

MOLECULAR INVESTIGATION OF POLYELECTROLYTE HYDROGEL UNDER MECHANICAL DEFORMATION

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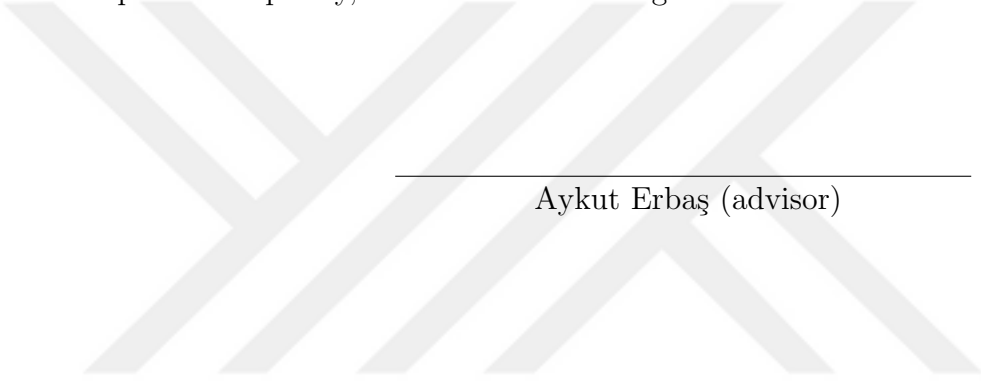
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Molecular investigation of polyelectrolyte hydrogel under mechanical deformation

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We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.



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ABSTRACT

MOLECULAR INVESTIGATION OF POLYELECTROLYTE HYDROGEL UNDER MECHANICAL DEFORMATION

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Polyelectrolyte hydrogels are fascinating materials that can produce electro-mechanical responses when they are electrically or mechanically deformed. However, the accurate molecular origins of such phenomenon are still unknown, even though it is often ascribed to the change in condensation of counterion levels or alteration of ionic conditions in the pervaded volume of the hydrogel. We used all-atom molecular dynamics (MD) simulations to investigate this behavior by utilizing a polyacrylic acid (PAA) hydrogel immersed in an explicit polar solvent as our model system. In the atomistic MD simulation, we investigated the swelling behavior of polyelectrolyte hydrogels, traditionally computed through the equilibrium of chemical potential and pressure between the system and reservoir. However, we discovered that achieving the equilibrium swelling state was non-trivial, as faster relaxation of the simulation box resulted in lower swelling ratios, while slower relaxation led to larger swelling ratios. To address this challenge, we employed theoretical calculations with a Gaussian state as the reference to estimate the hydrogel's swelling ratio effectively. In our computational study, we investigated the response of PAA polyelectrolyte hydrogel from weak to highly swollen (i.e., between 60 to 90% solvent content) when subjected to uniaxial mechanical compression and extension. Our primary aim is to compute the condensed counterions at different deformations at the microscopic level. We found out that condensation of counterion shows highly non-monotonic behavior when they are mechanically deformed, with an overall increase in total counterion condensation when the PAA hydrogel is uniaxially compressed or stretched. However, this effect diminishes for weakly swollen gel because a large fraction of counterions are already condensed on the polyelectrolyte polymer. Upon closer examination, we found that counterion condensation increases along the stretched chains in the hydrogel. on the one hand, this increase reaches to maximum value for certain

deformation ratios after that, we see a decline in the condensation of counterions when the hydrogel chains are stretched further. On the other hand, we see a very minimal increase in condensation when the hydrogel is compressed, and chains are collapsed state. We also analyzed the single polyelectrolyte chains, which also displayed a qualitatively similar response. This observation gives us insight that polymer chain conformations affect the distribution of counterions in the gel. We further investigated the counterion condensation behavior for polyelectrolyte solutions at their critical concentration level. However, we don't see any deformation-dependent counterion condensation. This suggests the importance of hydrogel topology, which constrains the polyelectrolyte chain ends and leads to the observed behavior. These extensive molecular dynamics simulations shed light on the interesting and heterogeneous behavior of counterion condensation when the hydrogel is deformed, showing a rich electrostatic response behavior. These findings contribute significantly to the understanding of the underlying behavior of mechanically deformed polyelectrolyte hydrogels.

Keywords: Polyelectrolyte Hydrogels, Molecular Dynamics Simulations, Charged Polymers, Polymer Physics, Statistical Physics.

ÖZET

POLİELEKTROLİT HİDROJELİN MEKANİK DEFORMASYON ALTINDA MOLEKÜLER İNCELENMESİ

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Polielektrolit hidrojeller, mekanik deforme olduklarında elektrik potansiyeli üretebilen etkileyici malzemelerdir. Genellikle karşı iyon seviyelerinin yoğunlaşmasındaki değişime veya hidrojin nüfuz eden hacmindeki iyonik koşulların değişimine atfedilse de, bu fenomenin kesin moleküler kökenleri hala bilinmemektedir. Model sistemimiz, all-atom moleküler dinamik simülasyonlarını kullanarak bu olağanüstü davranışı araştırmak için belirgin bir polar çözücüye daldırılmış bir poliakrilik asit (PAA) hidrojel kullanılmaktadır. Hesaplamalı çalışmamızda, PAA polielektrolit hidrojinin tek eksenli mekanik sıkıştırma ve uzamaya maruz kaldığında zayıftan çok şişmişe (yani, %60 ila %90 solvent içeriği) tepkisi incelenmektedir. Birincil amacımız, mikroskobik düzeyde farklı deformasyonlardaki yoğunlaşmış karşıt iyonları hesaplamaktır. PAA hidrojelini tek eksenli olarak sıkıştırıldığında veya gerildiğinde, karşı iyon yoğunlaşmasının, mekanik olarak deforme edildiğinde toplam karşı iyon yoğunlaşmasında genel bir artışla oldukça monoton olmayan bir davranış sergilediği görülmektedir. Ancak, bu etki, karşı iyonların önemli bir kısmının polielektrolit polimer üzerinde zaten yoğunlaşmış olması gerçeğinden dolayı, zayıf şekilde şişmiş jel için azalır. Daha yakından incelendiğinde, hidrojeldeki gerilmiş zincirler boyunca karşı iyon yoğunlaşmasının arttığını bulunmaktadır. Bu artış, belirli deformasyon orantıları için maksimum değere ulaşır, bundan sonra hidrojel zincirleri daha fazla gerildiğinde karşı iyon yoğunlaşmasında bir azalma gözlemlenmektedir. Öte yandan, hidrojel sıkıştırıldığında ve zincirler çökmüş durumdayken, karşı iyon yoğunlaşmada çok az bir artış görülmektedir. Tekli polielektrolit zincirlerini analiz edildiğinde, niteliksel olarak benzer tepki sergilediğini gözlenmektedir. Bu gözlem, polimer zincir yapılarının jeldeki karşı iyonların dağılımını etkilediğine dair bir fikir verilmektedir. Kritik konsantrasyon seviyelerinde polielektrolit

çözeltileri için karşı iyon yoğunlaşma davranışı daha fazla araştırıldı ve deformasyona bağlı karşı iyon yoğunlaşması gözlemlenmemektedir. Bu, polielektrolit zincir uçlarını sınırlayan ve gözlemlenen davranışa yol açan hidrojel topolojisinin önemini ortaya koymaktadır. Bu kapsamlı moleküler dinamik simülasyonları, hidrojel deforme olduğunda zengin bir elektrostatik tepki davranışı göstererek, karşı iyon yoğunlaşmasının ilginç ve heterojen davranışına ışık tutmaktadır. Bu bulgular, mekanik olarak deforme olmuş polielektrolit hidrojellerin temel davranışının anlaşılmasına önemli ölçüde katkıda bulunmaktadır.

Anahtar sözcükler: Polielektrolit Hidrojeller, Moleküler Dinamik Simülasyonları, Yüklü Polimerler, Polimer Fiziği, İstatistiksel Fizik.

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Chapter 1

Introduction

Polymers are large molecules comprised of lots of small repeating units called monomers. These small units are combined chemically together to form macromolecules. Polymers can be found both naturally and synthetically [1]. Proteins, deoxyribonucleic acid (DNA), and cellulose are examples of natural polymers, whereas polyacrylic acid (PAA), polyvinyl chloride (PVC), polyethylene, etc., are examples of synthetic polymers.

If a polymer chain contains ionizable groups like carboxylic acid ($-\text{COOH}$), ammonium ($-\text{NH}_2$) along their molecular chains can lose or gain H^+ ions when dissolved in a solvent, such as water, leaving behind the charged polymer chains and counterions [2]. The presence of the charged groups gives rise to unique properties of the polymer, like electrostatic interactions with other charged species and improved water solubility. The charged polymer chain can be classified into two groups:

Cationic polymers: These polymers comprise functional groups such as ammonium or phosphonium, which gain H^+ forming positively charged polymeric chains (Figure 1.1 a (i)).

Anionic polymers: These polymers consist of ionizable groups, such as carboxylic acid, sulfonate, etc., that can dissociate in water, forming a negatively

charged polymer chain (Figure 1.1 a (ii)).

The Onsager-Manning-Oosawa mean-field theories imply that counterion condensation can occur for rod-like macromolecules such as DNA or charged polymers. During this process, a fraction of the counterions that neutralize the charges on the rod is restricted within a critical radial distance from the macromolecule's axis of rotation [3, 4, 5]. In contrast, the leftover counterions disperse to the surrounding bulk solution. This counterion condensation transition has significant implications for charged polymers' static and dynamic properties of various laboratory or biological fluids.

The Manning condensation is characterized as a critical value ζ , also known as the Manning condensation parameter. The Manning parameter is defined as the ratio of the distance between charged groups on the macromolecule and the characteristic Debye length of the solution, which describes the screening length of electrostatic interactions in the solvent [6]. Manning parameter (ζ) is defined as the product of the counterion valency (q), the Bjerrum length (l_B), and the line charge density λ . According to the Onsager-Manning-Oosawa theory, counterion condensation occurs when the Manning parameter exceeds 1 ($\zeta = ql_B\lambda > 1$) [3, 4, 5, 7].

The Poisson-Boltzmann (PB) equation can be solved analytically for "only counterion case" within a finite cylindrical cell, also known as the cell model [8]. This model provides a simple expression for the counterion condensation within the threshold distance, referred to as the Manning radius (r_M) Figure 1.1 b (i), and the fraction of condensed counterions denoted as f . According to PB theory, the fraction of condensed counterions, f , is given by the expression $f = 1 - 1/\zeta$ [9, 10]. This prediction of PB theory is independent of the cell size [6]. To exemplify, for DNA, it is argued that approximately 75% of the ions are condensed within a radius of about 1 nm [11]. The Poisson-Boltzmann equation is beneficial for systems where the electrostatic coupling is not excessively strong and when dealing with monovalent ions [8, 12].

Polyelectrolyte (PE) hydrogels are three-dimensional networks constructed

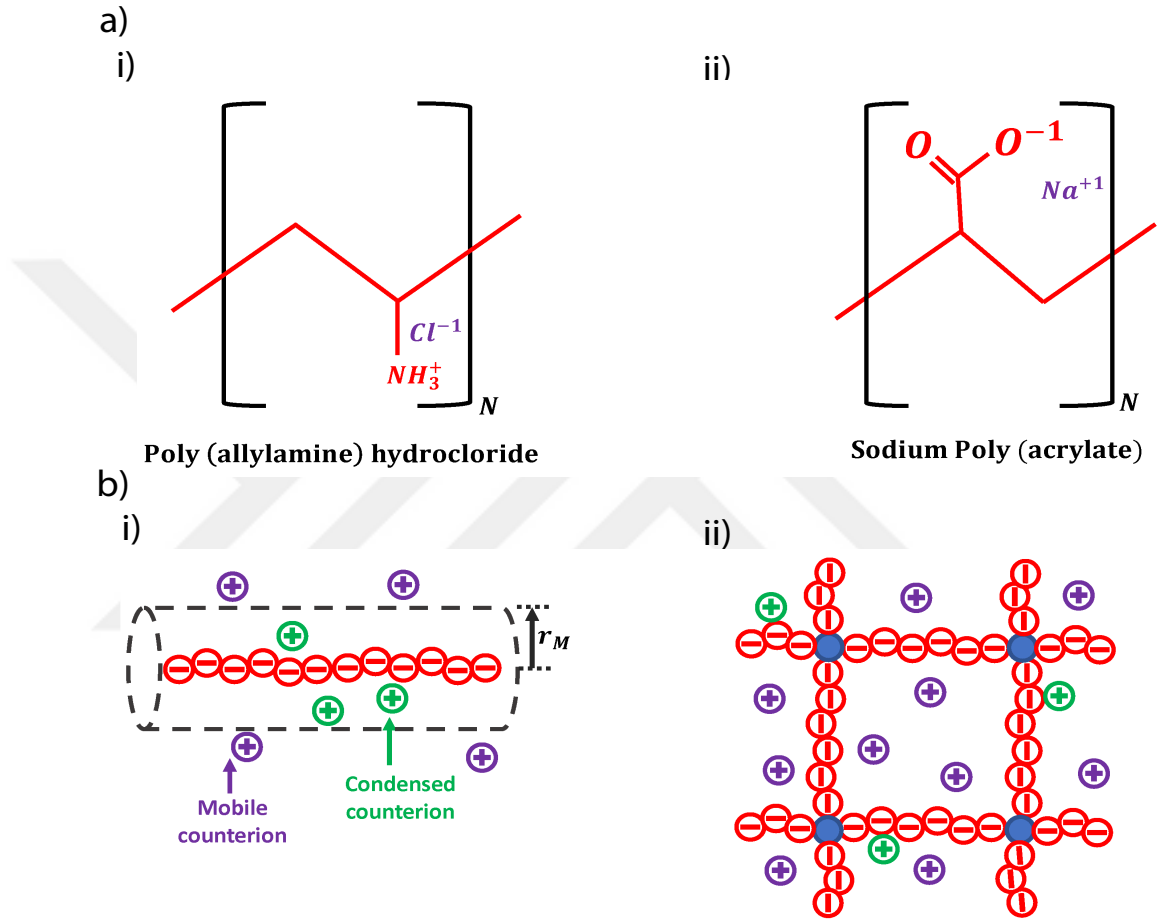


Figure 1.1: The chemical formula of different single monomer units are shown, which form a positive and negatively charged polymer a) i) Poly (allylamine) hydrochloride represented, which will accept H^+ ion to get positively charged. ii) Poly (acrylic) acid monomer unit is shown, which dissociates H^+ ions to form the negatively charged polymer. b) i) The coarse-grain model of charged polymer is shown in which each Kuhn monomer carries a $-1e$ charge and rod-like charged polymer is surrounded by the counterions (purple). If the radial distance between the charged polymer backbone and counterion is $r \leq r_M$, (i.e., Manning radius) the counterion is considered to be condensed (green). ii) Charge polymers are linked together to form a polymer network called polyelectrolyte hydrogel.

from the crosslinking of charged polymers (Figure 1.1 b (ii)). The charged polymers can be crosslinked using chemical or physical bonding [2]. The PE hydrogel network consists of hydrophilic and charged polymers with a strong affinity for polar solvent molecules like water [1]. The PE hydrogels cause polar solvents or biological fluids to be absorbed and retained in the network. Therefore, PE hydrogels can be used in superabsorbent applications like diapers, hygiene products, etc. PE hydrogels have also emerged as an ideal biomaterial, which can be used for diverse biomedical applications such as drug delivery and tissue engineering. These fascinating materials are imbued with electrostatic interactions, making them unique and intriguing materials to study for scientific study and technological purposes.

The electrostatic interactions between charged polymer chains and counterions released by ionizable groups are at the core of PE hydrogel. The electrostatic repulsion due to the charges on the polymer chains contributes to the osmotic pressure in the PE hydrogels and favors the swelling of the three-dimensional hydrogel network [13, 14]. In contrast, the entropic nature of polymeric chains resists network swelling [15, 16]. The balance between osmotic pressure due to charges and chain elasticity is reached with high solvent content [16]. This equilibrium between elastic and electrostatic components can be disturbed when external stimuli such as mechanical deformation, electric field, or magnetic field are applied [13, 17, 18, 19, 20, 21]. PE hydrogels change their counterions distribution or chain conformation when external stimuli such as mechanical deformation or electric field are applied [18]. This makes PE hydrogels an exciting area to study for different applications such as biosensing, water desalination, energy storage, bio-mimetic tissues, signal transfer, and sensing [17, 22, 23, 24, 25, 26, 27].

When an external electric field is applied to PE hydrogels, fixed electric charges on polymer backbone chains and mobile counterions of opposite charges tend to move in opposite directions [28, 13]. This effect leads to a transient non-uniform distribution of counterions. Consequently, resulting in non-uniform elastic energy throughout the pervaded volume of the PE hydrogel and leads to the hydrogel's macroscopic deformation [29, 30, 31]. Similarly, the electrostatic interactions and possibly counterionic distribution are modified when mechanical deformation

is applied. It has been illustrated in experimental studies that several orders of millivolts of electrostatic potential were generated when PAA hydrogel was compressed. Likewise, the mechanical deformation-dependent electrical potential was observed in another study as the polymethacrylic hydrogel was stretched [20].

Based on the coarse-grained molecular dynamics (MD) simulations, where the solvent was represented without actual solvent molecules in the simulation box but with a consistent dielectric constant, it was observed that when a model hydrogel was mechanically compressed, there was an increased electrostatic interaction between counterions and backbone charges. This indicates that ions' distribution depends on the hydrogel's deformation [17, 32].

The counterion condensation theory may describe the counterion distribution around the constituting chains of a PE hydrogel originally suggested for dilute PE solutions [7]. The condensation model dictates that not all but some of the counterions are released to the surrounding solution while a fraction of the counterions *condense* near the chain backbone, effectively renormalizing the net of charge of the PE chain [3, 4]. Accordingly, if the line charge density of a chain is $1/\ell_0$, the counterion condensation occurs if the ratio, also known as Manning parameter, obeys $\xi = \ell_B/\ell_0 > 1$, where the Bjerrum length ℓ_B characterizes the strength of the Coulomb coupling in a solvent with dielectric constant, ϵ . Nevertheless, the theory assumes an infinitely long, straight chain embedded in a uniform-dielectric medium. In a hydrogel structure, constituting chains can accept different conformation properties depending on the solvent content inside the pervaded volume of the network (i.e., swelling ratio). Furthermore, in a deforming hydrogel, individual chains can readily be collapsed or stretched to adjust the total volume or shape of the hydrogel. In turn, such conformational changes can affect the counterion distribution of the constituting PE chains in a highly non-trivial way. To make matters even more complicated, counterion distributions near the PE chains of the hydrogel can be affected by the dielectric heterogeneities near the PE chains [33, 34]. Such heterogeneity can easily arise due to the dipole nature of water molecules surrounding the hydrophobic and hydrophilic moieties of PE chains [35, 36].

In this work, to investigate the effect of weak-to-intermediate uni-axial compression and stretching on the counterion distribution in a hydrogel, we use all-atom molecular dynamics (MD) simulations of a defect-free PAA hydrogel. In our atomistic simulations, all water molecules, backbone charges, and counterions are considered explicitly with their partial charges, dipoles, and steric interactions, allowing us to consider the microscopic "condensation" of counterions on the backbone charges of the hydrogel chains under mechanical deformation. Our simulations suggest that deformation affects the counterion condensation and electrostatics in a highly non-monotonic way, depending on the swelling ratio of the hydrogel. Simulations with semi-dilute PAA solutions and single PAA chains reveal that alterations in the ionic distributions are due to conformational changes of constituting chains and, thus, could be a generic property of weak PEs.

Chapter 2 of this thesis introduces fundamental concepts from statistical physics, specifically the NVT and NPT ensembles, which serve as the basis for defining our polyelectrolyte hydrogel system. The chapter then delves into a comprehensive discussion on the swelling behavior of hydrogels, exploring the underlying principles of the Poisson-Boltzmann theory. Subsequently, we provide a thorough theoretical background on classical molecular dynamics and the OPLS AA force field, both of which are employed to define our polyelectrolyte hydrogel system. Additionally, we elucidate the water chemical using Widom's method, and we will insert water molecules into the hydrogel structure using Grand Canonical Monte Carlo (GCMC) method. The ensuing section describes the algorithms utilized to maintain constant pressure and temperature during simulations, which is crucial for accurately characterizing the system. Finally, we outline the analytical approaches employed to examine the behavior of counterion condensation as the polyelectrolyte hydrogel undergoes deformation.

In Chapter 3, we shift our focus to modeling the polyelectrolyte hydrogel network, specifically investigating the impact of deformation along a uniaxial direction on the condensation of counterions. Furthermore, we conduct a comparative analysis by examining a single polymeric charged chain in implicit and explicit solvent cases, enabling us to discern differences in counterion condensation between

the two scenarios. Lastly, we emphasize the significance of the periodic topology of the hydrogel network, which plays a vital role in observing non-monotonic behavior in counterion condensation.



Chapter 2

Theoretical Background

2.1 Statistical Mechanics

Statistical mechanics provides the theoretical framework to study polyelectrolyte hydrogels. Depending on the nature of the physical problem, different ensemble approaches can be applied to represent the system, and properties of the interest can be studied. If the system is isolated, i.e., no exchange of energy or particle with the surround and volume remains fixed, it can be described using a microcanonical (NVE) ensemble. A system with a fixed number of particles, volume, and temperature can best represent using a canonical (NVT) ensemble. For a system with constant particles, pressure, and temperature isobaric-isothermal (NPT) ensemble.

2.1.1 Canonical ensemble

The canonical ensemble is one of the most common ensembles used to describe physical systems. The number of particles, volume, and temperature are kept fixed in a canonical ensemble; that's why it is also known as the “NVT” ensemble. In the canonical ensemble, the system can exchange energy with the surroundings

(reservoir) to keep the system's temperature fixed. The system can be described entirely using the partition function $Q(N, V, T)$ and the free energy $F(N, V, T) = -k_B T \ln(Q(N, V, T))$ [37]. The partition function of the NVT ensemble can be derived from the integration of the Boltzmann factor taken over the entire phase space $(\vec{r}^N, \vec{p}^N)$, where $\vec{r}^N$ and $\vec{p}^N$ represent the position and momenta of all the particles [37]:

$$Q(N, V, T) = \frac{1}{h^{3N} N!} \int_{V^N} d^{3N} r \int_{\mathbb{R}^{3N}} d^{3N} p e^{-\beta H(\vec{r}^N, \vec{p}^N)} \quad (2.1)$$

Where h is Planck's constant, β is the inverse of the product of Boltzmann constant k_B and absolute temperature T , and H is the Hamiltonian function of the system. If the system is composed of different species j , the partition function of the system can be represented as follows:

$$Q(N_j, V, T) = \prod_j \frac{1}{h^{3N_j} N_j!} \int_{V_j^{N_j}} d^{3N_j} r \int_{\mathbb{R}^{3N_j}} d^{3N_j} p e^{-\beta H(\vec{r}^{N_j}, \vec{p}^{N_j})} \quad (2.2)$$

The system's total energy is the sum of the kinetic energy and potential energy of all the particles.

$$H = \underbrace{\sum_j \sum_k^{N_j} \frac{\vec{p}^2(k, j)}{2m_j}}_{\text{Kinetic Energy}} + \underbrace{\sum_j U(\vec{r}^{N_j})}_{\text{Potential Energy}} \quad (2.3)$$

The potential energy function, U , only depends on the position of particles, and it is independent of the particles' momenta. This allows us to rewrite the partition function separately into the dimensionless “kinetic partition function” Q_{kin} and the dimensionless “configuration partition function” Q_{conf} [37].

$$Q(N_j, V, T) = \underbrace{\prod_j \frac{1}{V^{N_j}} \int_{V_j^N} d^{3N_j} r e^{-\beta U(\vec{r}^{N_j})}}_{Q_{conf}} \underbrace{\prod_j \frac{V^{N_j}}{N_j! h^{3N_j}} \int_{\mathbb{R}^{3N_j}} d^{3N_j} p e^{-\beta \sum_j \sum_k^{N_j} \frac{\vec{p}^2(k,j)}{2m_j}}}_{Q_{kin}} \quad (2.4)$$

In an ideal gas, particles don't interact with each other. Therefore, potential energy $U(\vec{r}^{N_j}) = 0$ and configuration partition function, $Q_{conf} = 1$. For a non-interacting system, the partition function can be obtained by integrating just the kinetic partition function, which can be solved analytically [37].

$$Q_{kin}(N_j, V, T) = \prod_j \frac{1}{N_j!} \left(\frac{V}{\lambda_j} \right)^{N_j} \quad (2.5)$$

Where λ_j is the thermal de Broglie wavelength of the species j .

However, in most natural systems, particles can interact with each other, and the configuration partition function is a complicated multidimensional integral that cannot be solved analytically. Sometimes simplified assumptions are made to get a numerical or analytical expression of the system's partition function.

The free energy of the system can be written as the sum of kinetic free energy and configuration free energy:

$$\begin{aligned} F(Q(N_j, V, T)) &= -k_B T \ln(Q(N_j, V, T)) \\ &= -k_B T \ln(Q_{kin}(N_j, V, T) \cdot Q_{conf}(N_j, V, T)) \\ &= F_{kin} + F_{conf} \end{aligned} \quad (2.6)$$

2.1.2 Isobaric-Isothermal ensemble

Pressure P , temperature T , and particle number are kept fixed for systems in an isobaric-isothermal ensemble; that's why they are referred to as the "NPT" ensemble. This ensemble is vital in studying experiments that occur under constant pressure and temperature. The total particles are M (reservoir + system), constant temperature T , and the volume V_o figure 2.1. We place our system in this

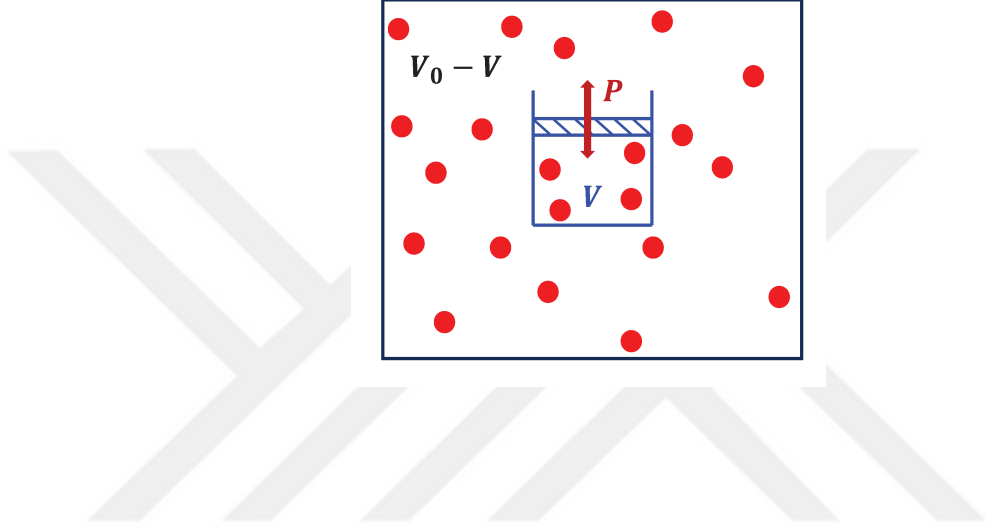


Figure 2.1: The system of volume V is immersed in an ideal gas reservoir with constant volume $V_0 - V$. The system and reservoir will reach an equilibrium when the pressure of an ideal gas reservoir $P_{reservoir}$ equals the pressure of the system P_{system} (i.e., $P_{reservoir} = P_{system} = P$). The system's pressure depends on the volume V of the system.

reservoir with constant particle number N , temperature T , and pressure P such that $M - N \gg N$. We assume that reservoir and system particles are identical for derivation, and we have a cubic simulation system with volume V , and the length of each side is $L = V^{1/3}$ [38]. We are using scaled the coordinates as $\mathbf{s}^N$ by using $\mathbf{r}_j = L\mathbf{s}_j$. We can compute the partition function of the whole system by simply taking the product of partition functions of the subsystems figure 2.1:

$$Q_{res+system}(N, V, T) = \frac{V_o^N (V_{res} - V_o)^{M-N}}{\lambda^{3M} N! (M - N)!} \int d\mathbf{s}^{M-N} \int d\mathbf{s}^N e^{-\beta(U(\mathbf{s}^N))} \quad (2.7)$$

Note that the integral over $\mathbf{s}^{M-N}$ scaled coordinates equals 1 and density ρ is constant, in the limit, such that $V_o \rightarrow \infty$, $M \rightarrow \infty$ and $\rho = (M - N)/V_o$ is constant [38]. Furthermore, the volume change of the system does not change the pressure of the system. Note that limit $V/V_o \rightarrow 0$ [38], we can write

$$(V_o - V)^{M-N} = V_o^{M-N} (1 - (V/V_o)^{M-N}) \rightarrow V_o^{M-N} e^{-(M-N)V/V_o} \quad (2.8)$$

Note that $M - N \rightarrow \infty$, $e^{-(M-N)V/V_o} \rightarrow e^{-\rho V}$ [38]. However, if a reservoir contains an ideal gas, we can write $\rho = \beta P$. Substituting this relationship will allow us to write the partition function for the system in an isobaric-isothermal ensemble as follows [38]

$$Q(N, P, T) = \frac{\beta P}{\lambda^{3N} N!} \int dV V^N e^{-\beta P V} \int d\mathbf{s}^N e^{-\beta(U(\mathbf{s}^N; L))} \quad (2.9)$$

To sum up, we can compute the thermodynamic variables of the systems which are in thermal equilibrium with fixed particle number N , temperature T , and either fixed pressure P or volume V .

In statistical mechanics, all system's information is contained in the partition function. However, we are only interested in the time average of the observable $C(\vec{r}^N, \vec{p}^N)$. For the isobaric-isothermal ensemble, we can write the expectation value of the observables as [38, 37]:

$$\langle C_{NPT}(\vec{r}^N, \vec{p}^N) \rangle = \frac{\int_{V^N} Q(N, V, T) e^{(-\beta P V) \beta P C(\vec{r}^N, \vec{p}^N)} dV}{Q_{N,P,T}} \simeq \frac{1}{T} \sum_{j=1}^T C_j \quad (2.10)$$

This shows that the ensemble average value of the observable can be approximated by the time average of the observable.

2.2 Theory of Charged Gels: Swelling and Deformation

This section will summarize the theoretical background of swelling of the gels based on the mean-field theory. We will focus primarily on the interplay of microscopic dynamics and macroscopic properties, such as the elasticity of the hydrogels. We will discuss the hydrogel model and derive the expression for the free energy contributions required for the equilibrated swelling of the hydrogel and corresponding osmotic pressure terms. Finally, we will discuss the theory of deformation of the hydrogel along the uniaxial direction.

2.2.1 Modeling of the Hydrogel

Consider a system with uniformly charged hydrogel in a polar solvent (i.e., water) with a monovalent salt solution of concentration c_s . Hydrogel comprises multiple gel strands n , each containing specified N Kuhn segments [39]. Gel strands are connected together by the N_c crosslinkers. Within specified Kuhn segments, there are z_p charged groups without any associated counterion adsorption. Considering counterion adsorption, the degree of ionization can be defined as α . Therefore, the concentration of counterions can be expressed as $\frac{\alpha z_p n N}{V} = \alpha z_p c$, where $c = nN/V$ is the monomer concentration [39].

After the synthesis and drying of a gel, it attains a certain initial volume, which may resemble its dry state. Regardless of the initial volume achieved during synthesis, we denote the volume of the gel in its dry state as V_d (Figure 2.3) [39]. As aforementioned that the gel consists of n strands, each containing N segments. We can express the dry volume as

$$V_d = nNv_1. \quad (2.11)$$

Where v_1 represents the volume associated with a single Kuhn segment, it is essential to note that v_1 can be determined using various approaches, such as

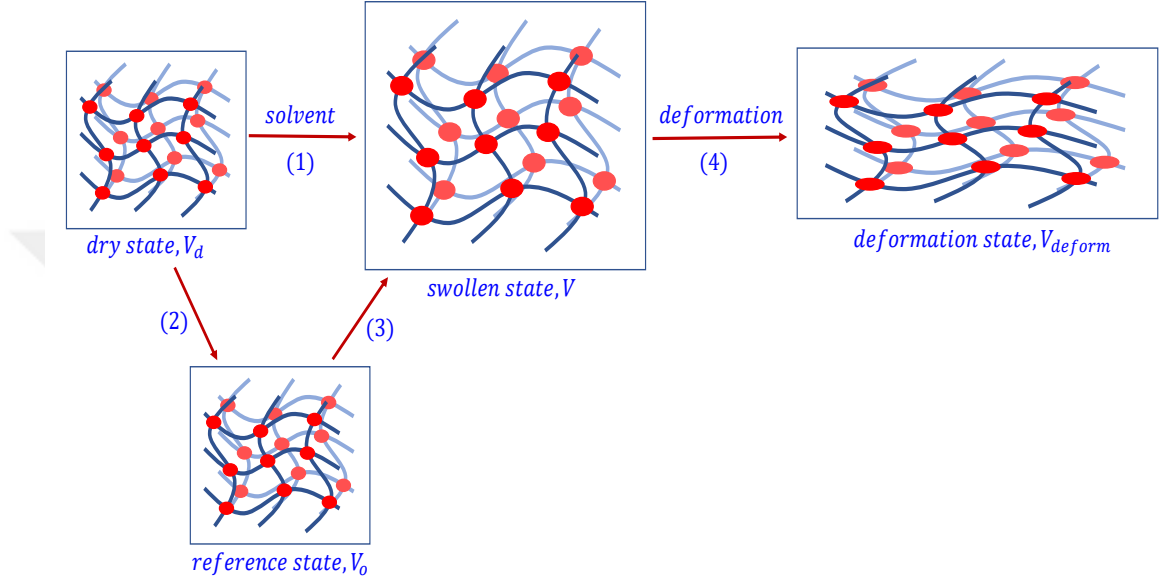


Figure 2.2: Initially hydrogel is in dry state V_d (1) solvent is added to the hydrogel, and it swells to a volume V (4) Swollen hydrogel is deformed to a deformed volume V_{deform} when it is subjected to an external mechanical force. Theoretical gel swelling is done in two steps (2) and (3), where dry gel volume is compared with the theoretical reference state volume V_0 , which obeys Gaussian statistics

the volume of the solvent molecule used in the Flory-Huggins theory or the cubic value of the Kuhn segmental length l^3 .

Hydrogel can be swelled by adding solvent into the initial dry state V_d to an equilibrated swollen state V . Applying uniaxial force/strain to deform the swollen hydrogel causes the hydrogel to be in a deformation state V_{deform} (Figure 2.3) [39]. It is vital to consider the proper chain statistics to develop a molecular theory of the hydrogel. For theoretical purposes, since the initial state of the dry gel is unfamiliar, it is suitable to use Gaussian chain statistics for capturing the chain conformation characteristics. Therefore, we consider the reference dry state in which polymeric strands between the crosslinkers follow the Gaussian statistics [39]. We can define the volume fraction of polymer in swollen state and

the reference state as follows:

$$\phi = V_d/V \quad (2.12)$$

$$\phi_0 = V_d/V_0 \quad (2.13)$$

Here, V_0 is the volume of the hypothetical reference state. In computational modeling of the gels, it is easier to build perfect gel networks without any defects, such as dangling chains and defective branching emerging from the crosslinking points [39]. A simple relationship can be made between the number of polymer chains and crosslinking points. For example, if the crosslinking is in the arrangement for the perfect network, this relationship can be written as

$$N_c = n/2 \quad (2.14)$$

2.2.2 Free Energy and Osmotic Pressure in Hydrogel

By considering Gaussian statistics for the theoretical modeling of the gel, the free energy can be divided into two main parts: the mean-field component and the fluctuation component [40, 41, 42, 39]. The free energy due to the mean-field results from the free energy of mixing between solvent particles and polymer chains, electrostatic interactions between charged particles and charged polymer segments, Donnan equilibrium of electrolyte, and free energy due to polymer elasticity in the gel [39]. The free energy due to fluctuation can arise from the changes in the polymer chain's conformations, charged particle distribution in the hydrogel, and variation in monomer concentration.

$$\Delta F = \underbrace{\Delta F_{mixing} + \Delta F_{elec} + \Delta F_{Donnan} + \Delta F_{elasticity}}_{\Delta F_{mean-field}} + \Delta F_{fluctuations} \quad (2.15)$$

The free energy ΔF depends on the volume fraction of the polymer ϕ , degree of ionization α , the concentration of salt c_s , Flory-Huggins interaction parameter χ , and crosslinking density [43, 44, 45]. The osmotic pressure Π and bulk modulus K at isothermal condition can be defined as

$$\Pi = - \left(\frac{\partial \Delta F}{\partial V} \right)_T = \phi^2 \frac{\partial}{\partial \phi} \left(\frac{\Delta F/V}{\phi} \right)_T \quad (2.16)$$

$$K = -V \left(\frac{\partial \Pi}{\partial V} \right)_T = \phi \left(\frac{\partial \Pi}{\partial \phi} \right)_T \quad (2.17)$$

The different contributions of change in free energies (mixing, electrostatics, Donnan, elasticity, and fluctuations) can be written in osmotic pressure terms. Gel equilibrium is reached when the sum of all these osmotic pressure contributions goes to zero.

$$\Pi = \Pi_{\text{mixing}} + \Pi_{\text{elec}} + \Pi_{\text{Donnan}} + \Pi_{\text{elasticity}} + \Pi_{\text{fluctuations}} = 0 \quad (2.18)$$

Here, Π is called the osmotic pressure of the gel, and $\Pi = 0$ is the equilibrium condition [39, 14].

2.2.2.1 Free Energy of Mixing

Let us consider n polymer chains comprising N Kuhn segments. These chains are immersed in a solvent of volume V and m number of solvent molecules. The free energy of mixing of solvent and polymer chains can be derived from Flory-Huggins theory [46] as

$$\Delta F = \frac{k_B T V}{v_1} \left(\frac{\phi}{N} \ln(\phi) + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right) \quad (2.19)$$

Here, we assume that the volume of the solvent molecules equals the Kuhn segment volume and χ represents the interaction between solvent and polymer. We can consider the whole polymer network as a single large molecule. This will allow us to ignore the mixing entropy contribution due to the gel network and we rewrite the free energy of mixing as

$$\frac{\Delta F}{k_B T} = \frac{V}{v_1} \left((1 - \phi) \ln(1 - \phi) - \chi \phi^2 \right) \quad (2.20)$$

The osmotic pressure due to mixing can be given as

$$\frac{\Pi_{mixing} v_1}{k_B T} = -\ln(1 - \phi) - \phi - \chi \phi^2 \quad (2.21)$$

2.2.2.2 Electrostatics Interactions

There will be electrostatic interaction energy among all segments of the hydrogel network, which can be defined as follows [40, 41, 42, 39]:

$$\frac{F_{elec}}{k_B T} = \frac{1}{2} \int_0^{nN} dx \int_0^{nN} dx' U(\mathbf{R}(x) - \mathbf{R}(x')) \quad (2.22)$$

Here, $\mathbf{R}(x)$ is the position vector of the x -th segment, and electrostatic energy between x -th and x' -th segments is represented by $U(\mathbf{R}(x) - \mathbf{R}(x'))$. The electrostatic interactions between x -th and x' -th segments can be expressed as

$$U(\mathbf{R}(x) - \mathbf{R}(x')) = \frac{\alpha^2 z_p^2 e^2}{4\pi\epsilon_0\epsilon k_B T} \frac{1}{|\mathbf{R}(x) - \mathbf{R}(x')|} \exp(-\kappa|\mathbf{R}(x) - \mathbf{R}(x')|) \quad (2.23)$$

Where ϵ_0 is the permittivity of vacuum, ϵ is the medium dielectric constant, and κ is the inverse of Debye screening length

$$\kappa^2 = \frac{e^2}{\epsilon_0\epsilon k_B T v_1} (\alpha z_p \phi + 2c_s v_1) \quad (2.24)$$

For intermediate salt concentrations, the free energy for electrostatic interactions can be expressed as [47]

$$\frac{F_{elec}}{k_B T} = \frac{1}{2} \frac{V}{v_1} \frac{\alpha^2 z_p^2 e^2}{\epsilon_0\epsilon k_B T l} \frac{(nN)^{2/3} \phi^2}{\kappa^2 l^2 (nN)^{2/3} + \frac{3^{4/3} \pi^{7/6} \phi^{2/3}}{2^{5/3}}} \quad (2.25)$$

Where l is the length of the Kuhn segment, in gels, the polymer's volume fraction is small, and the total number of Kuhn segments is large such that $\phi^{2/3}$

$\ll \kappa^2 l^2 (nN)^{2/3}$ [39]. By considering this approximation, we can simplify the electrostatic free energy expression:

$$\frac{F_{elec}}{k_B T} = \frac{1}{2} \frac{V}{v_1^2} \frac{\alpha^2 z_p^2 e^2}{\epsilon_0 \epsilon k_B T \kappa^2} \phi^2 = \frac{1}{2} \frac{V}{v_1} \frac{\alpha^2 z_p^2 \phi^2}{\alpha z_p \phi + 2c_s v_1} \quad (2.26)$$

We can write the electrostatic interaction energy expression for the limiting cases as follows:

$$\frac{F_{elec}}{k_B T} = \frac{V}{v_1} \begin{cases} \frac{\alpha z_p \phi}{2} & (\text{salt-free}, c_s = 0) \\ \frac{\alpha^2 z_p^2 \phi^2}{4c_s v_1} & (\text{high-salt}) \end{cases} \quad (2.27)$$

We can note that salt concentration is inversely proportional to the volume, and the osmotic pressure due to electrostatic interaction goes to zeros at a specific salt concentration

$$\frac{\Pi_{elec} v_1}{k_B T} = 0 \quad (2.28)$$

2.2.2.3 Free Energy due to Elasticity

We can use classical rubber elasticity theory to write the free energy expression for gel elasticity along three principal orthogonal axes ($\vec{x}$, $\vec{y}$, and $\vec{z}$) [46]. The stretching ratio along three different orthogonal directions can be defined as $\lambda_x = \frac{L_x}{L_0}$, $\lambda_y = \frac{L_y}{L_0}$, and $\lambda_z = \frac{L_z}{L_0}$. The free energy for elasticity can be written as

$$\frac{F_{elasticity}}{k_B T} = \frac{n}{2} \{ \lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 - \ln(\lambda_x \lambda_y \lambda_z) \} \quad (2.29)$$

Considering $\lambda_x = \lambda_y = \lambda_z = \lambda$. We can rewrite the equation (2.29) as

$$\frac{F_{elasticity}}{k_B T} = \frac{3n}{2} \{ \lambda^2 - 1 - \ln(\lambda) \} \quad (2.30)$$

Using equations (2.65), (2.66), and (2.67). Note that $V = V_o \lambda^3$, we will get

$$\frac{F_{elasticity}}{k_B T} = \frac{3n}{2} \left\{ \left(\frac{\phi_0}{\phi} \right)^{2/3} - 1 - \frac{1}{3} \ln \left(\frac{\phi_0}{\phi} \right) \right\} \quad (2.31)$$

We can obtain the osmotic pressure for the elasticity using equations (2.16) and (2.31). We assume that gel swells isotropically

$$\frac{\Pi_{elasticity} v_1}{k_B T} = -\frac{1}{N} \left(\phi_0^{2/3} \phi^{1/3} - \frac{\phi}{2} \right) \quad (2.32)$$

Note that osmotic pressure for elasticity contribution is negative, which means that free energy due to elasticity does not favor the swelling of the gel. The crosslink density can be computed for the reference state of the gel as $S\phi_0^3 \equiv \frac{2N_c v_1}{V_0}$, where S is the cross-link density parameter [46, 48]. In terms of crosslink parameter S , osmotic pressure due to elasticity can be expressed as

$$\frac{\Pi_{elasticity} v_1}{k_B T} = -S\phi^3 \left\{ \left(\frac{\phi}{\phi_0} \right)^{1/3} - \frac{1}{2} \frac{\phi}{\phi_0} \right\} \quad (2.33)$$

The aforementioned formulas are derived under the assumption that the size of polymer strands is long enough and weak stretching forces are acting on them so that the Gaussian statistic remains valid. However, if polymer strand size (root mean square end-to-end distance) becomes comparable with the contour length of the polymer, the finite extensibility of chains needs to be considered.

2.2.2.4 Donnan Equilibrium and Osmotic Pressure due to Electrolyte

The mobile ions will be transferred between the salt ions reservoir (outside the gel) and inside the gel network until equilibrium is reached. This is also known as the Donnan equilibrium [16]. In equilibrium, there will be no net exchange of ions between the reservoir and the gel, and the chemical potential of the electrolyte will equal inside and outside the gel [49].

$$\mu_{ions}^{in} = \mu_{ions}^{out} \quad (2.34)$$

Assuming that electrolyte ions are monovalent. The osmotic pressure due to the mobile can be given as

$$\frac{\Pi_{Donnan} v_1}{k_B T} = \sqrt{\alpha^2 z_p^2 \phi^2 + 4 v_1^2 c_s^2} - 2 v_1 c_s \quad (2.35)$$

2.2.2.5 Free Energy due to Fluctuations

An intriguing resemblance can be made between semidilute solutions above the overlap concentration and swollen gels that free energy per correlation volume ζ^3 is comparable to the thermal energy $k_B T$. Here, ζ is the correlational length associated with the monomer concentration fluctuations emerging from polymer chain connectivity. According to the double screening theory, the free energy arising from the conformational fluctuations can be expressed as [40, 42]

$$\frac{\Delta F_{fluctuation}}{k_B T} \sim \frac{V}{\zeta^3} \quad (2.36)$$

The correlation length ζ can be related to the Debye screening length κ^{-1} . In salt-free case $\zeta \sim \phi^{-1/2}$ whereas, in high salt concentration case $\zeta \sim \phi^{-3/4}$. The Debye-Hückel theory provides free energy due to coulombs interactions correlations for electrolyte case, which can be given as

$$\frac{F_{DH}}{k_B T} = -\frac{1}{4\pi} \left(\frac{V}{v_1} \right) \left\{ \ln(1 + \kappa l) - \kappa l + \frac{1}{2} \kappa^2 l^2 \right\} \quad (2.37)$$

Furthermore, local polymer concentration can also play an essential role in the free energy of fluctuations. For the scope of this thesis, we only focus on free energy arising from mean-field theory.

2.2.3 Swelling Equilibrium of Gel

Using equation (2.18) to write the total osmotic pressure of the gel, which can be expressed as [39]

$$\frac{\Pi v_1}{k_B T} = \underbrace{-\ln(1 - \phi) - \phi - \chi \phi^2}_{\Pi_{mixing}} + \underbrace{\sqrt{\alpha^2 z_p^2 \phi^2 + 4c_s^2 v_1^2} - 2c_s v_1}_{\Pi_{Donnan}} - \underbrace{\frac{1}{N} \left(\phi_0^{2/3} \phi^{1/3} - \frac{\phi}{2} \right)}_{\Pi_{elasticity}} \quad (2.38)$$

To get the swelling equilibrium, total osmotic pressure goes to zeros ($\frac{\Pi v_1}{k_B T} = 0$). We can see the limiting case where the swollen gel has no salt ($c_s = 0$) by setting the total osmotic pressure to zero, $\frac{\Pi v_1}{k_B T} = 0$, and salt concentration $c_s = 0$ in equation (??)

$$-\ln(1 - \phi) - \phi - \chi \phi^2 + \alpha z_p \phi = \frac{1}{N} \left\{ \phi_0^{2/3} \phi^{1/3} - \frac{\phi}{2} \right\} \quad (2.39)$$

The logarithmic term on the left-hand side of the above equation can be expanded if $\phi \ll 1$, and $\alpha z_p \gg \frac{1}{2N}$. Consequently, we will get

$$\phi^{2/3} = \frac{\phi_0^{2/3}}{\alpha z_p N} \quad (2.40)$$

The swelling ratio of the gel can be expressed as the volume of gel divided by the dry gel volume

$$\frac{V}{v_d} = \frac{1}{\phi} = \frac{(\alpha z_p N)^3 / 2}{\phi_0} \quad (2.41)$$

2.2.4 Deformation of Swollen Gels

Once we have the swollen gel, we can deform the gel by either compression or elongation along the uniaxial direction (z -axis) and other directions (x - and y -axes) to be equivalent [39, 50]. Consider that $\lambda_s = \frac{L_z}{L}$ is the stretching ratio compared to swollen gel and $\lambda_z = \frac{L_z}{L_0}$ is the stretching ratio with respect to the

Gaussian or reference state of the gel. We can write stretching ratio in terms of volume fraction as $\frac{L}{L_0} = (\frac{\phi}{\phi_0})^{1/3}$ [50] and we will get

$$\lambda_z = \frac{L_z}{L_0} = \frac{L_z}{L} \frac{L}{L_0} = \lambda_s \left\{ \frac{\phi_0}{\phi} \right\}^{1/3} \quad (2.42)$$

Here, $\frac{\phi_0}{\phi}$ does not change because of deformation and it stays a constant. We also assume that the gel is incompressible, meaning the volume of the swollen gel does not change because of the deformation

$$\lambda_z \lambda_x \lambda_y = \frac{V}{V_0} = \frac{\phi_0}{\phi} \quad (2.43)$$

Hence,

$$\lambda_x = \lambda_y = \sqrt{\frac{\phi_0}{\lambda_z \phi}} = \frac{1}{\sqrt{\lambda_z}} \left\{ \frac{\phi_0}{\phi} \right\}^{1/3} \quad (2.44)$$

Therefore, the change in free energy due to deformation can be expressed as

$$\Delta F_{elasticity} = \frac{nk_B T}{2} \left\{ \lambda_s^2 \left(\frac{\phi_0}{\phi} \right)^{2/3} + \frac{2}{\lambda_s} \left(\frac{\phi_0}{\phi} \right)^{2/3} - 3 - \ln \left(\frac{\phi_0}{\phi} \right) \right\} \quad (2.45)$$

The normal tensile stress σ_z on the swollen gel is given as

$$\sigma_z = \frac{1}{L^2} \frac{\partial \Delta F_{elasticity}}{\partial L_z} = \frac{1}{L^3} \frac{\partial F_{elasticity}}{\partial \lambda_s} \quad (2.46)$$

This equation can be rewritten as

$$\sigma_z = \frac{nk_B T}{V} \left(\frac{\phi_0}{\phi} \right)^{2/3} \left(\lambda_s - \frac{1}{\lambda_s^2} \right) = \frac{k_B T}{N v_1} \phi_0^{2/3} \phi^{1/3} \left(\lambda_s - \frac{1}{\lambda_s^2} \right) \quad (2.47)$$

We can compute Young's Modulus E from the above equation

$$E = \left(\frac{\partial \sigma_z}{\partial \lambda_s} \right)_{\lambda_s \rightarrow 1} = \frac{3k_B T}{N v_1} \phi_0^{2/3} \phi^{1/3} \quad (2.48)$$

2.2.5 Bulk Modulus of the Salt-Free Swollen Gel

Using equations (2.17 and 2.38), a bulk modulus K equation can be derived for the swollen gel [39]

$$\frac{Kv_1}{k_BT} = \frac{\phi}{1-\phi} - \phi - 2\chi\phi^2 + \sqrt{\alpha^2 z_p^2 \phi^2 + 4c_s^2 v_1^2} - 2c_s^2 v_1 - \frac{1}{3N} \left\{ \phi_0^{2/3} \phi^{1/3} - \frac{3\phi}{2} \right\} \quad (2.49)$$

By considering salt-free limit $c_s = 0$, $\phi \ll 1$, and ignoring higher order terms ϕ^2 , we can simplify above equation

$$\frac{Kv_1}{k_BT} \simeq \left\{ \alpha z_p + \frac{1}{2N} \right\} \phi - \frac{\phi_0^{2/3} \phi^{1/3}}{3N} \quad (2.50)$$

Finally, if $\alpha z_p \gg \frac{1}{2N}$, we will get

$$\frac{Kv_1}{k_BT} \simeq \frac{2\alpha z_p \phi}{3} \quad (2.51)$$

Hence, the mean-field theory predicts that osmotic bulk modulus for no salt case is proportional to the product of volume fraction and degree of ionization αz_p . This result is similar to the shear modulus when the swollen gel undergoes shear stress.

2.3 Poisson-Boltzmann equation

Polyelectrolytes are a class of polymers that can dissociate when they are placed in polar solvents. This leads to the charged polymers, along with mobile counterions. The charged polymers are of great interest in the biochemistry and molecular biology field since most of the proteins and biopolymers, such as DNA, microtubules, etc., exhibit polyelectrolyte behavior [51]. Furthermore, cell membranes possess a charged nature, and electrostatic interactions hold significant importance in understanding interactions and functional and conformational properties of biomolecules.

The charged polymers require an understanding of an exquisite interplay of long-range coulombic interactions and a conformational degree of freedom of polymers [10]. The Poisson-Boltzmann (PB) equation based on the mean-field theory

approximation can be used to study charged systems. For the PB equation to work, we will neglect any quantum mechanical effects, and we use classical mechanics for the theoretical description of polyelectrolytes. Another simplification we need to consider is that solvent is implicit, meaning that the effects of solvent can be simulated as a dielectric continuum with no local dielectric effects of solvent. The cell model can be used to describe the charged macromolecules [8, 9]. It assumes that the charged polymers will have mutual pair interactions that are repulsive since monomeric units carry the same charge. The cell model approximates polyelectrolyte polymers by enclosing them in cylindrical cells and ignores the cylindrical caps effects by assuming that the polymer is infinitely long. The cylindrical cell model helps study the electrostatic interaction between macromolecules and mobile ions (i.e., salt ions and counterions) and the interaction between solvent and charged polymer enclosed in a cylinder [10].

Let's consider linear charge polymers dissolved in a solvent with density n_p and let the Bjerrum length of the solvent is l_B [10]. The charged polymers have a uniform charge density $\lambda = e\tilde{\lambda} > 0$, and they have a radius r_o and length L surrounded by monovalent counterions. Now consider that each polyelectrolyte is enclosed in a cylinder with a radius R and length L such that the density of the polyelectrolyte can be expressed as $n_p = \frac{1}{\pi R^2 L}$. From this equation, we can obtain the radius of the cylindrical cell [10].

The polyelectrolyte polymers will dissociate $N_c = \tilde{\lambda}L$ monovalent counterions in a solution. Let's say the average number of counterions dissociated by all these rods is $\tilde{n}_c = n_p N_c = \frac{\tilde{\lambda}}{\pi R^2}$. It is important to note that the average density of counterions does not depend on the length of the cell. The coordinates of the ion can be described as the density $n(\mathbf{r})$ because of cylindrical symmetry, ions position only depends on radial coordinates.

The Poisson-Boltzmann density functional can be expressed as [52]:

$$F_{PB}[n(\mathbf{r})] = \int_V d^3\mathbf{r} \left(z e n(\mathbf{r}) \left(\frac{\psi(\mathbf{r})}{2} + \psi_f \mathbf{r} \right) + k_B T n(\mathbf{r}) (\ln(n(\mathbf{r}) \lambda_T^3) - 1) \right) \quad (2.52)$$

where $z = -1$ is the valency of counterions and charged monomer unit, $n(\mathbf{r})$ is

ion density, ψ is the electrostatic potential due to mobile ions, ψ_f is the electrostatic potential due to fixed charged density, and $\lambda_T = \frac{h}{\sqrt{2\pi mk_B T}}$ is the de Broglie wavelength. We can find the density $n(\mathbf{r})$ by setting a functional derivative with respect to density $\delta F_{PB}[n]/\delta n$ to zero. This ensures that (i) charge density and electrostatic potential follows the Poisson equation and (ii) conversation of particles in the system. To satisfy first constraint, an additional term $\mu_0(n(\mathbf{r}) - \frac{N}{V})$ is introduced in the integrand of the equation (2.52). Here, μ_0 is the Lagrangian multiplier. The second term can be fulfilled by writing $\psi(\mathbf{r})$ in terms of $n(\mathbf{r})$ [10]. The functional derivative can be expressed as

$$0 = \frac{\delta F[n(\mathbf{r})]}{\delta n} = \mu(\mathbf{r}) = \mu_0 + ze(\psi(\mathbf{r}) + \psi_f(\mathbf{r})) + k_B T \ln(n(\mathbf{r})\lambda_T^3) \quad (2.53)$$

This equation is composed of two simplified terms (i). The electrostatic energy is associated with charge distribution in the presence of its own potential and external potential ψ_f . (ii) The entropy contribution as particles effectively behave as an ideal gas with density $n(\mathbf{r})$.

We can express $\mu(\mathbf{r}) = 0$ as:

$$n(\mathbf{r}) = \lambda_T^{-3} \exp(-\beta(ze\psi_{tot}(\mathbf{r}) + \mu_0)) = n_0 \exp(-\beta ze\psi_{tot}(\mathbf{r})) \quad (2.54)$$

Where $\psi_{tot} = \psi + \psi_f$ showing total electrostatic potential and n_0 and μ_0 are constant due to the particle conservation law. Moreover, n_0 represents a density when the total electrostatic potential $\psi_{tot} = 0$ and equation (2.54) shows that charged particle density is proportional to the Boltzmann factor. Substituting equation (2.54) into Poisson equation $\Delta\psi_{tot}(\mathbf{r}) = -\frac{e}{\epsilon_0\epsilon_r}(zn(\mathbf{r}) + n_f(\mathbf{r}))$ will give Poisson-Boltzmann equation [10]

$$\Delta\psi_{tot}(\mathbf{r}) = -\frac{e}{\epsilon_0\epsilon_r} (zn_0 \exp(-\beta ze\psi_{tot}(\mathbf{r})) + n_f(\mathbf{r})) \quad (2.55)$$

The Poisson-Boltzmann equation is a mean-field theory that works well for understanding charged systems. Nevertheless, it assumes that the dielectric due to solvent is constant throughout the system. In other words, it ignores the medium's local dielectricity due to its charges and polymer heterogeneities, and it ignores all correlations [10].

The Poisson-Boltzmann can be solved in cylindrical coordinates between r_0 and R by assuming that the charged rod is infinitely long using the following differential equation.

$$y''(r) + \frac{y'(r)}{r} = \kappa^2 e^{y(r)} \quad (2.56)$$

Here, $\kappa = \sqrt{4\pi l_B n(R)}$. The solution $y(r)$ is the dimensionless electrostatic potential that can be expressed as $y(r) = \frac{\psi(r)}{\beta e}$. The values of the electric field can give the boundary conditions which satisfy the above differential equation at $r = r_0$ and $r = R$ [10]

$$y'(r_0) = -\frac{2\zeta}{r_0} \text{ and } y'(R) = 0 \quad (2.57)$$

Where $\zeta = \tilde{\lambda} l_B$ is the dimensionless charge parameter, which accounts for the charge density along the Bjerrum length of the rod.

The differential equation (2.56) was first solved independently by Fuoss et al. ([53]) and Alfrey et al. ([54]). The solution is given as

$$y(r) = -2 \ln \left(\frac{r}{R} \sqrt{1 + \gamma^{-2}} \cos \left(\gamma \ln \frac{r}{r_M} \right) \right) \quad (2.58)$$

where $\gamma = \sqrt{\frac{\kappa^2 R^2}{2} - 1}$ is the dimensionless integration constant. Using boundary conditions (2.57), we can get the general solution for γ and r_M [10]

$$\gamma \ln(r_0/r_M) = \arctan\left(\frac{1-\zeta}{\gamma}\right) \quad (2.59)$$

$$\gamma \ln(R/r_M) = \arctan(1/\gamma) \quad (2.60)$$

By subtracting equations (2.59) and (2.60), we can write equation in only γ terms as

$$\gamma \ln(R/r_0) = \arctan(1/\gamma) + \arctan((\zeta - 1)/\gamma) \quad (2.61)$$

For equation (2.61) to give a real solution, it has to satisfy $\zeta > \zeta_{min}$, where ζ_{min} can be expressed as

$$\zeta_{min} = \frac{\ln R/r_0}{1 + \ln \frac{R}{r_0}} \quad (2.62)$$

This solution is essential for studying strongly charged density cases. Let's consider that $P(r)$ denotes the fraction of counterions present between r_0 and r radial distance of the charged rod. By considering $n(r) = n(R)\exp(y(r))$ and substituting it into the equation (2.58, 2.59, and 2.60), we can derive the expression for the function $\phi(r)$, which shows the spatial distribution of counterions

$$\phi(r) = \frac{1}{\lambda} \int_{r_0}^r 2\pi \tilde{r} n(\tilde{r}) d\tilde{r} = 1 - \frac{1}{\zeta} + \frac{\gamma \tan\left(\gamma \ln \frac{r}{r_M}\right)}{\zeta} \quad (2.63)$$

Here, r_M is known as the "Manning radius." If we wanted to find the fraction of condensed counterions within Manning radius r_M , we need to set $r = r_M$, and we will get $P(r_M) = 1 - \frac{1}{\zeta}$ [55, 3]. The PB theory gives valuable insight into the phenomena of Manning condensation, which gives a distance until which counterions are said to condense. This phenomenon can be seen by plotting a log plot of integrated counterions distribution with respect to radial distance, which will give an inflection point that can be considered as Manning distance [9, 6]

2.3.1 Manning Condensation

The counterions distribution surrounding the charged polymers or rod shows an intriguing behavior that can be elucidated by simple consideration. Let's consider a very dilute system with only a single counterion. The radial distribution of this system in the canonical ensemble is given as $\frac{e^{-\beta H(r)}}{\text{Tr}\{e^{-\beta H(r)}\}}$ and Hamiltonian can be expressed as $\beta H(r) = 2\zeta \ln \frac{r}{r_0}$. However, the trace (per unit length) over the coordinate space is [10]

$$\text{Tr}\{e^{-\beta H}\} = \int_{r_0}^{\infty} 2\pi r e^{-2\zeta \ln \frac{r}{r_0}} = 2\pi r_0^2 \int_1^{\infty} x^{1-2\zeta} dx \quad (2.64)$$

If $\zeta < 1$, the integral above will diverge, and normalization of the counterion distribution function cannot be achieved; such rod will not have localized counterions. However, if $\zeta > 1$, counterions get localized around the charged cylindrical rod. The charged rod condenses the fraction of counterions $1 - 1/\zeta$ such that they renormalize its charge parameter to an effective value of 1. In contrast, the remaining ions disperse in bulk solution (or not localized) [3]. This phenomenon is referred to as "Manning Condensation."

2.4 Molecular Dynamics Simulation

We employ Newton's equation of motion to determine the trajectories of all particles present in the system. Consider that our system comprises N particles, and each particle i experiences a conservative force due to interactions with other particles in the surroundings [38]. The force-acting on particle i is following:

$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \frac{d\mathbf{p}_i}{dt} = -\nabla E_{pot}(\mathbf{r}_i) \quad (2.65)$$

where t is time, m_i is the mass of the particle i , $\mathbf{r}_i$ its position, $\mathbf{F}_i$ force on particle i , and $\mathbf{p}_i$ is the momentum of particle i . The kinetic energy of particle i is given as:

$$T_i = \frac{m_i v_i^2}{2} = \frac{p_i^2}{2m_i} \quad (2.66)$$

If we differentiate kinetic energy with respect to the linear momentum of the particle i , we will get

$$\frac{dT_i}{dp_i} = \frac{p_i}{m_i} = v_i = \frac{dr_i}{dt} \quad (2.67)$$

Equations 2.65 and 2.67 are the Hamilton equations and provide the time evolution of the coordinates $\mathbf{r}_i$ and momenta $\mathbf{p}_i$ for each particle in the system [38]. It is important to note that these Hamiltonian equations cannot be solved analytically. Thus, they are needed to be solved numerically.

If we know the positions and the velocities of each particle at time t , we can use a Taylor expansion around a known point $\mathbf{r}(t)$ to find the position $\mathbf{r}(t + \Delta t)$ of the particles at time $t + \Delta t$ as follows:

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \Delta t \frac{d\vec{r}(t)}{dt} + \frac{\Delta t^2}{2!} \frac{d^2\vec{r}(t)}{dt^2} + \dots \quad (2.68)$$

where

$$\frac{d^2\vec{r}(t)}{dt^2} = -\frac{1}{m} \frac{dV(\vec{r}(t))}{dr}$$

and

$$\frac{d\vec{r}(t)}{dt} = \vec{v}$$

Therefore, we can get the updated position of particles as follows:

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \Delta t \vec{v}(t) + \frac{\Delta t^2}{2m} \frac{dV(\vec{r}(t))}{dr} \quad (2.69)$$

Similarly, we can do a Taylor expansion for velocities around known points $\vec{v}(t)$ and $\frac{d\vec{v}(t)}{dt}$, and we will get the following equations, respectively:

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \Delta t \frac{d\vec{v}(t)}{dt} + \frac{\Delta t^2}{2!} \frac{d^2\vec{v}(t)}{dt^2} + \dots \quad (2.70)$$

$$\frac{d\vec{v}(t + \Delta t)}{dt} = \frac{d\vec{v}(t)}{dt} + \Delta t \frac{d^2\vec{v}(t)}{dt^2} + \dots \quad (2.71)$$

Equation (2.71) can be rearranged as following to get the value for $\frac{\Delta t^2}{2!} \frac{d^2\vec{v}(t)}{dt^2}$:

$$\Delta t \frac{d^2\vec{v}(t)}{dt^2} = \frac{\Delta t}{2} \left(\frac{d\vec{v}(t + \Delta t)}{dt} - \frac{d\vec{v}(t)}{dt} \right) \quad (2.72)$$

By plugging in the equation (2.72) into the equation (2.70), we will get the following:

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \Delta t \frac{d\vec{v}(t)}{dt} + \frac{\Delta t}{2} \left(\frac{d\vec{v}(t + \Delta t)}{dt} - \frac{d\vec{v}(t)}{dt} \right) \quad (2.73)$$

where

$$\frac{d\vec{v}(t + \Delta t)}{dt} = -\frac{1}{m} \frac{dV(\vec{r}(t + \Delta t))}{dr}$$

and

$$\frac{d\vec{v}(t)}{dt} = -\frac{1}{m} \frac{dV(\vec{r}(t))}{dr}$$

Hence, we will get the updated velocities using the following equation:

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \Delta t \frac{d\vec{v}(t)}{dt} - \frac{\Delta t}{2m} \left(\frac{dV(\vec{r}(t + \Delta t))}{dr} + \frac{dV(\vec{r}(t))}{dr} \right) \quad (2.74)$$

We should provide each particle's initial positions and velocities (i.e., initial conditions) at the start of the simulations. Moreover, we should have a conservative potential function to compute the force acting on each particle.

Initial coordinates can be taken from the experiments, or we can guess from suitable theoretical models. At the same time, initial velocities can be taken from Maxwell-Boltzmann or Gaussian distribution at the desired temperature. The gradient of the potential function can be computed using the OPLS-AA force field.

2.4.1 OPLS-AA force field

The interaction potential between the atoms dictates the behavior of the system. A force field is a simple equation that relates the potential energies of the system with the internal coordinates of the particles present in the system. Most force

fields can be divided into bonded and non-bonded interactions:

$$V_{total} = \underbrace{\sum_{i=1}^{N_{bonds}} V_{bonds} + \sum_{j=1}^{N_{angles}} V_{angles} + \sum_{k=1}^{N_{dihedrals}} V_{dihedrals}}_{Bonded} + \underbrace{\sum_{l=1}^{N_{non-bonded}} V_{non-bonded}}_{Non-bonded} \quad (2.75)$$

While simulating the polymeric system, it is vital to consider that polymer atoms are bonded. In all-atom simulations, we consider the detailed structure of the polymeric chains, which can have interactions between two atoms (bonded interactions), three atoms (angle interactions), and four atoms (dihedral interactions and improper interactions). If more than four atoms separate interacting particles, they are considered non-bonded interactions. In the OPLS-AA force field, bonded interactions are given as follows:

$$V_{bonded} = \sum_{i=1}^{N_{bonds}} \frac{k_b(r - r_o)^2}{2} + \sum_{j=1}^{N_{angles}} \frac{k_\theta(\theta - \theta_o)^2}{2} + \sum_{k=1}^{N_{dihedrals}} \sum_i^{M=4} \frac{K_i(1 + (-1)^i \cos(i\phi))}{2} \quad (2.76)$$

Where r_o is the equilibrium distance between two atoms, θ_o is the equilibrium angle between three atoms, and ϕ is the angle between the two planes formed by atoms ijk and jkl (Figure 2.3 a). Furthermore, k_b , k_θ , and K_i define the bond, angle, and dihedral, respectively, stiffness coefficients. The non-bonded interactions are represented by Lennard-Jones (LJ) potential and Coulombic interactions. The LJ potential combines two types of interactions (i) repulsive due to the Pauli-exclusion principle and (ii) attractive interactions due to momentary dipole interactions, also known as van Der Waals interactions (Figure 2.3 b). The non-bonded interactions are calculated using the following equation:

$$V_{non-bonded} = \sum_{i>j} \underbrace{\frac{q_i q_j}{4\pi\epsilon_o r_{ij}}}_{Coulombs\ interaction} + \underbrace{4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right)}_{LJ-potential} \quad (2.77)$$

where q_i and q_j are charge on particle i and j that are r_{ij} distance apart and ϵ_o is the electric permittivity in vacuum. ϵ_{ij} and σ_{ij} for pair particles are computed using geometric and arithmetic rules, respectively, $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and $\sigma_{ij} = (\sigma_i +$

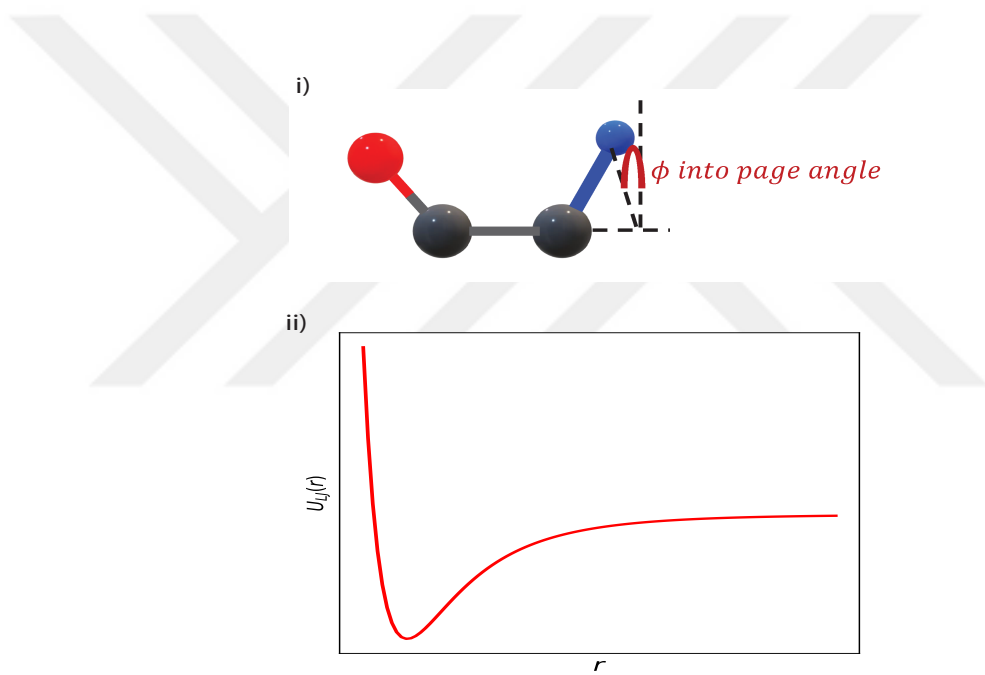


Figure 2.3: i) Spheres represent the atoms and dihedral angle ϕ is achieved into or out of plane twisting around the axis of center atoms. ii) represents the Lennard-Jones potential $U_{LJ}(r)$ between pair atoms with respect to the distance r .

$\sigma_j)/2$ For electrostatic interaction, the cut-off distance, $r_c = 1.5$ nm, is used. In other words, if the interacting particles are within r_c , their electrostatic interactions are computed using coulombic interaction part in equation 2.77. Otherwise, they are computed using a PPPM solver, which solves electrostatic interaction in Fourier space with the precise 10^{-5} .

2.4.2 Nose-Hoover algorithm

Depending on the problem of interest, different materials can be studied under different conditions. Therefore, our system needs to maintain these conditions to understand the system's behavior under given conditions. This thesis used the Nose-Hoover algorithm to control and maintain the temperature and pressure. This thermostating and barostatting method introduces dynamic variables that, coupled with molecular dynamics equations for velocities and dimensions of the simulation box, respectively, regulate and control the temperature and pressure of the system.

$$\dot{\mathbf{r}}_i = \frac{\dot{\mathbf{p}}_i}{m_i} + \frac{p_\epsilon \mathbf{r}_i}{W} \quad (2.78)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \underbrace{\frac{p_\epsilon \mathbf{r}_i}{W}}_{\text{pressure control}} - \underbrace{\frac{p_\zeta}{Q} \mathbf{p}_i}_{\text{Temperature control}} \quad (2.79)$$

$$\dot{V} = \frac{dV p_\epsilon}{W} \quad (2.80)$$

$$\dot{p}_\epsilon = dV(P_{int} - P_{ext}) - \frac{p_\zeta p_\epsilon}{Q} \quad (2.81)$$

$$\dot{\zeta} = \frac{p_\zeta}{Q} \quad (2.82)$$

$$\dot{p}_\zeta = \sum_{i=1}^N \frac{\dot{\mathbf{p}}_i^2}{m_i} + \frac{p_\epsilon^2}{W} - (N_f + 1)kT \quad (2.83)$$

Where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the i th particle's position and momentum vector, respectively. V and p_ϵ represent the volume and barostat momentum. ζ and p_ζ shows position and momentum due to thermostat. $\mathbf{F}_i$ is the conservative force depending on the particle positions. P_{ext} and P_{int} are the external and internal pressure acting on the box, respectively. The pressure is controlled many by changing the dimensions of the simulation box. Q and W are relaxation rates for thermostats and barostats. If the values of Q and W are large, we will have weak coupling, which will take a long time to get the target temperature and pressure. Similarly, if the values of Q and W are small, we will have a strong coupling, and target temperature and pressure can be achieved rather faster. However, our system's temperature and pressure values will fluctuate a lot. Therefore, we must choose relaxation rate values such that the simulation should not take too long to relax with minimum fluctuation from the target temperature and pressure.

2.4.3 Monte Carlo Simulations

The Monte Carlo simulations allow us to calculate the ensemble average of the system. It is important to note that Monte Carlo simulations do not produce a trajectory or time evolution of the system like molecular dynamics simulations, which produce a system's trajectory by solving classical Newton's equations. As we know in statistical mechanics, all information of the system is contained in the partition function, and we can represent the probability of the system P_i in state i as

$$P_i = \frac{\sum_i \frac{1}{h^{3N} N!} \exp(-\beta H)}{Q} \quad (2.84)$$

Where Q is the partition function. The ensemble average of C can be calculated by summing the product C_i and probability P_i in the state i , which can be written as follows

$$\langle C \rangle = \sum_i C_i P_i \simeq \frac{1}{N} \sum_s C_s \quad (2.85)$$

The second sum is over all the samples acquired from the collected data.

In the Metropolis algorithm, detailed balance is a fundamental principle that ensures the proper sampling of the equilibrium distribution. It establishes an equilibrium condition where the probability of transitioning $P(i \rightarrow j)$ from one state i to another j is balanced by the probability of transitioning in the opposite direction.

According to the principle of detailed balance, the ratio of these transition probabilities should be equal to the ratio of the equilibrium probabilities of the two states:

$$\frac{P(i \rightarrow j)}{P(j \rightarrow i)} = \frac{P_{eq}(i)}{P_{eq}(j)} \quad (2.86)$$

Here, $P_{eq}(i)$ represents the equilibrium probability of being in state i , and $P_{eq}(j)$ represents the equilibrium probability of being in state j .

A suitable acceptance criterion is employed to achieve detailed balance in the Metropolis algorithm. It is based on the Metropolis-Hastings rule, which states that a proposed transition from state i to state j is accepted with some probability, denoted as $acc_{i \rightarrow j}$. This acceptance probability is given by:

$$acc_{i \rightarrow j} = \min \left\{ 1, \frac{P_{eq}(j)}{P_{eq}(i)} \right\} \quad (2.87)$$

This criterion ensures that if the equilibrium probability of state j is greater than that of state i , the transition from i to j is always accepted. However, if the equilibrium probability of state j is lower, the transition is accepted with a probability proportional to the ratio of the equilibrium probabilities.

By utilizing this acceptance criterion, the Metropolis algorithm generates a Markov chain of states that eventually converges to the equilibrium distribution. It allows for efficient sampling of the equilibrium ensemble while maintaining the detailed balance condition, which is crucial for obtaining reliable statistical results.

2.4.3.1 Widom's Method

For the swelling of the polyelectrolyte hydrogel, we need to immerse the hydrogel into the reservoir (large water body). Water molecules will get absorbed by hydrogel until the chemical potential of the solvent outside is the same as that of the solvent inside the gel $\mu_{in}^{solvent} = \mu_{out}^{solvent}$. Moreover, the osmotic pressure of the gel is equal to the external pressure due to the water reservoir $\Pi_{total} = P_{reservoir}$ [49].

To compute the chemical potential of the SPC/E solvent $\mu_{out}^{solvent}$, we used Widom's particle insertion method. We modeled three pure SPC/E NVT simulation systems with average density $\rho_{SPC/E} \sim 1.0g/cm^3$ to compute the reservoir's average chemical potential and external pressure. The chemical potential of solvent is defined as $\mu_{sol} = \left(\frac{\partial F}{\partial N_{sol}} \right)_{NVT}$, where F is the Helmholtz free energy. The chemical potential is the sum of the ideal and excessive chemical potential, $\mu = \mu^{id} + \mu^{ex}$. The ideal chemical potential can be computed analytically. However, we will compute the system's potential energy with $N + 1$ particle by adding one particle at a random position into the N particle system. The change in potential can be represented as $\Delta U \equiv U(\mathbf{s}^{N+1}) - U(\mathbf{s}^N)$ and we can write the equation for excessive chemical potential [38]

$$\mu_{ex} = -k_B T \ln \int d\mathbf{s}_{N+1} \langle \exp(-\beta \Delta U) \rangle_N \quad (2.88)$$

where $\langle \dots \rangle$ represents the canonical ensemble averaging. We simulated 4000 SPC/E (pure water) using a canonical ensemble keeping the system's temperature constant at 300 K and density $\rho \simeq 1g/cm^3$. This system's chemical potential μ can be considered as the chemical potential of the reservoir, and pressure P can be regarded as the pressure of the reservoir [49]. Figure (2.4a) represents the excess chemical potential of the pure SPC/E system with respect to time, and the mean excess chemical potential is $\langle \mu_{ex} \rangle = 2.0$ kcal/mol (blue line in Figure (2.4a)).

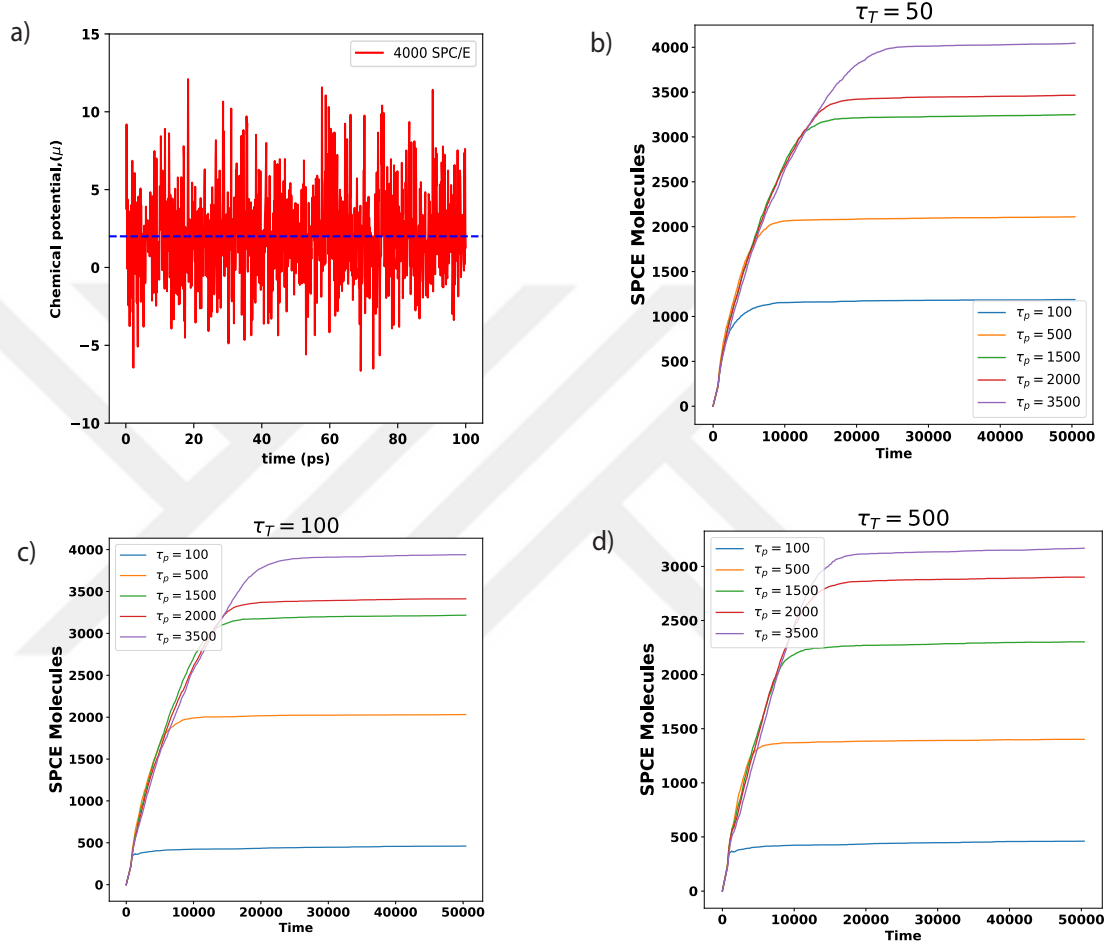


Figure 2.4: a) The pure SPC/E water is simulated. Excess chemical potential is plotted with respect to time, the excess chemical potential is computed using Widom's particle insertion method (red), and the dashed blue line represents the average excess chemical potential $\mu_{ex} = 2$ kcal/mol. b-d) The water insertion into the simulation box using GCMC is shown at different temperatures and pressure relaxation rates τ_T and τ_P ii) $\tau_T = 50$ and τ_P varying from 100 to 3500, we see a different number of water molecules being inserted at the equilibrium with slow relaxation rate (i.e., $\tau_P = 3500$) takes more water molecules as compared to faster relaxation ($\tau_P = 100$)

2.4.3.2 Grand Canonical Monte Carlo (GCMC) Method

The Grand Canonical Monte Carlo (GCMC) is a statistical approach in which the system can exchange particles and energy with a reservoir. The particle's insertion into or deletion from the system is determined by the chemical potential μ . Therefore, the number of particles in the system is not fixed, but rather they can fluctuate. The particle is inserted into the system at the randomly selected position with some acceptance probability P_{insert} , which is computed as

$$P_{insert} = \min(1, \exp(-\beta(\Delta U + \mu) \frac{\omega_{insert}}{\omega_{delete}})) \quad (2.89)$$

Where ΔU is the change in the system's potential energy when the particle is inserted or deleted, μ is the chemical potential of the reservoir, ω_{insert} and ω_{delete} is the configurational bias for particle insertion or deletion from the system. Similarly, particles are deleted from the system with a certain probability that can be measured as

$$P_{delete} = \min(1, \exp(-\beta(\Delta U - \mu) \frac{\omega_{delete}}{\omega_{insert}})) \quad (2.90)$$

Figure (2.4 (b-d)) shows the water molecules being inserted into the hydrogel at a constant chemical potential and pressure. As discussed earlier in the Nose-Hover algorithm section, pressure and temperature are relaxed with some relation rate determined by the damping constant τ_p and τ_T . In Figure (2.4 (b-d)), we used different relation rates for temperature and pressure. When the τ_P is large, the hydrogel system takes longer to relax the system's dimensions to reach equilibrium. We will have a larger volume to insert water molecules, and we will see more particles being inserted into the system than the smaller τ_P values, which relax the system's dimensions, and a lower number of water molecules are inserted. These results show our attempts to get the equilibrium state in which hydrogel contains a constant but fluctuating number of water molecules and the system is in equilibrium with the particle reservoir at fixed temperature and external constant reservoir pressure. Unfortunately, we couldn't get this equilibrium state because different pressure damping constant τ_P values leads to a different number of water molecules.

2.5 Analysis

In this thesis, we used mainly two analysis methods for studying the behavior of condensation of counterions. In method one, i.e., microscopic perspective, we look for the counterions within the vicinity of the oxygen atoms in the carboxylic group since most of the negative charge for poly (acrylic) acid (PAA) is found there. Method two, i.e., macroscopic perspective, looks for the overall distribution of counterions around the PAA polyelectrolyte polymer as considered in a cell model. These two methods will allow us to comprehensively study the condensation of counterion as the charged polymer and polyelectrolyte hydrogel are deformed.

2.5.1 Microscopic Perspective

We use this method to look for counterions within the vicinity of the oxygen atoms of the PAA polymer due to attractive electrostatic potential. We also wanted to measure how the fraction of condensed counterion changes with the uniaxial deformation. We measured this by computing the distance between oxygen atoms in PAA and counterion. If this distance $r \simeq r^{Na^+} + r^{O^-} \simeq 0.25$ nm, the counterion is said to be condensed and said to be it is literal in contact with the oxygen atom of PAA polymer. Since it is possible that oxygen atoms in the monomer of the PAA can get close to each other, meaning $r \leq 0.25$ nm, we ensured that only one counterion could be adsorbed to one monomer only. This also allows us to provide no overcounting of the counterions.

2.5.2 Macroscopic Perspective

We will deform the periodic PAA polymer along the z direction. We consider the PAA carbon backbone as an axis for the cylinder to calculate the counterion distribution using a cell model. The average value where the axis of the cylinder lies can be measured by calculating the center of mass of all carbon backbone

atoms of the PAA polymer as follows [6]

$$\vec{r}_{cylinder} = (x_{cylinder}, y_{cylinder}) = \frac{\left\{ \sum_j^{N_C} x_{C,j}, \sum_j^{N_C} y_{C,j} \right\}}{N_C} \quad (2.91)$$

Where $N_C = 50$ represents fifty carbon atoms in the PAA backbone, with each monomer containing two backbone carbon atoms. Each monomer dissociates one hydrogen ion into the water. Therefore, we added 25 Na^+ counterion to keep the system electro-neutral. The average counterion distribution around the PAA carbon backbone can be computed as follows [6]

$$\rho_{Na^+}(r) = \frac{\sum_{t=0}^T \sum_k^{N_{Na^+}} \delta(|\vec{r}_{cylinder} - \vec{r}_{Na_k^+}|)}{T} \quad (2.92)$$

Here, $|\vec{r}_{cylinder} - \vec{r}_{Na_k^+}|$ shows the distance between the PAA carbon backbone and the sodium counterion, and it summed up over all of the counterions. As the radial distance r from the carbon backbone increases, we can count the number of counterions that fall between the cylindrical value of r and $r + dr$ and form a distribution function with respect to the r . We can define a bulk density of species i as $\rho_i = \frac{N_i}{V}$, where V is the volume of the simulation box. We use the following formula to compute the cylindrical radial distribution for counterions and water molecules:

$$n_i(r) = \frac{\rho_{Na^+}(r)}{2\pi r dr L_z \rho_i} \quad (2.93)$$

The denominator of equation (2.93) represents the volume of the cylindrical shells around the polymeric chains extended along the z-axis. The dr is the histogram bin size, and r is the midpoint of these bins.

Chapter 3

Simulations, Results, and Discussion

3.1 Methods

3.1.1 Hydrogel model

A defect-free PAA hydrogel network with a cubic topology is employed as a model system in all molecular dynamics simulations [56]. The cubic topology has been used previously in well-documented studies [57, 58, 59] and offers the advantage of calculating the ionic density around the PAA polymer chains aligned in the $\hat{x}$, $\hat{y}$, and $\hat{z}$ directions. The PAA polymer chains are cross-linked by bonding each chain's end to a charge-neutral crosslinker bead to obtain a hydrogel structure with no free dangling ends (see Figure 3.1a). The polymer chains are flexible, and the network nodes are free to move (not fixed at the lattice positions), which accounts for any fluctuations. The number of acrylic acid (AA) monomers between two crosslinkers is $n = 10$. The cubic network structure is periodic and comprises 240 AA monomer units and eight crosslinkers. The periodic structure is obtained by bonding each chain to its image in the neighboring periodic box

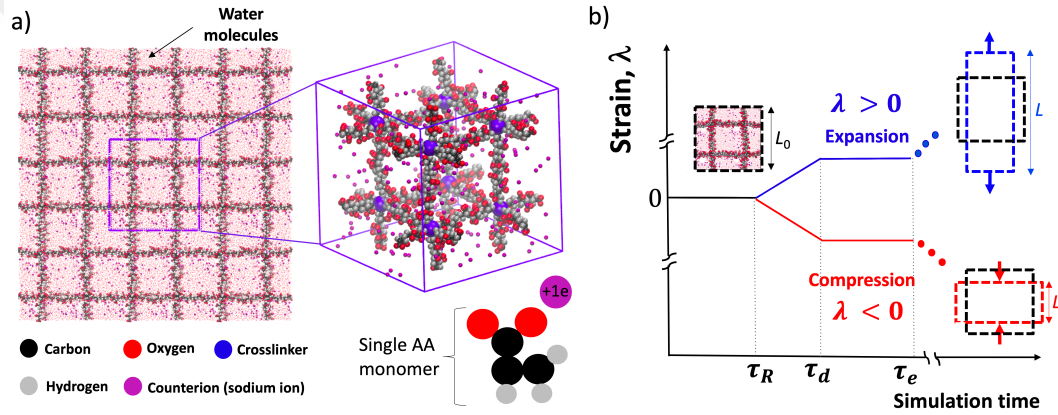


Figure 3.1: The molecular model of the polyacrylic (PAA) hydrogel and schematics of the deformation simulations. a) The representative simulation snapshot of the unit hydrogel cell with cubic topology and its surrounding periodic images. In the close-up 3d view of the simulation box, the water molecules are not shown for clarity, and crosslinker beads are drawn larger than they are in the simulations (see the text for details). b) The schematics of quasi-static deformation simulations. The hydrogel is either compressed or stretched with discrete steps to reach a prescribed strain $\lambda \equiv (L_0 - L)/L_0$. The hydrogel is deformed within a time period of τ_d . Then, the height of the simulation box L is kept constant for a time period of τ_e before considering the simulation data for analysis at each strain value.

(Figure 3.1a). For this study, the crosslinker beads are modeled as charge-neutral dummy atoms that can bond to six chain ends with a molecular mass equivalent to that of a carbon atom [56]. A single AA monomer consists of a single carboxylic group and can become negatively charged by releasing its H^+ counterion when the polymer is dissolved in water (see Figure 3.1a). In order to model counterions, initially, 240 Na^+ ions are added in the simulation box at random positions to fulfill the electroneutrality condition throughout the box. The total number of atoms throughout simulations is constant (i.e., canonical ensemble) [56]. Note that the dissociation degree of the PAA chain in water depends on the pK value of its monomers and on the solution properties such as pH and salinity since it is a weak polyelectrolyte [60, 61, 32, 62]. In this study, we are using only water as the solvent. Therefore, we assume that the pH is seven during all the simulations and PAA chains are fully ionized at $\text{pK} \approx 4.26$ (i.e., $\text{pH} - \text{pK} \approx 3$) [63], and we ignore the variations in pK values [17].

3.1.2 Swelling hydrogels

The swelling capability of a polymer network is described by the swelling ratio, which is the weight ratio of dry (i.e., unswollen) and swollen states. After assuming an affine deformation, a microscopic swelling ratio can be defined as [50]

$$\phi \equiv V/V_0 \approx (R/R_0)^3 \quad (3.1)$$

where V and V_0 are the volumes of swollen and unswollen (i.e., reference) states, R is the average end-to-end size of the chains between two crosslinkers in the swollen hydrogel, and R_0 is the end-to-end distance in the reference state. Our aim is to construct a physical, highly-swollen hydrogel structure in a salt-free solution. For the reference state, R_0 obeys random-walk statistics in melt conditions and is $R_0 \approx b(N)^{1/2}$ [50]. For a swollen hydrogel of flexible PE chains, we may write a scaling relationship for the end-to-end distance as $R \approx bN$ [7]. Thus, Eq. 3.1 becomes $\phi \approx N^{3/2}$. After assuming a Kuhn segment number of $N \approx 5$ for our 10-mer PAA (i.e., roughly 2 AA units are equivalent to one Kuhn monomer [64]), a swelling ratio of around $\phi \approx 10$ (i.e., 1000% swelling) is predicted [56]. To

obtain such a highly swollen hydrogel, we dissolve the PAA hydrogel with 8000 water molecules without encountering any numerical issues. This setup leads to a hydrogel volume $V = 62 \times 62 \times 62 \text{ nm}^3$ in the swollen state. Independently, we run the simulation with a dry (charge-neutral) gel and obtain a reference volume of $V_0 = 29 \times 29 \times 29 \text{ nm}^3$ and obtain a swelling ratio of $\phi = V/V_0 \approx 9$, which is consistent with our scaling prediction and provides a highly swollen hydrogel network [56].

In addition to our highly-swollen hydrogel system, by changing the number of water molecules in the simulation box and equilibrating the hydrogel under $T = 300 \text{ K}$ at an isotropic pressure of $P = 1 \text{ atm}$, we obtain toy models with three additional swelling ratios Figure (3.2). Specifically, we use 2000, 4000, and 6000 water molecules to obtain $\phi \approx 300, 500, 700\%$, respectively. The SPC/E water model is used in all simulations for explicit solvent [65, 66].

3.1.2.1 MD parameters

In simulations, all bonded interactions are taken care of via the OPLS-AA force field, which is a commonly employed force field to study polymeric systems at the atomic resolution, including PAA chains [67, 68, 69]. All bonded and non-bonded interactions are calculated by using the tabulated pair-wise interaction coefficients [70, 69]. Specifically, the short-range Coulomb interactions between two atoms with charges q_i and q_j separated by a distance r_{ij} are calculated via

$$U_C(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon r_{ij}} \quad (3.2)$$

Where ϵ_0 is the vacuum permittivity. Eq. 3.2 applies only if two charges are within a cut-off distance of $r_C = 1.5 \text{ nm}$. Beyond the cut-off distance, a PPPM Ewald solver with an accuracy of 10^{-5} is used to calculate the long-range electrostatics [71, 72].

Initially, the solvated hydrogel system, including chain monomers, ions, and water molecules, is treated by the steepest descent minimization to remove the nonphysical contacts between the atoms. After minimization, a $\tau_R \approx 60\text{--ns}$ long

canonical-ensemble simulation is performed to relax the hydrogel structure with a timestep of 2 fs at $T = 300$ K and $P = P_z \approx P_x \approx P_y \approx 1.0$ atm Figure (3.2). The Nose-Hover algorithm is used to maintain the temperature and pressure. The Zimm relaxation time of a chain segment composed of N Kuhn segments in good solvent could be approximated as $\tau_Z \approx N^{3/2}\tau_0 \approx 10$ ns, where the self-diffusion time of a Kuhn monomer to travel a distance equivalent to its own size is taken as the upper limit for the monomeric relaxation time, $\tau_0 \approx k_B T / 6\pi\eta b \approx 1$ ns. In this calculation, we take the Kuhn size of the PAA chain $b \approx 0.6$ nm [64] and $\eta = 10^{-3}$ Pas. Thus, our relaxation simulations are sufficiently long to avoid any effect due to initial chain configurations. The relaxed hydrogel configuration is used for uni-axial stretching and compression simulations.

The deformation is applied in a discrete and quasi-static fashion (Figure 3.1b). The simulation box is deformed in the $\hat{z}$ direction within a time period of $\tau_d = 3$ ns by an amount of $\delta L = 0.15$ nm and $\delta L = 0.175$ nm for compression and expansion, respectively under a constant-volume ensemble while maintaining the temperature at $T = 300$ K with a timestep of 1 fs. Once the box height is reached the prescribed value L to obtain the prescribed strain, $\lambda = (L - L_0)/L_0 \equiv \Delta L/L_0$, the pressure control is switched on; the pressure in the unconstrained $\hat{x}$ and $\hat{y}$ directions are $P_x \approx P_y \approx 1.0$ atm while the pressure along the $\hat{z}$ -axis is determined by the mechanical equilibrium Figure (3.2). The simulation in each deformation ratio is run for a time period of minimum $\tau_e \approx 40$ ns or more with a timestep of 2 fs. For the data analyses, only the last 25 ns of these simulations are considered.

3.1.3 Calculation of counterion condensation under deformation

The amount of condensed counterions is calculated by analyzing the trajectories of the individual Na^+ counterions around each constituting chain of the hydrogel. In order to calculate the population of microscopically condensed counterions, we define the condensation with respect to the localization of a counterion to an oppositely charged backbone (i.e., oxygen) atom [73]. If the distance between the

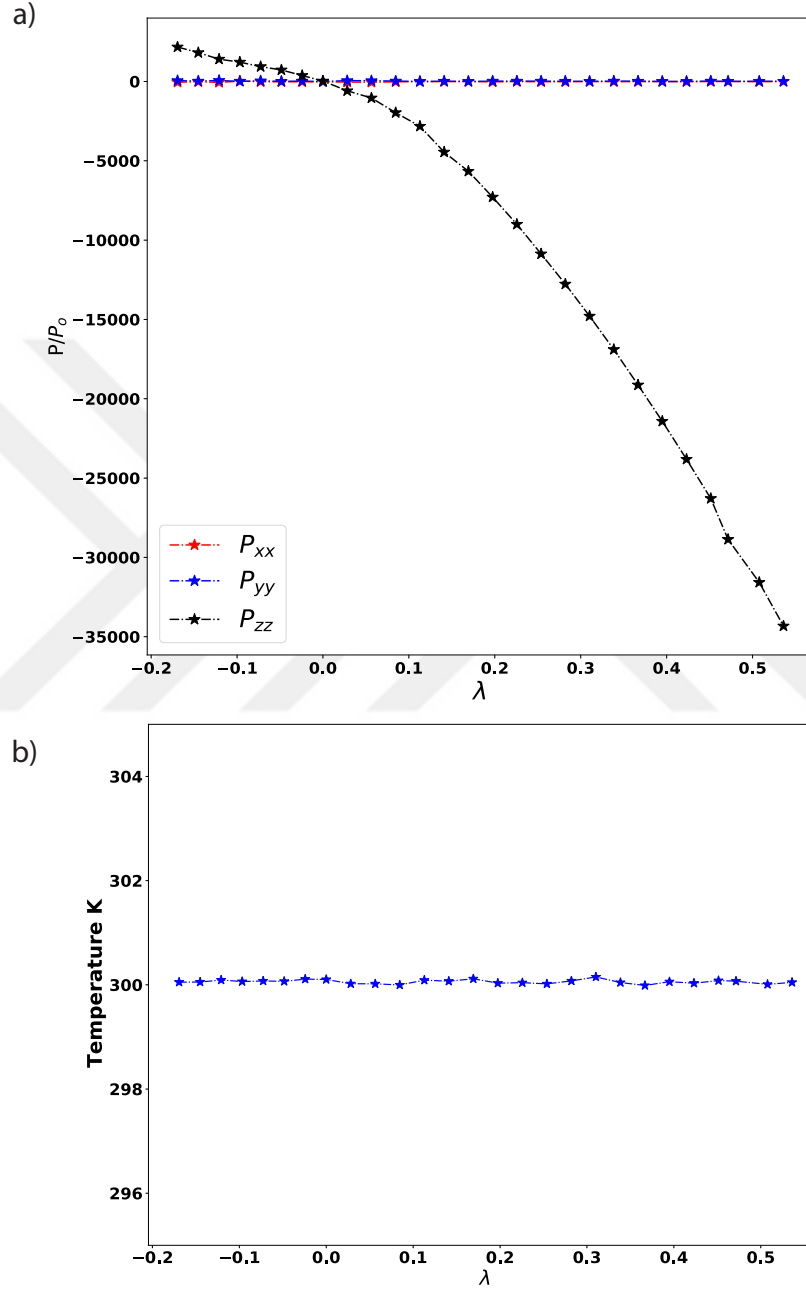


Figure 3.2: Pressure and temperature during the deformation are shown. a) pressure along $\hat{x}$ and pressure along $\hat{y}$ remains at 1 atm throughout all the deformation steps. Pressure along $\hat{z}$ changes as the hydrogel is compressed and elongated. The pressure along $\hat{z}$ is $P \geq 1$ atm and $P \leq 1$ atm for compression and elongation, respectively. b) Temperature of the system is maintained throughout the deformation at $T = 300$ K.

backbone charge and the counterion $d \leq 0.25$ nm, then the counterion is considered to be condensed (see Figure 3.4a). The threshold distance d corresponds to a steric contact between the oxygen atom and the counterion. We also calculate the distribution of the counterions around the individual polymer chains in the cylindrical coordinates [9, 8]. The main axis of the cylindrical coordinate system for each chain is determined by the positions of the terminal crosslinker beads. The number of counterions $n(\rho)$ within any radius, ρ , is calculated, and the distribution is integrated to obtain the cumulative number of condensed counterions via [61]

$$Q(\rho) = \int_{\rho_0}^{\rho} n(\rho') d\rho', \quad (3.3)$$

Where $\rho_0 = 0.15$ nm is taken as the effective radius of a strongly stretched PAA chain. No counterion is counted twice such that one counterion can condense only on either around a single chain or an oxygen atom of the AA monomer. The distributions are normalized by the total number of counterions in order to calculate percentiles. Unless otherwise noted, all data presented in this work are averaged over time, and the chains are aligned in the same direction.

3.2 Results and discussion

3.2.1 Condensation of counterions under deformation

In MD simulations, we focus on the quasi-equilibrium deformation of a periodic PAA hydrogel network with cubic topology (see Figure 3.1a). The hydrogel is applied either a uniaxial compression or stretching in the $\hat{z}$ -direction by varying the strain, λ , in discrete steps (see Figure 3.1b and Methods section). At each deformation ratio, the concentration of condensed counterions around the hydrogel chains, the chain conformations, pairwise-interaction energies, and pressure components are monitored to ensure a steady-state behavior Figure (3.3). To distinguish condensed and free counterions, a counterion is counted as condensed if and only if the distance between the center of mass of the counterion and the nearest backbone oxygen is $d \leq 0.25$ nm (see Figure 3.4a). This cut-off distance

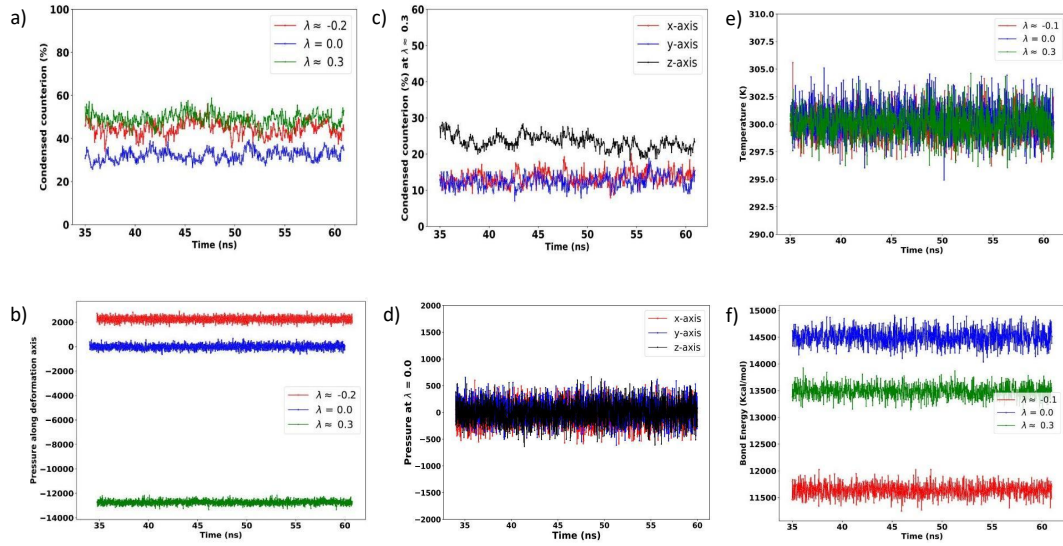


Figure 3.3: a) Total condensation of counterions for three different deformation ratios, λ , b) the pressure along the deformation $\hat{z}$ -direction for various λ cases are shown, c) the amount of condensed counterion around the chains aligned in all three directions at $\lambda \simeq 0.3$, d) the pressure at $\lambda = 0.0$. for three different orthogonal directions are shown e) Temperature is maintained at $T = 300$ K, f) bonded interactions as a function of simulation time

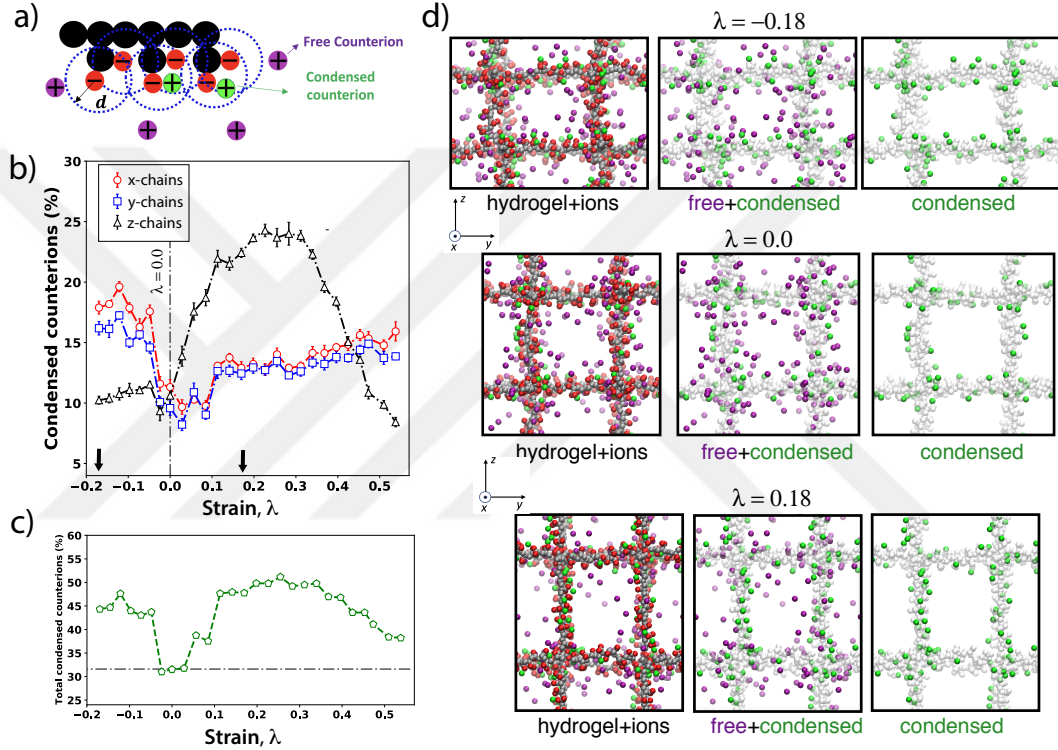


Figure 3.4: Vertical compression and stretching alter the counterion condensation anisotropically. a) Schematics of the definition of condensed and free ions. b) The percentage of condensed counterions around the chains aligned in $\hat{x}$, $\hat{y}$, and $\hat{z}$ directions. The vertical dashed line indicates the deformation-free case (i.e., $\lambda = 0$). The data symbols are joined to guide the eye. The error bars are not shown if they are smaller than the symbol size. c) The total percentage of condensed counterions. d) The representative snapshots showing the conformation of the hydrogel unit cell for two deformation cases indicated in (b) by arrows along with the $\lambda = 0$ case. The right panels show the snapshots highlighting the Na⁺ ions condensed around the chains aligned in the $\hat{z}$ direction. The condensed ions are shown in green only if their distance to a backbone oxygen atom of the PAA chain is $d \leq 0.25$ nm.

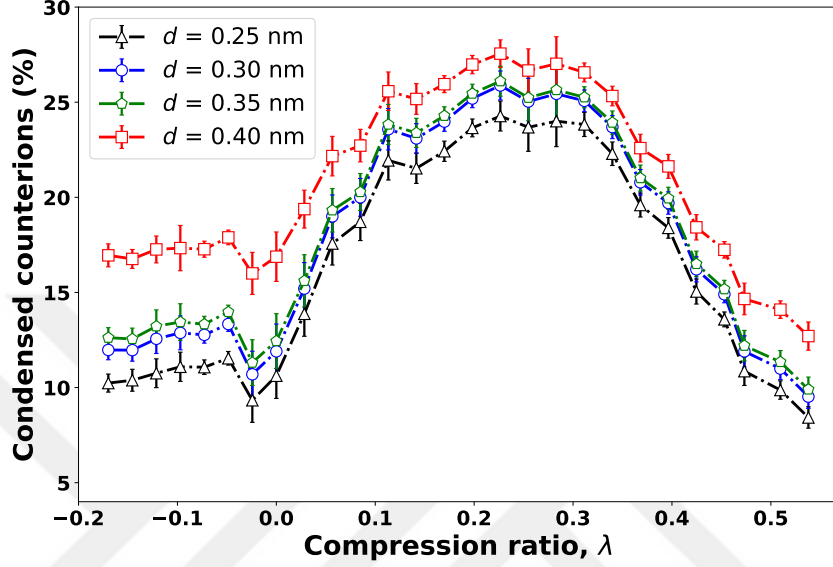


Figure 3.5: This figure represents that we will see a similar pattern of condensation of counterion if different cut-off d are chosen with smaller increases in condensation percentage as d values increase.

is slightly smaller than the distance between two backbone charges, $\ell_0 = 0.32$ nm.

In Figure 3.4b, the percentage of condensed counterions in $\hat{x}$, $\hat{y}$, and $\hat{z}$ directions are shown as a function of the deformation ratio λ . At $\lambda = 0$, the hydrogel is undeformed, and the ionic condensation levels around the chains aligned in all three directions are equivalent to each other within the error bars. The total fraction of condensed ions calculated by considering all chains is $f \approx 0.3 \pm 0.02$. Note that individual counterions near the chains change dynamically, but their average number exhibits a steady-state behavior Figure (3.3). The condensation value for f is lower than the values estimated via the Manning condensation theory, which is $f_M = 1 - \ell_0/\ell_B = 1 - 1/\xi \approx 0.55 > f$ after assuming a Bjerrum length $\ell_B = e^2/\epsilon_0\epsilon k_B T \approx 0.7$ nm for water and a thermal-energy value of $k_B T \approx 4$ pN $\times$ nm at room temperature. We attribute this difference to our choice of the condensation cut-off, d , since this value can alter the numerical value of f [73]. Nevertheless, as we will discuss further in the next sections, our main conclusion

is not affected by the methodology of counting the condensed counterions Figure (3.5).

If the hydrogel is stretched in the $\hat{z}$ -direction (i.e., $\lambda > 0$), the number of condensed counterions around the chains aligned in the $\hat{z}$ -direction increases more than 2-fold at $\lambda \approx 0.2$ (see black triangles in Figure 3.4b). If the stretching is further increased towards $\lambda = 0.5$, the condensation in the $\hat{z}$ direction decreases gradually from its maximum value and becomes slightly lower than the values at $\lambda = 0$ (see Figures 3.4b,d). In the lateral (i.e., $\hat{x}$ and $\hat{y}$) directions, the condensation levels also increase roughly 50% in each direction at the maximum stretching (see circles and squares in Figure 3.4b). The increase in the condensation levels in the lateral directions is weaker and monotonic as compared to the condensation profile in the $\hat{z}$ direction. Note that as the hydrogel is stretched in the $\hat{z}$ -direction, the chains in the $\hat{x}$ and $\hat{y}$ directions are slightly collapsed to preserve the total volume of the hydrogel. As a result, even at the maximum stretching (i.e., $\lambda = 0.5$), the gel volume increases only 2% Figure (3.6).

If the hydrogel is compressed in the $\hat{z}$ -direction (i.e., $\lambda < 0$), the condensation around the chains aligned in the $\hat{z}$ -direction does not change for the maximum compression, $\lambda \approx -0.2$, that we achieve here (see Figure 3.4b). However, the condensation levels in the $\hat{x}$ and $\hat{y}$ directions increase with increasing compression (see Figure 3.4b). Note that as the hydrogel is compressed at $\lambda < 0$, the chains aligned in the $\hat{x}$ and $\hat{y}$ directions are stretched. This conformational change is accompanied by an increase in the counterion condensation similar to the chains aligned in the $\hat{z}$ -direction at $\lambda > 0$.

The representative snapshots shown in Figure 3.4d, in which condensed and free counterions are shown by green and purple colors, respectively, are consistent with the condensation patterns in Figure 3.4b, while there are visually more condensed counterions near the chains aligned in the $\hat{z}$ direction at $\lambda > 0$ (see Figure 3.4d), there are fewer ions localized near the chains aligned in the $\hat{z}$ direction at $\lambda < 0$. Overall, these compression and stretching simulations suggest that condensation increases for the stretched chains of the hydrogel. However, over-stretching of the chains reduces the number of condensed ions.

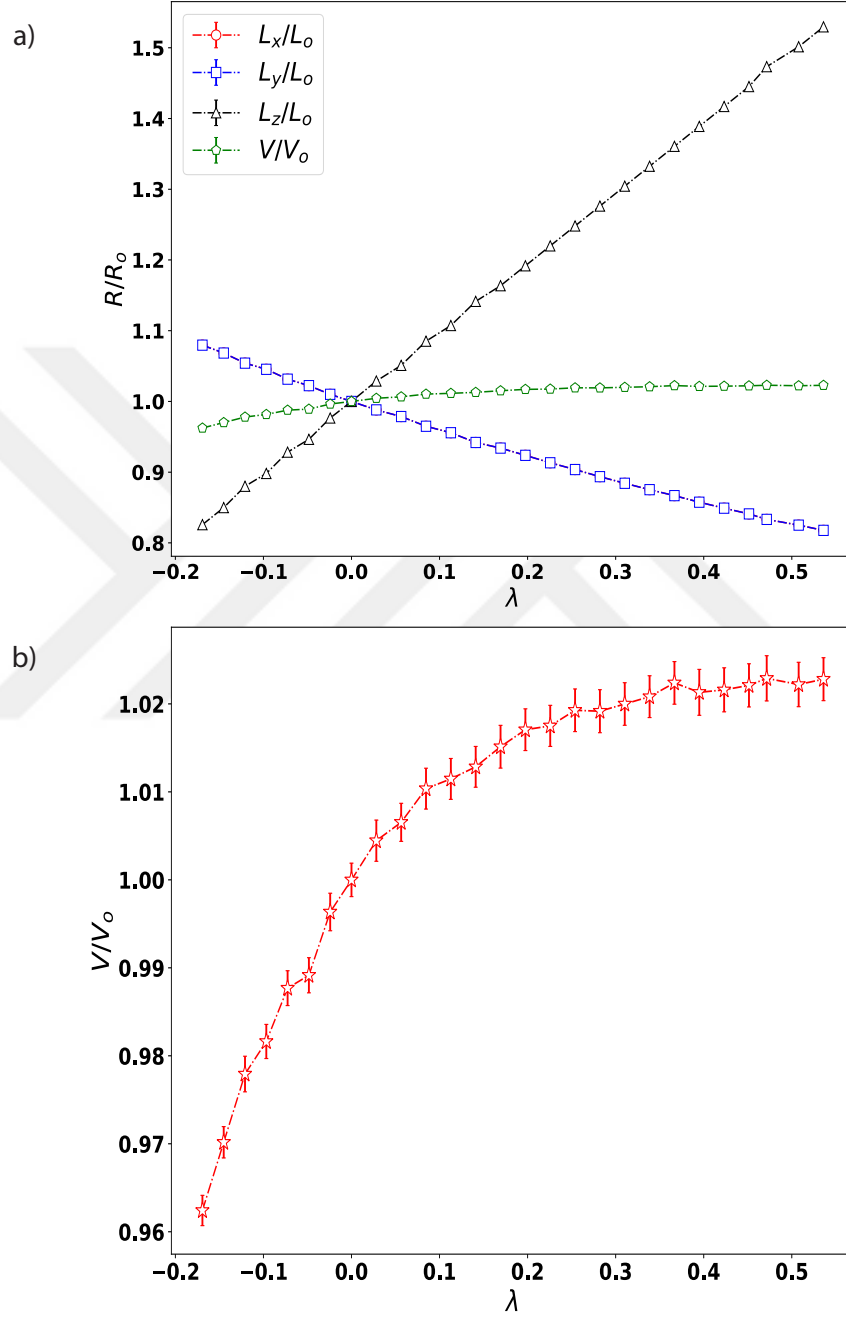


Figure 3.6: The change in dimension and volume with deformation are shown. a) It shows the deformation of the hydrogel along $\hat{x}$ (red) and $\hat{y}$ (blue) direction. The deformation along $\hat{z}$ is a straight line (black) since the hydrogel is deformed along the z-direction. b) The change in volume of the hydrogel is also shown, indicating that the volume of the hydrogel changes when it is deformed. However, the volume change is within 5% change compared to the relaxed NPT state.

If we sum the number of condensed ions around all hydrogel chains, we observe a highly non-monotonic behavior as a function of strain (see Figure 3.4c). Since the hydrogel tends to preserve its total volume under deformation, there are always relatively more stretched and more collapsed chains. For instance, in the compressive deformation (i.e., $\lambda < 0$), while the chains aligned in the $\hat{z}$ direction are collapsed, chains aligned perpendicular to the $\hat{z}$ direction are stretched further (see Figure 3.4d). As a result, both compression and stretching of the hydrogel lead to an increase in the total amount of condensed counterions around the constituting chains of the hydrogel.

In simulations, we observe a weak volume change (i.e., less than 4% for compression and 2% for stretching cases Figure (3.6b)). A considerable volume change can affect the translational entropy of free counterions and could be the reason for the variations in the ionic condensation levels that we observe [25, 61]. If we can approximate the translational free energy per ion as $F_t \sim k_B T \log(V)$, where V is the deformation-free volume available for ion diffusion at $\lambda = 0$, the translational free energy change with respect to the volume at the maximum compression, V_λ , could be written as $\Delta F \sim k_B T \log(V/V_\lambda)$. This leads to a translational energy change per ion $\Delta F \sim 10^{-2} k_B T$ per ion. This change is significantly weaker than the energy that an ion can gain upon condensation, which is on the order of $\sim 0.1 k_B T$ Figure (3.8). Therefore, we conclude that the alterations in the fraction of condensed counterions cannot be due to the deformation-dependent swelling or shrinkage of the hydrogel but rather due to conformational changes of the individual chains composing the hydrogel.

Finally, to confirm that the deformation-dependent condensation phenomenon that we observe does not depend on the method used to distinguish between condensed and free counterions, we calculate the radial distribution functions for counterions around the constituting chains of the hydrogel for various strain values. The average distribution of counterions is obtained by counting the counterions within an imaginary cylindrical cell positioned around each PE chain aligned in the $\hat{z}$ -direction (see Figure 3.7a) [7]

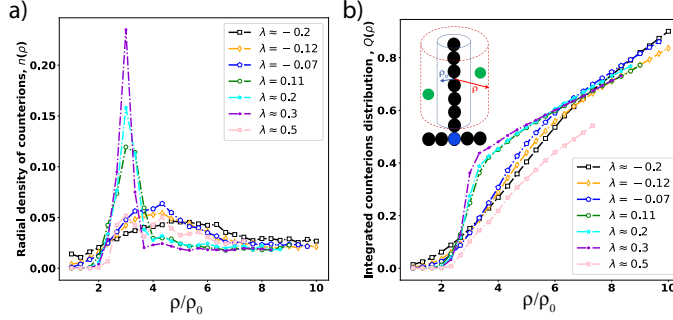


Figure 3.7: Ionic distribution around the hydrogel chains aligned in the $\hat{z}$ direction. a) Radial distribution functions and b) integrated counterion distributions as a function of the distance from the center of each chain, normalized by the effective thickness of the polymer backbone ρ_0 . The distributions are plotted for various strain values given in Figure 3.4b for the $\hat{z}$ direction. Notice that at $\lambda \approx 0.2$, the distribution differs from other cases, consistent with the results in Figure 3.4. The schematics in the inset show that the charge-neutral crosslinks (blue bead) are not considered for the calculations.

Once the counterion distribution is calculated as a function of the radial distance ρ , the cumulative number of counterions around the chains can be obtained by integrating the distribution data. In Figure 3.7, we show the radial distributions and integrated distributions defined in Eq. 3.3. Consistent with the data in Figure 3.4, the chain extension leads to an increase in the concentration of ions around the chains. For compressed and strongly stretched chains, on the other hand, we observe fewer counterions nearby the chains. Thus, the condensation patterns in Figure 3.7 are qualitatively similar to the data shown in Figure 3.4, suggesting that deformation-induced condensation alterations are not a side effect of the method used to determine the condensed counterions.

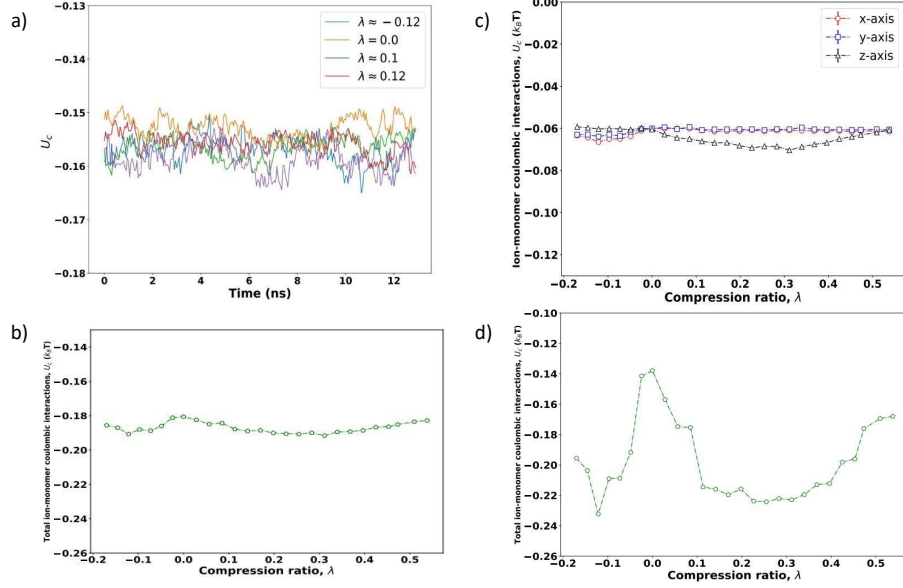


Figure 3.8: Coulomb interactions between the negative charge on monomers of hydrogel and sodium counterions are computed at the cut-off distance, $r_c = 1.5$ nm. a) The total Coulomb energy change during the last 13 ns of simulations for different deformations cases are shown b) The change in the Coulomb energy along the three different axes as the hydrogel is deformed at $r_c = 1.5$ nm c) The total Coulombic interactions as a function of strain, d) Sort-range pairwise Coulomb interactions per ion at $d < 0.25$ nm.

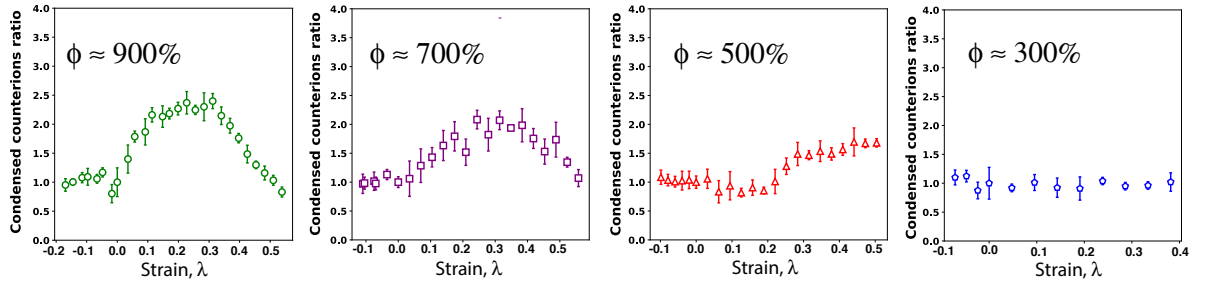


Figure 3.9: Counterion condensation along the deformation axis for PAA hydrogels with various swelling ratios as a function of strain. The percentage of condensed counterions is normalized by their value at zero strain. The error bars are not shown if they are smaller than the symbol size.

3.2.2 Weakly-swollen hydrogels display vanishing condensation alterations under deformation

While our highly-swollen PAA hydrogel shows deformation-dependent changes in its counterion distribution, we ask the question if this phenomenon has a dependence on the swelling ratio. Since the swelling ratio is related to the conformation of chains between two crosslinkers under the affine deformation assumption (Eq. 3.1), we anticipate that solvent content can affect the condensation profiles significantly. By decreasing the number of solvent molecules in our equilibrated hydrogels, we obtain various swelling ratios. Note that the swelling ratios we obtain by decreasing water content are not truly physical but rather serve as a tool to decipher the elastic and electrostatic effects, as we will discuss further. We run mechanical stretching and compression simulations with these hydrogels to monitor how condensation profiles change with deformation (Figure 3.9). The condensation profiles in Figure 3.9 are normalized by their value at zero strain. As the amount of water content inside the pervaded volume of the hydrogel decreases, the total amount of condensed counterions in the deformation-free hydrogels increases (see Supporting Information Figure S5). However, deformation-dependent variations in condensation levels diminish with decreasing water content (Figure 3.9), consistent with weak electrostatic changes in weakly swollen hydrogel networks under deformation [74]. Since most of the ions are already near the PAA chains in the less swollen hydrogels, deformation does not change the ionic distribution drastically. Thus, the deformation-dependent condensation phenomena that we observe here are stronger in highly-swollen PE hydrogels, and it weakens as the hydrogel loses solvent.

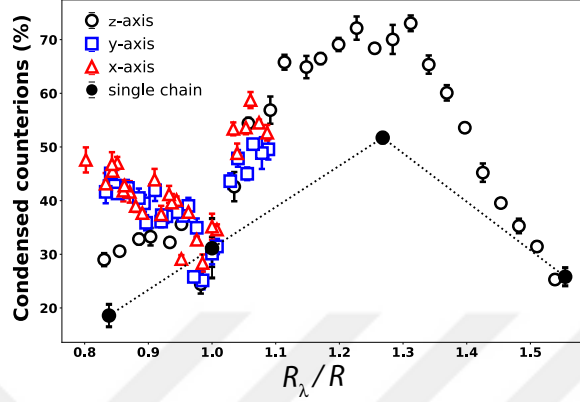


Figure 3.10: Counterion condensation around an end-constrained single chain and hydrogel chains aligned in $\hat{x}$, $\hat{y}$, and $\hat{z}$ directions. A single chain is composed of 25 AA monomers and aligned in the $\hat{z}$ direction. R_λ is the chain end-to-end distance in deformed states, and R is the size in the strain-free cases (i.e., $\lambda = 0$). The symbols are joined to guide the eye.

3.2.3 A single PE chain also exhibits stretch-dependent condensation

To test if the condensation phenomenon is a consequence of conformational changes of the PE chains in the hydrogels, we run simulations with isolated, practically infinite 25-mer single PAA chains, and 25 Na^+ counterions are added into the system to maintain the electroneutrality condition. We added 8000 SPC/E explicit water molecules into the system. The PAA chains are flexible, and they can fluctuate (i.e., they are not fixed to the lattice points) (see also Figure 3.11). These chains are obtained by bonding one end of the chain to the other terminal monomer throughout the periodic boundaries. We define the $\lambda = 0$ state by considering the box dimensions at the isotropic pressure of $P = 1.0$ atm, similar to the hydrogel simulations. At this state, the chain is stretched, and their end-to-end distance is $R \approx 6.2$ nm.

By stretching or compressing the simulation box, we stretch or compress the chain. This scheme allows us to control the end-to-end distance of the chain in the stretching/collapsing direction. In Figure 3.10, we plot the percentage

of condensed counterions for various stretching and compression cases as well as for $\lambda = 0$ for the single chain and hydrogel chains. To be able to compare the single chain and hydrogel cases, we plot the hydrogel data in Figure 3.4 but as a function of the chain sizes in the corresponding direction. The non-monotonic condensation profile that we observe for the hydrogel chains aligned in the stretched directions is in qualitative agreement with the single-chain results (Figure 3.10); the condensation exhibits a maximum as the chains are stretched (i.e., $\lambda \approx 0.2$). Both hydrogel chains and single-stretched chains show a similar increase. Further, for both hydrogel chains and single PAA, under weak compression and strong stretching, counterions are less localized near the backbone charges, which results in a less number of condensed counterions. Overall, our single-chain simulations validate that the deformation-dependent counterion condensation is due to conformational changes of constituting chains of the hydrogel and further demonstrate that this effect can occur in other hydrogels composed of longer PE chains.

3.2.4 Implicit solvent leads to a monotonic increase in counterion condensation

In our simulations, when the single-chain is stretched to a prescribed end-to-end distance, R_λ , the projected distance between backbone charges in the stretching direction becomes $\ell \approx R_\lambda/N \approx (1 + \lambda)R/N$. Such conformational changes could decrease the effective 1d concentration of the backbone charges to $1/\ell$ from $1/\ell_0$. The decrease in the 1d charge density can attract fewer counterions towards the backbone charges and decrease the counterion condensation. In the opposite case of chain compression, the 1d charge density can increase, and more counterions can be attracted toward the backbone charges. This scenario is analogous to the alterations in the concentration of charged chain monomers in an isotropically shrinking or swelling hydrogel and consequent changes in the condensation levels [32]. Tentatively, the changes in the 1d charge density upon deformation may be Incorporated into the Manning condensation parameter; after assuming that the Bjerrum length does not depend on the deformation, one can write

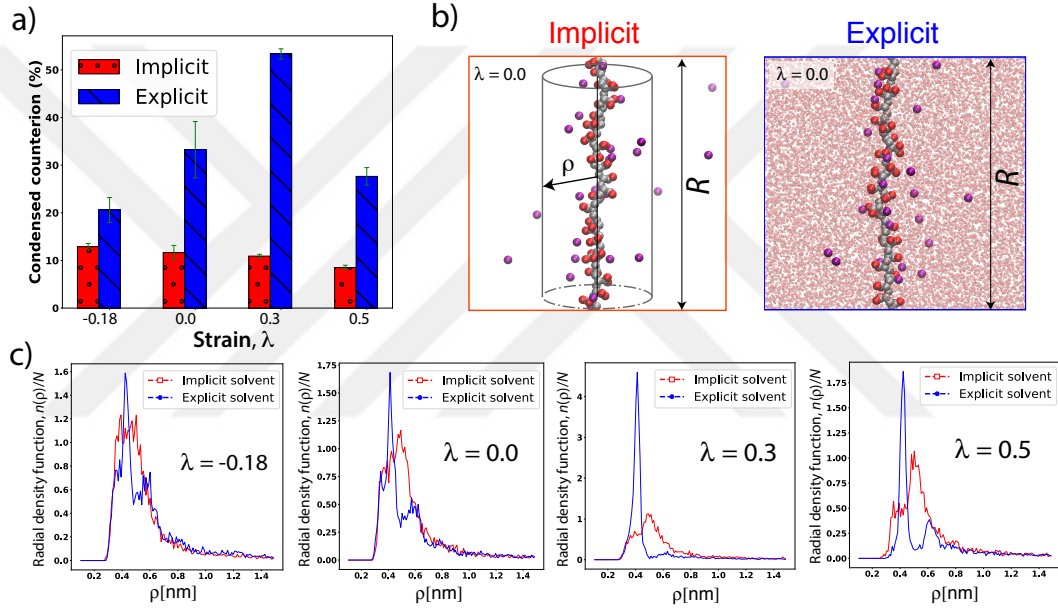


Figure 3.11: Counterion condensation around an end-constrained single chain in an explicit and implicit solvent; a) Calculated percentage of condensed counterions for explicit (default) and implicit water simulations for various strain values exhibiting the lowest and the highest condensation behavior for the $\hat{z}$ direction-aligned chains of the hydrogel. b) Representative simulation snapshots are taken from explicit and implicit water simulations at $\lambda = 0$. In explicit cases, water molecules are shown in red (oxygen) and white (hydrogen) spheres. The borders of the snapshots correspond to the actual size of the simulation boxes. c) Radial distribution functions of counterions near the chain calculated in the cylindrical coordinates for implicit and explicit-solvent cases.

$f_M(\lambda) = 1 - [(1 + \lambda)R/N\ell_B]$, which leads to a decreasing counterion condensation at $\lambda > 0$. However, in our single-chain and hydrogel-deformation simulations, we rather observe an increase until moderate stretching levels (i.e., $\lambda \approx 0.2$) followed by a decrease at strong stretching (i.e., $\lambda > 0.3$) Figure (3.11 a). This suggests that, at least in part, increasing condensation levels at weak deformations are not due to a Manning-type condensation modification. One possible effect influencing the condensation behavior could be the water molecules nearby the chains. These explicitly-modeled water molecules can either sterically modify the condensation (e.g., by competing with the ions to bind to the chain backbone) [75]. or alter the dielectric constant near the chain [33, 73] Figure (3.12).

To quantify the role of the explicit nature of water molecules in the counterion condensation phenomenon that we observe, we run implicit solvent simulations, in which all the water molecules in the simulation box are removed, and a Langevin description is used to model the effect of solvent molecules [57, 7]. Note that such an implicit-solvent model cannot describe either excluded volume or the dipole-related properties of individual water molecules. Interestingly, single-chain implicit solvent simulations do not show non-monotonic condensation behavior (see Figure 3.11a,c). Instead, as the end-to-end distance of the chain is increased (i.e., as λ is increased), the condensation decreases monotonically. As discussed in the previous paragraph, such a decrease is expected from a mean-field level behavior, in which the distance between backbone charges decreases, the fraction of condensed counterions decreases. Consistently, previous coarse-grained simulations with implicit solvent and analytical models, in which solvent was treated as a continuum, predicted a decrease in the counterion condensation (i.e., an increase in ionization) as the molar volume of hydrogel is increased, and chains are more stretched [32, 17] As a final note, if we set our condensation condition to a cut-off of $d = 0.25$ nm, we observe almost no condensation in the implicit simulations (see Supporting Information Figure S6). Only if the cut-off is set to $d = 0.3$ nm a percentage of counterion condensation comparable to the explicit cases is obtained (see Figure 3.11b). This indicates that the absence of water molecules somewhat decreases the adsorption of counterions to the corresponding backbone charges.

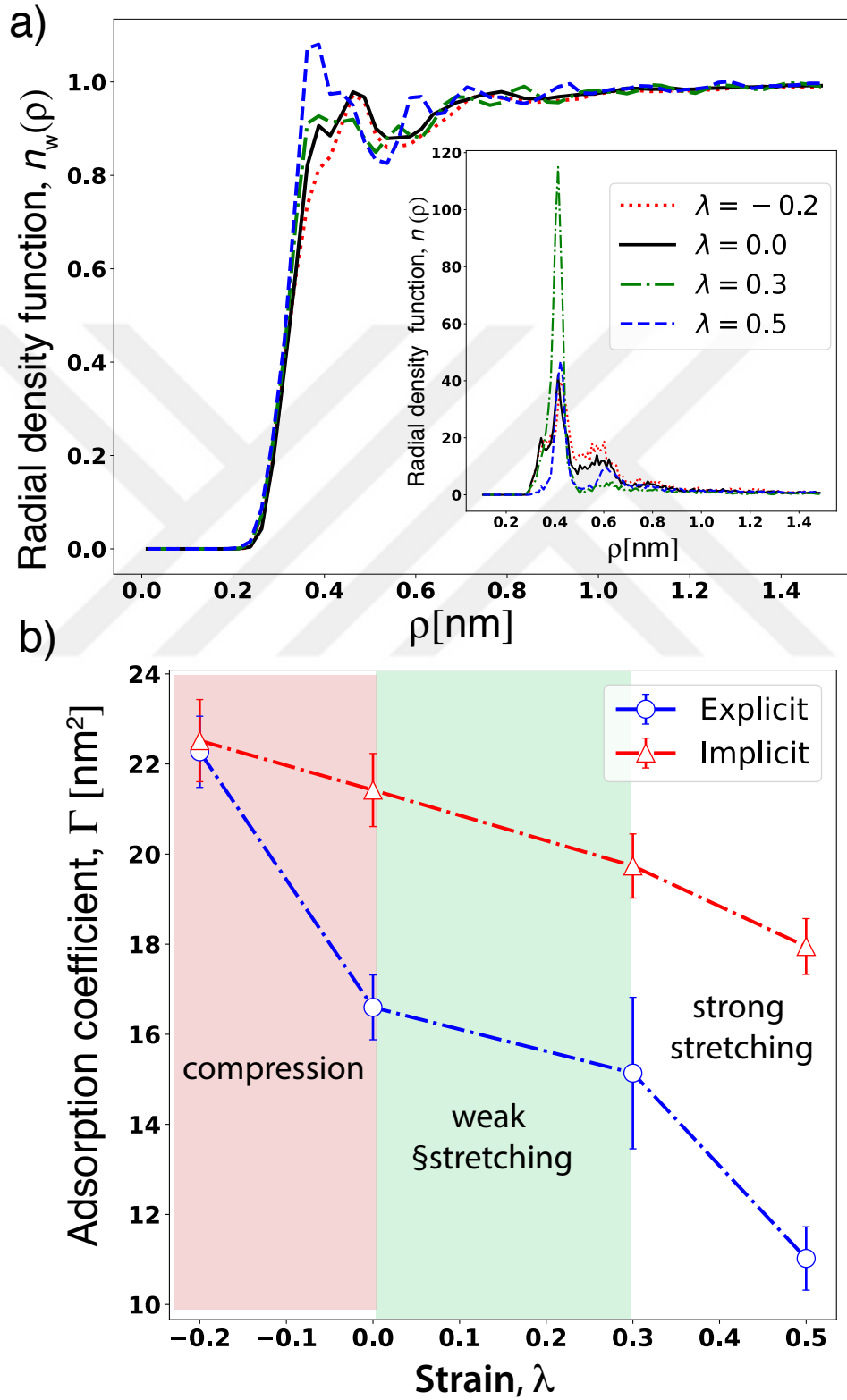


Figure 3.12: a) The cylindrical radial distribution function of PAA chains and explicit water is shown for different deformation ratios b) The first term of the solubility parameter is defined using equation (3.5) for implicit and explicit solvent

We can analyze the exhibit water simulations to understand the structure of water around PAA chains. For this purpose, we used the cylindrical radial distribution of the PAA carbon backbone and water, $n_w(\rho)$ shown in Figure (3.12). We plotted radial distribution for the four different deformations of PAA polymer chains. We see a large peak for the largest deformation $\lambda = 0.5$ case, and this peak value gradually decreases for the lower deformation (i.e., loosening of the PAA chains) cases. One can compute the Gibbs radius R_G for the PAA polyelectrolyte chains in cylindrical coordinates, which shows the effective radius of the polymer chain.

$$R_G^2 = 2 \int_0^\infty (1 - n_w(\rho)) \rho d\rho \quad (3.4)$$

It is important to note we see this water structure near the polyelectrolyte chains, and this structure vanishes as we move further away from the polyelectrolyte chains, and radial distribution $g_w(r)$ approaches a value of 1 (bulk density).

3.2.5 Solubility effects on the condensation around a deformed single PAA chain

To qualitatively characterize the counterion condensation by using the solution theories, we calculate the solubility parameter in cylindrical coordinates, defined as

$$\Gamma = 2\pi \int_0^\infty (n(\rho) - 1) \rho d\rho + \pi R_G^2 \quad (3.5)$$

Where R_G is the Gibbs radius, we compared the solubility parameter for explicit and implicit solvents by subtracting the second term in the equation (3.5) [76]. Since R_G^2 is much smaller than the first term and becomes smaller as the chains are stretched (i.e., $R_G = 0.44\text{nm}$ and $R_G = 0.38\text{ nm}$ for $\lambda = -0.2$ and $\lambda = 0.5$, respectively, this approach doesn't affect our comparison. The comparison in Figure (??) shows that the Γ becomes smaller as the chain is stretched in implicit and explicit cases, suggesting less condensation in Figure (3.12b).

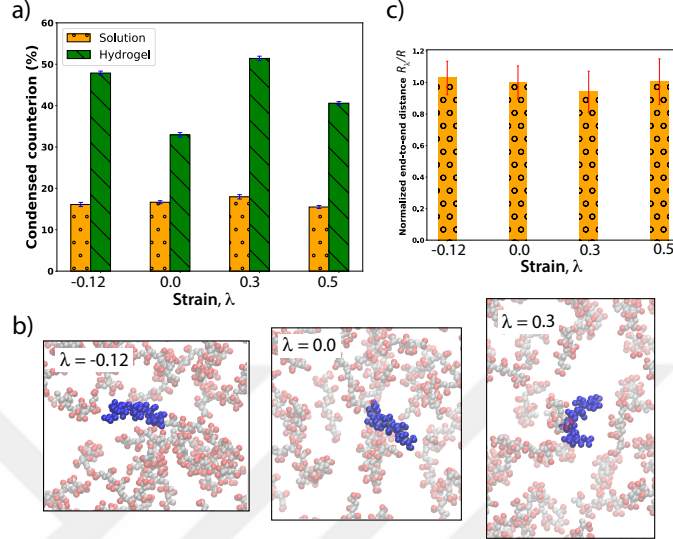


Figure 3.13: Counterion condensation in a PAA solution at the overlap concentration; a) a Calculated percentage of condensed counterions for various strain values. The average end-to-end distance of the 10-mer chains for the strain values in (a) is normalized by the chain size at $\lambda = 0$. b) Representative simulation snapshots taken for various deformation cases. An arbitrarily selected chain is highlighted by rendering all its constituting atoms blue. The water molecules are not shown for clarity. The borders of the snapshots correspond to the actual size of the simulation boxes.

However, in the explicit case, Γ exhibits a plateau-like regime at the moderate stretching range, $\lambda = 0 - 0.3$. Notably, this is the range that we observe an increase in the condensation levels with stretching in our simulations in Figure (3.12b). We speculate that dangling groups (e.g., carboxylic acid) and hydration layers surrounding counterions are re-organized as the chain is stretched, allowing more ions to condense on the chains. The exact molecular nature of this increase can involve dielectric mismatches near the chain due to the re-ordering of water dipoles, which can be analyzed in more detail in a future study.

3.2.6 Condensation in polyelectrolyte solution does not show deformation-dependence

The deformation-induced condensation demonstrated in our simulations requires PE chains to be constrained by both ends. We, therefore, hypothesize that the deformation-induced changes in the condensation profiles should not occur in solutions of PE chains or in dangling chains of a hydrogel that does not contribute to the elasticity of the hydrogel. To test this idea, we run additional MD simulations for a PE solution containing free PAA chains at the overlap concentration, equivalent to the hydrogel’s chain concentration (i.e., $\phi^* \approx N/R^3$). In the simulation box, $n = 24$ 10-mer PAA chains solvated by a similar number of water molecules as in a 900%-swollen hydrogel system. The chains are in physical contact with each other at the overlap concentration [50], but they are not cross-linked (see Figure 3.13). We deform the simulation box to obtain box dimensions as in our hydrogel’s compression and extension deformation simulations. As expected, the simulation box containing the solution does not change its total volume; thus, the concentrations of polymer monomers and ions do not change. As the box is deformed, the individual chains change their orientation to adjust new box dimensions. However, these orientation changes do not affect the fraction of condensed counterions per chain in compression or stretching cases (Figure 3.13a,c). The chain end-to-end distance does not change consistently as the simulation box is deformed. Consequently, the deformation simulations with a PE solution confirm that PE chains constrained by the hydrogel’s network 3d topology are the main driving reason for the observed condensation profiles in deformed hydrogels.

3.3 Conclusion

In this study, by employing all-atom simulations of a weak polyelectrolyte (i.e., polyacrylic acid) hydrogel and by explicitly considering water molecules and

counterions, we show that deformation of a hydrogel alters counterion condensation around the constituting chains of the polymer network in a deformation-dependent manner. The stretched chains of the hydrogel network exhibit a non-monotonic condensation profile, in which the ionic condensation increases at moderate chain stretching and decreases as the chains are strongly stretched. Since the hydrogel tends to preserve its volume under deformation by adjusting the conformation of its constituting chains, uniaxial compression and stretching manifest as changes in the total counterion distribution. This effect in turn could lead to electrostatic potential fluctuations inside the hydrogel by changing the ionic degree of the hydrogel or by creating heterogeneous ion distributions. Our simulations with implicit water also confirm that water molecules nearby the chains are of paramount importance for this phenomenon to occur, possibly by affecting the local dielectric properties. Importantly, the deformation-induced phenomenon in our single-chain simulations indicates that the stretch-dependent effect can be generic for weak and flexible polyelectrolyte chains as they undergo large extensional conformation deformations. Such deformation-dependent effects may be probed by micro-manipulation apparatus (e.g., AFM) [77] or extensional flow fields [78]. Our results also suggest that anisotropic hydrogels (e.g., longer chains in one direction than those in the others) can exhibit a much richer behavior of deformation-dependent condensation profiles. Such condensation responses can be used to tune the permeability of hydrogel membranes or build mechano-electrical systems such as biomimetic skin or muscles.

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