = 1$, decrease. **For $p = 2$ the deviations change their sign with magnitude nearly unaffected. For $p = 3$ there is an increase of the deviations. For $p > 3$ the deviations are either nearly unaffected**

or a little decreasing in magnitude. Fig. 4 (insert) shows that the average of the moduli of the relative errors over all the Rouse modes decreases with increasing density.

Fig. 5 plots the relative errors for different shapes of $V(r; l, s)$ (see also Fig.2). The overall agreement of the SM3 model with the numerical results is better for stiff potentials ($l = 11, s = 12$) **in that the magnitude of the deviations decreases for all but the modes with $p = 3, 4, 9$ with respect to the other floppier potentials.**

5 Discussion

The above first results need to be complemented by more detailed studies which go beyond the purpose of the present paper. However, some preliminary conclusions may be drawn.

The negligible temperature dependence of the statics of the Rouse modes was noted elsewhere [15,17,20]. At higher temperatures the truncation procedure of the potential, Eq.10, (and then the SM3 model itself) becomes questionable since the high kinetic energy of the monomer allows the latter to sense a wider portion of the interaction potential, including the attractive tail.

As noted above, for a system with constant volume and fixed interactions the potential energy landscape (PEL) is fixed and changing the temperature varies its sampling [22]. Differently, changing the density and the intermolecular potential (apart from the special case of molecular interactions being proportional to a common inverse-power of distances) affects the rugged character of the PEL and then the fragility of the system [23,24]. From this respect it is interesting to note a difference in Figs. 3,4,5 . **Changing the temperature affects in an uniform way the plot since it lifts up the relative error of the $\mathbf{X}_p$ mode (Fig. 3) reducing the deviations of the modes with the lowest indexes. Instead, increasing the density and the potential stiffness results in a sort of clockwise rotation of the curves reducing, again, the deviations of the modes with the lowest indexes (long length scales) , but showing a tendency to increase the deviations for the modes with the highest indexes (short length scales), see Figs. 4,5**.

The SM3 model implies via Eq.8 ideal gaussian properties of the chain at large scales [2]. When the density increases, the accuracy improvement of the model to account for the chain conformations on long length scales is taken as a consequence of better screening of the excluded volume and then of increasing ideality [2]. This is also supported by the preliminary observation of the decrease of the characteristic ratio C_{10} with increasing density (data not shown) [2,3]. On the other hand, when the potential stiffness increases, the accuracy improvement of the model to account for the chain conformations on long length scales is ascribed at least in part to better localization of the intra-chain monomer-monomer interactions, the central assumption of the Rouse model [2].

6 Conclusions

We have shown that excluded volume effects on single-chain statics may be introduced by analytic corrections to the Rouse results. The final expressions do not depend on free parameters. In particular, the SM3 version of the above approach has been compared with numerical simulations of a polymer melt for different values of the temperature, the density and the interaction potential. Density and interactions control the PEL of the system. Changing the temperature just allows for PEL exploration. The overall agreement between the SM3 model and the moduli of the Rouse modes **does not depend markedly on the temperature with some improvement for the first modes (large length scales)**. Differently, increasing the packing and the stiffness of the monomer-monomer interaction reduces the deviations for the first modes , whereas it leaves the magnitude of the deviations for the high-indexes modes (short length scales) nearly unaffected **or with some tendency to increase**.

Acknowledgements

Luca Larini is warmly thanked for helpful discussions. Financial support from MIUR within the PRIN project "Aging, fluctuation and response in out-of-equilibrium glassy systems" is gratefully acknowledged.

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Figure captions

Fig. 1. Top: the polymer model under study: a fully-flexible linear chain with M monomers pictured as soft spheres with bond length b_0. The portion between the m-th monomer and the $(m+2)$-th one is emphasized. Bottom: the definition of the bond (or valence) angle γ_m between the m-th bond and the $(m+1)$-th one.

Fig. 2. Plot of the interaction potential between the non-bonded monomers $V(r; l, s)$, Eq.12, with $\sigma = 1, \epsilon = 1$.

Fig. 3. Relative error of the moduli of the Rouse modes $e = 10^2 \times (\langle |\mathbf{X}_p|^2 \rangle^{(\mathrm{SM3})} / \langle |\mathbf{X}_p|^2 \rangle - 1)$ between MD data and the SM3 model for different temperatures. $M = 10, \rho = 0.8$, potential parameters $l = 6, s = 12$. **Inset: temperature dependence of the average modulus of the relative error**. No parameter was adjusted.

Fig. 4. Relative error of the moduli of the Rouse modes $e = 10^2 \times (\langle |\mathbf{X}_p|^2 \rangle^{(\mathrm{SM3})} / \langle |\mathbf{X}_p|^2 \rangle - 1)$ between MD data and the SM3 model for different densities. $M = 10, T = 1.2$, potential parameters $l = 6, s = 12$. **Inset: density dependence of the average modulus of the relative error**. No parameter was adjusted.

Fig. 5. Relative error of the moduli of the Rouse modes $e = 10^2 \times (\langle |\mathbf{X}_p|^2 \rangle^{(\mathrm{SM3})} / \langle |\mathbf{X}_p|^2 \rangle - 1)$ between MD data and the SM3 model for different shapes of the interaction potential between non-bonded monomers $V(r; l, s)$, Eq.12 (see Fig. 2) . $M = 10, T = 1.2, \rho = 0.8$

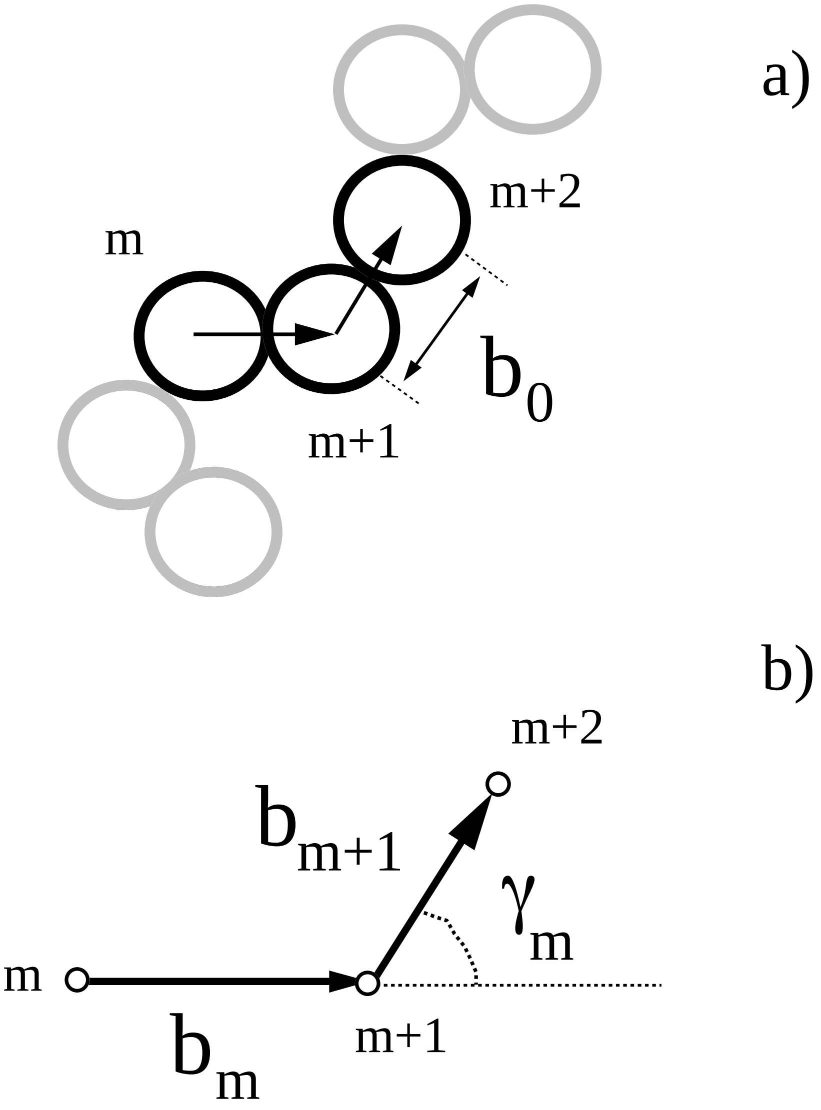

FIGURE 1

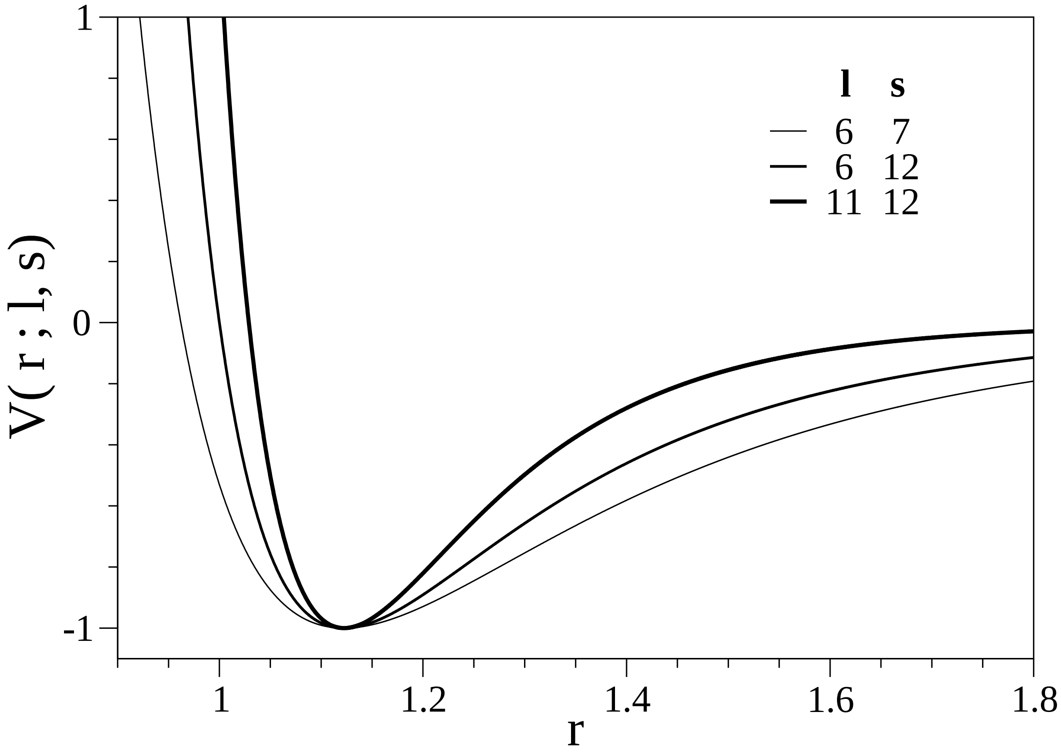

FIGURE 2

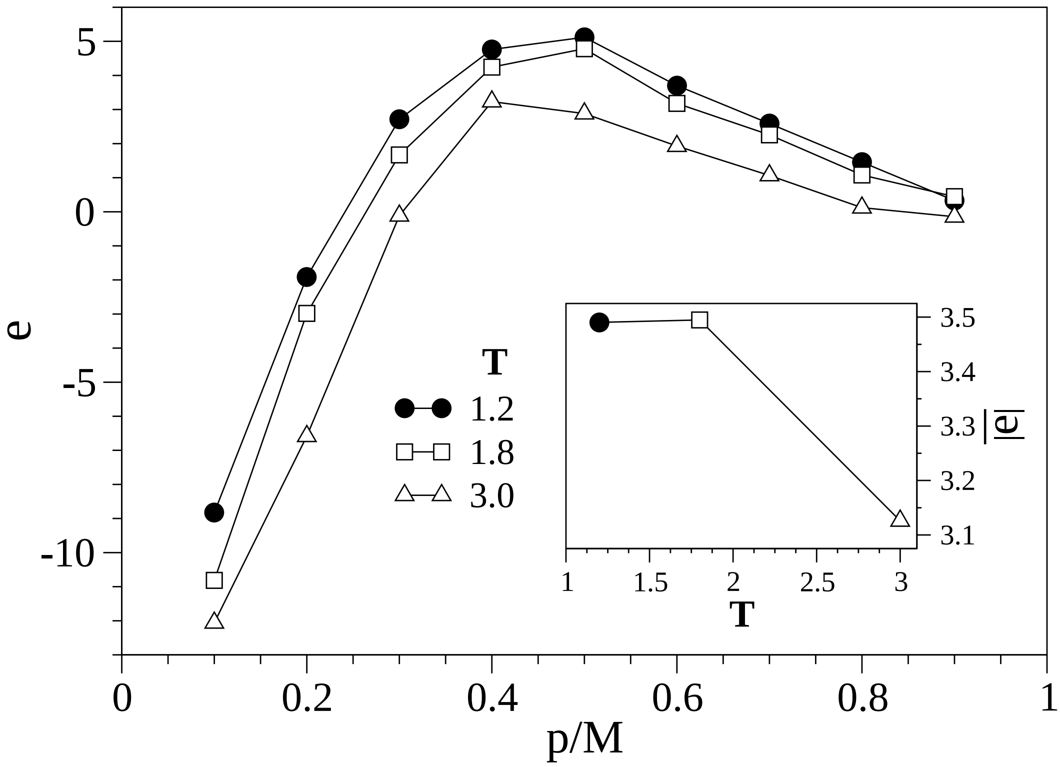
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FIGURE 3

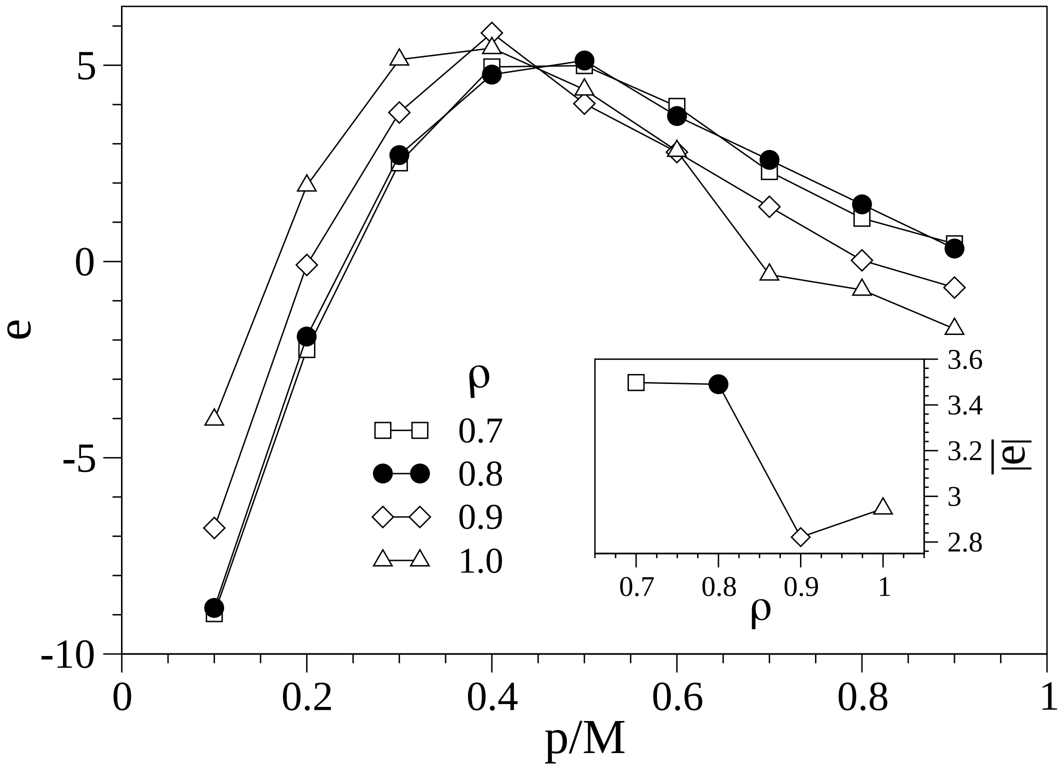
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FIGURE 4

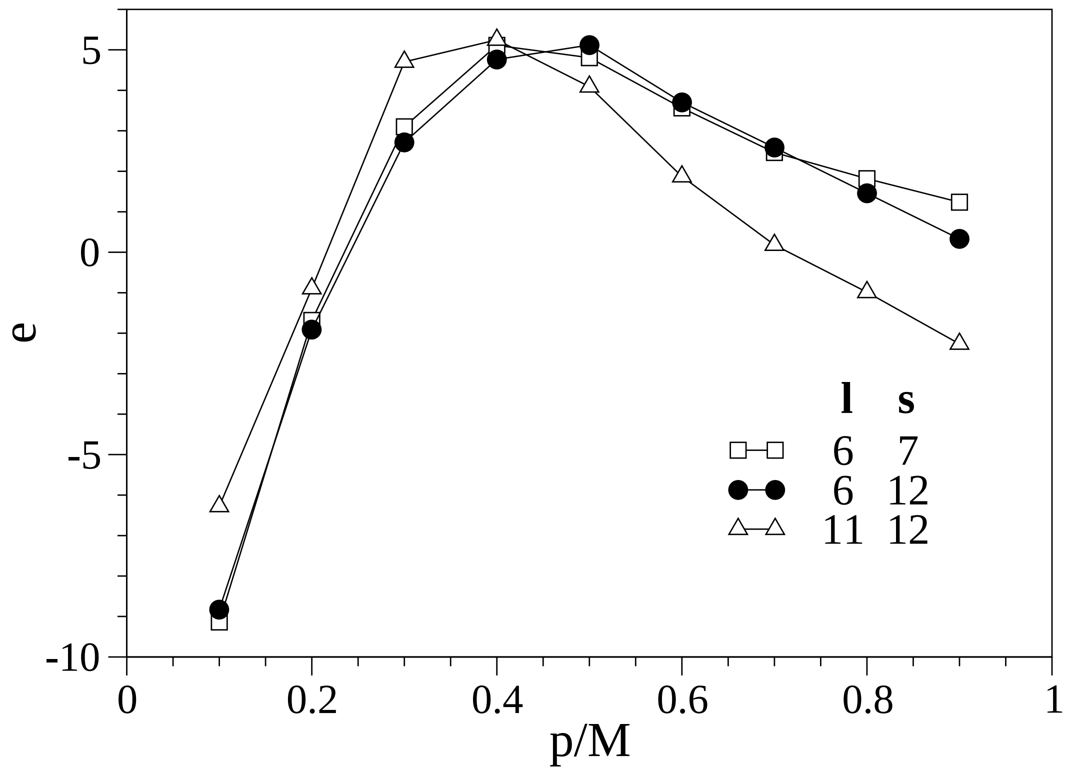

FIGURE 5