Chapter 7

Slow Relaxation Dynamics in Coacervates and Syneresis

7.1 Introduction

Many systems from both the living and inorganic world display slow relaxation kinetics of energy fluctuation [1-6]. One interesting feature that has recently been arousing interest is the relaxation to pressure equilibrium of local or distributed pressure fluctuation. Slow energy relaxation is naturally associated with the presence of a hierarchy of relaxation times. Nevertheless, the origin of such hierarchy is not always easy to pinpoint. A common assumption is that multiple time scale arises because of the roughness of the energy landscape, i.e. lots of local minima of different depths whose sequence enroute to equilibrium determines a hierarchy of decay times. In experimental observations, the slowing down of the dynamics is due to the spontaneous formation of dynamical structures which persist for long times and play the same role as metastable states observed in glasses. These dynamical structures were found to consist of random distributions of pinned or weakly mobile breathers [1]. The existences of breathers, i.e., localized nonlinear periodic oscillations in extended discrete nonlinear systems, show up spontaneously in the dynamics of nonlinear systems and may change substantially system characteristics. The lower the density of breathers, the weaker the rate of energy transfer will be [1]. Heat dissipation experiments in metallic nano-clusters in solution have revealed that the approach to equilibrium follows stretched-exponential relaxation behaviour [7]. The functional form such as exponential, non-exponential and stretched exponential behavior for the slow dynamics is neither quantitatively nor qualitatively is understood. However, such a picture (exponential relaxation behavior) would be compatible with our current understanding of syneresis; the phenomenon in which the separation of liquid from a system is caused by contraction (as in cheese making) from simple coacervate system is described in this chapter. The time behavior of the system only depends on the pressure difference \( \Delta P = P_{\text{int}_{t \to 0}} - P_{\text{int}_{t \to \infty}} \) and the objective is to study the system relaxation to a pressure \( P_{\text{int}_{t \to \infty}} < P_{\text{int}_{t \to 0}} \).
Bungenberg proposed [8] the idea of the existence of low and highly dispersed states of colloids that phase separate under unfavorable thermodynamic conditions. The phase separated colloid-rich phase (coacervate) remains for some reason or other in a very highly dispersed state. Considered from the two-phase standpoint, the mutual surface of contact between the colloid-rich and the colloid-poor phase (supernatant), is very large in these systems. This is manifested in the observation of spontaneous syneresis [9], which can fruitfully be described as the extrusion of a colloid-poor phase from a colloid-rich phase. As the system attempts to minimize the interfacial energy time-dependent changes in the microscopic properties of the coacervate phase ensues. The observation of syneresis proves that no equilibrium prevails inside the polymer-rich coacervate phase. The same has been routinely observed in many coacervates. The features associated with coacervation have been summarized in detail in several references [10-12]. The coacervation kinetics of aqueous gelatin solutions and its phase separation behaviour have been discussed at length earlier [13].

When a homogeneous polyelectrolyte solution [14,15] undergoes coacervation through charge neutralization, alike in an aqueous gelatin system, a sequence of morphological changes occurs that precedes the liquid-liquid phase separation, which leads to coacervation ultimately. We have observed this in gelatin coacervates prepared under different pH, ionic strength and temperature conditions [13]. It is well known, that the supernatant phase is an extremely dilute polymer solution compared to its thermodynamic partner, the coacervate. Let \( V_1, N_1 \) and \( V_2, N_2 \) represent the volume and polymer chain density in the supernatant and the coacervate phase respectively [10]. In coacervates, \( N_2 > N_1 \) and \( V_2 << V_1 \). Hence, \( N_2/V_2 >> N_1/V_1 \). The osmotic pressure difference between the coacervate and the supernatant \( (P_2 - P_1) \) will be [10]

\[
p_{\text{int}} = P_2 - P_1 = k_BT \left( \frac{N_2}{V_2} - \frac{N_1}{V_1} \right) - \frac{\sqrt{\pi}}{3} e^3 \frac{1}{(k_BT)^{1/2}} \left[ \left( \frac{N_2}{V_2} \right)^{3/2} - \left( \frac{N_1}{V_1} \right)^{3/2} \right] \quad (7.1)
\]

where \( k_B \) is Boltzmann constant, \( T \) is absolute temperature and \( e \) is electronic charge.

\[ k_BT >> \frac{\sqrt{\pi}}{3} e^3 \frac{1}{(k_BT)^{1/2}} \text{ and } N_2/V_2 >> N_1/V_1 \quad (7.2) \]

It immediately follows that \( P_2 >> P_1 \), which establishes the cause for syneresis rather explicitly. However, this treatment does not provide any insight into the kinetics of
fluctuations prevailing inside the coacervate phase. In this chapter, the issue of syneresis is addressed explicitly within the framework of non-equilibrium thermodynamics.

This phase-space dynamics in complex systems is elaborately discussed by S. F. Edwards and K. F. Freed [16,17] through the formalism of second quantization. The syneresis problem has been formulated here by taking Coarse-Grained models [18] from generalized considerations. The utility of order parameter approach is very important for describing the kinetics of phase transitions. Typically, kinetic processes are comprised of various fluctuating modes, and the order parameter is the slowest one, both in terms have spatial and temporal modulations. Thus, one needs coarse-grained models for the description of order parameter kinetics, which are valid on length scales larger than typical lattice spacings, and time-scales longer than microscopic relaxation times. It is of relevance to derive such macroscopic models from microscopic formulations like the kinetic Ising model [18]. The Langevin equation for phase-space dynamics reduces to a stochastic differential equation for the particle position in the high-friction limit in the Brownian motion problem. This is identical to the motion of a polymer chain in highly densed phase where the medium viscosity is very high.

The details of preparation of gelatin coacervates, and the experiments performed on coacervates pertaining to the rheological and AFM studies have been discussed in details earlier [19]. Mainly coacervate state is a partially charge neutralized macroionic phase. The ions (on the surface of the polyampholyte) and the counter-ions (free from the surface) play the major role in driving the system towards the energy minimization state. Results obtained from small angle neutron scattering (SANS) and rheology experiments confirmed the existence of a length-scale hierarchy inside this material [11, 12]. The length scale hierarchy is also discussed within the purview of spinodal decomposition models [20,21]. The relevant length scale in syneresis is the viscoelastic length measured through rheology.

7.2 Results and Discussion

7.2.1 Equation of state of coacervate

The three independent contributions of pressure cause syneresis inside the coacervate; (i) the pressure caused by cross links (P_1) [9], (ii) the ensemble of chains are randomly linked but not so linked that there are many units capable of moving around in the volume
$V_0$ which will exert pressure in local environment and also on the wall ($P_2$) \cite{9}, and (iii) the concentration fluctuations always build up a local stress which produces excess pressure inside the system ($P_3$) \cite{11}. Furthermore, its spatial variation, and the build up pressure will be relaxed at a certain rate which is characterized by viscoelastic properties of the system \cite{11}. The pressure due to excluded volume interaction is zero as we have neglected excluded volume interaction by assuming the polymer chains overlap and interpenetrate each other. The condition $P_{\text{int}} = P_1 + P_2 - P_3 = 0$ occurs when the contraction of the system caused by the cross links and stress relaxation balances the pressure exerted by the chains on their local environment. Negative sign is due to the reduction of pressure due to cross-links and stress relaxation. Cross linking are equivalent to an attractive force as $P_1$ is a monotonically decreasing function of number of cross-links. Physically, it is clear that the pressure will reduce until $P_{\text{int}} = 0$, and thereafter it will shrink in order to maintain zero pressure. As far as our coacervate system is concerned, it is indeed appropriate to make the physical identification of the energy of the system with time derivative of pressure at constant number of polymers chains or solute.

$$\frac{\partial P_{\text{int}}(r,t)}{\partial t} = \left( \frac{\partial P_{\text{int}}}{\partial C} \right) \frac{\partial C(r,t)}{\partial t} + \left( \frac{\partial P_{\text{int}}}{\partial m} \right) \frac{\partial m(r,t)}{\partial t} + \left( \frac{\partial P_{\text{int}}}{\partial \rho} \right) \frac{\partial \rho(r,t)}{\partial t}$$

Where $C$ is the concentration at highly densed phase and diluted phase, $m$ is the number of cross links and $\rho$ is the density of free chains. We defined the volume of solvent from coacervate i.e. Syneresis $\propto \frac{\partial P_{\text{int}}(r,t)}{\partial t}$ and

$$P_1 \propto \frac{\partial m}{\partial t},$$

$$P_2 \propto \frac{\partial \rho}{\partial t},$$

$$P_3 \propto \frac{\partial C}{\partial t}.$$

At equilibrium, $P_2 = P_1 + P_3$ as $P_{\text{int}} = 0 \Rightarrow \frac{\partial P_{\text{int}}}{\partial t} = 0$. From the famous article “Cross linkage problem of polymers III. Dense cross linked system of polymers” by S. F. Edwards and K. F. Freed \cite{9}, we have $P_2 = -\frac{mK_BT}{V}$ and $P_3 = \frac{nNK_BT}{V}I^{\frac{1}{2}}\rho^{\frac{1}{2}}Z$. One can write the pressure due to concentration fluctuation i.e. $P_1 = C \frac{K_BT}{V}$. Finally,
\[ \begin{aligned}
P_{\text{int}} &= -mK_B T/V + nNK_B T l^{3/2} \rho^{1/2} Z - C K_B T/V \\
\Rightarrow P_{\text{int}}V &= K_B T[-m + nNl^{3/2} \rho^{1/2} Z - C], \text{ the equation of state of coacervate.}
\end{aligned} \]

Here, \( P_{\text{int}} \) is the total internal pressure, \( V \) is the volume of solvent coming out from the coacervate, \( K_B \) is the Boltzman constant, \( T \) is the temperature, \( N \) is the number of units, \( l \) is the step length, \( n \) is the number of cuts in polymer network and \( Z \) is a constant. The relationship between \( P_{\text{int}} \) and \( V \) has been discussed in the slow relaxation dynamics is the following.

### 7.2.2 Slow Relaxation Dynamics

Suppose that entropy \( S \) is given as a function of extensive variables on which entropy \( S \) depends. In the following analysis of coacervate system, these symbols are referred to the densities of these thermodynamic quantities. Then \( TdS = P_{\text{int}}dV \), where

\[ P_{\text{int}} = \left( \frac{dS}{dV} \right)_{E^{\text{int}}} T \]

\( E^{\text{int}} \) is the internal energy of the dense polymer system is equal to zero or constant. The basic thermodynamics potential in equilibrium thermodynamics is depending on the conditions, the internal energy (\( U \)) or a variation such as enthalpy (\( H = U+PV \)), Helmholtz free energy (\( F - TS \)) or Gibbs free energy (\( G = U+PV-TS \)). However, in non equilibrium thermodynamics it is entropy (\( S \)) that takes center stage. Non-equilibrium thermodynamics is a branch of thermodynamics concerned with studying time-dependent thermodynamic systems, irreversible transformations and open systems. Irreversible transformations are characterized by net entropy production.

Non-equilibrium thermodynamics applies to situations where the system under study is not in thermodynamic equilibrium but can be broken into subsystems which are sufficiently small to be in equilibrium, while still being large enough that thermodynamics is applicable. Though the coacervate phase is heterogeneous, its microscopic structures observed through SANS data are assumed to form the subsystems that are in equilibrium, and generalize the whole system. This is consistent with the hypothesis of local equilibrium. In some cases, there will be a discrete collection of subsystems interacting with each other through a discrete collection of channels. Continuous systems are studied by measuring extensive quantities per unit volume (as
densities), and assuming that intensive quantities have locally defined values; this means that all thermodynamic variables can be represented by fields. Difference or Gradients of intensive parameters are thermodynamic forces and they cause flow of the extensive variables. A manifestation is the Cahn-Hilliard (CH) equation for the phase separation of a binary system which is governed by [18]

\[
\frac{\partial V(r,t)}{\partial t} = D \nabla^2 \left( \frac{\partial F}{\partial N} \right)
\]  

(7.3)

where, \( \partial V = dV = v \, dN \) is the volume of the solvent coming out the coacervate due to change in chemical potential \( (\partial F/\partial N) \). The volume \( \partial V \) is equal to \( dV \) because of the same volume \( \partial V \) decreases from the initial volume of the coacervate with respect to spatial and temporal scale. Here, \( F \) is the free energy change with respect to number of solvent molecules \( (N) \) coming out in the process of syneresis, and \( v \) is defined as the volume of single solvent molecule. Eq. 7.3 corresponds to the case of constant diffusion coefficient \( (D) \). But in the coacervate system the diffusion coefficient could depend on the local order parameter. The temporal release of the supernatant and the time-dependent decrease in viscoelastic length scale is shown in Figure 7.1.

Figure 7.1: Weight of the supernatant released versus time at 25 °C, contains 5-10% error arising from losses during measurement. Inset is the viscoelastic length versus time obtained from the storage modulus data [11]. Note the damped oscillatory nature of supernatant release.
The basic thermodynamic potential is the internal energy. In a dense fluid system, the energy density \( u \) depends on the matter density \( \rho \) and the entropy density \( s \) at temperature \( T \), in the following way.

\[
du = Tds + m \rho \quad (7.4)
\]

where \( m \) is either pressure or chemical potential. Thus

\[
ds = \left( \frac{1}{T} \right) du - \left( \frac{m}{T} \right) d\rho \quad (7.5)
\]

The extensive quantities \( u \) and \( \rho \) are conserved, and their flows satisfy continuity equations.

\[
\frac{\partial u}{\partial t} + \nabla \cdot J_u = 0 \quad (7.6)
\]

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot J_\rho = 0 \quad (7.7)
\]

The gradients of the conjugate variables of \( u \) and \( \rho \), which are \( T/m \) and \(-m/T\), are thermodynamic forces and they cause flow of the extensive variables. Partial derivative was taken by assuming that \( u \) and \( \rho \) are both function of space and time. In the absence of heat flow

\[
J_\rho = -K^* \nabla \left( \frac{m}{T} \right) \quad (7.8)
\]

and, in the absence of matter flow

\[
J_u = K^* \nabla \left( \frac{1}{T} \right) \quad (7.9)
\]

In our problem, we have assumed that there is no heat flow, thus Eq. 7.8 will prevail. The fluxes are proportional to the thermodynamic forces by proportionality constants, which are normally transport coefficients. Both coefficients \( K^* \) and \( K^\rho \) are measured in the same units of temperature times mass density due to Onsagar reciprocity relations [16]. Thus, the rate of release of supernatant \( \left( \frac{dV}{dt} \right) \) as \( V \) is replaced by \( \rho \) in our system, constitutes the divergence of flux \( \nabla \cdot J_\rho \) which is proportional to driving force \( \nabla . P_{\text{int}} \). The corresponding transport coefficient \( (K^*) \) incorporates the time-scale of phase separation. Thus

\[
\vec{J}_\rho = -\frac{K^*}{T} \nabla P_{\text{int}} \quad \text{with} \quad m = P_{\text{int}} \quad (\text{excess internal pressure})
\]

Combining Eqs. 7.7 and 7.10, we can write
\[
\frac{\partial V}{\partial t} = \nabla \cdot \frac{K^*}{T} \nabla P_{\text{int}} = \frac{K^*}{T} \nabla^2 P_{\text{int}}
\]  

(7.11)

So,
\[
\frac{\partial V}{\partial t} - \frac{K^*}{T} \nabla^2 P_{\text{int}} = 0
\]  

(7.12)

By introducing a constant, \( K = \frac{\partial V}{\partial P_{\text{int}}} \) (volume of supernatant released is linearly dependent on internal pressure of coacervate) we can rewrite Eq. 7.12 as
\[
K \frac{\partial P_{\text{int}}}{\partial t} - \frac{K^*}{T} \nabla^2 P_{\text{int}} = 0
\]  

(7.13)

Eq. 7.13 is similar to the three dimensional diffusion equation [22,23] which at equilibrium, \( \frac{\partial P_{\text{int}}}{\partial t} = 0 \), reduces to three dimensional Laplace equation giving \( \nabla^2 P_{\text{int}} = 0 \). It implies when there is no pressure difference inside the coacervate system; there is no syneresis. The solution to Eq. 7.13 can be obtained as follows: let \( P_{\text{int}}(r, t) = X(r) Y(t) \). Here, \( r \) symbolizes a length scale which changes with respect to time. Then,
\[
\frac{dP_{\text{int}}}{dt} = X(r) \frac{dY}{dt} \quad \text{and} \quad \frac{d^2 P_{\text{int}}}{dr^2} = Y(t) \frac{d^2 X(r)}{dr^2}
\]  

(7.14)

Using Eq. 7.14 in Eq. 7.13, we have
\[
\frac{K^*}{T} Y(t) \frac{d^2 X(r)}{dr^2} - KX(r) \frac{dY(t)}{dt} = 0,
\]
\[
\frac{K^*}{T} \cdot \frac{1}{X(r)} \frac{d^2 X(r)}{dr^2} = K \cdot \frac{1}{Y(t)} \frac{dY(t)}{dt} = \mu \quad \text{(say)}
\]  

(7.15)

Here the variables are separated taking \( \mu \) as constant of separation. There are three possible solutions for Eq. 7.15 corresponding to \( \mu = 0, \lambda^2 \) and \( -\lambda^2 \) out of which two solutions (for \( \mu = 0 \) and \( \lambda^2 \)) yield \( Y(t) \) increasing with respect to time, which are not physical. The only physical solution corresponds to \( \mu = -\lambda^2 \), giving
\[
X(r) = P_{\text{int}}(r) = A \cos \left( \frac{\lambda^2 T}{K^*} \right)^{1/2} r + B \sin \left( \frac{\lambda^2 T}{K^*} \right)^{1/2} r ; \quad Y(t) = P_{\text{int}}(t) = C \exp(-t\lambda^2 / K)
\]  

(7.16)
Thus, the final solution is

\[
P^{\text{int}}(r, t) = A \cos \left( \left( \frac{\lambda^2 T}{K} \right)^{1/2} r \right) + B \sin \left( \left( \frac{\lambda^2 T}{K} \right)^{1/2} r \right) \times C \exp \left( -\frac{\lambda^2}{K} \right) \quad (7.17)
\]

Here, A, B and C are constants of integration. Determination of exact values of these constants from boundary conditions is not trivial. Similarly, attributing exact physical meanings to \( \lambda \) and \( K'' \) is difficult at this stage. Eq. 7.17 predicts the damped periodic fluctuation of excess internal pressure prevailing inside the polymer-rich coacervate phase with the relaxation time being given by \( K/\lambda^2 \). Since, \( P^{\text{int}} \) drives the release of supernatant; the volume of supernatant released is expected to mirror identical time dependence behaviour. Moreover, the coacervate system will contract upon inter-chain crosslinking until the pressure caused by the restriction of a chain by entanglement with its neighbors balances the negative pressure due to the cross links.

Figure 7.2 depicts the time-dependent behaviour of internal pressure inside the coacervate which follows a damped oscillatory behavior and relaxes shortly with time during syneresis, independent of amplitude (numerically plotted using Eq. 7.17). At small relaxation time (\( K = 10 \)), robust breathers are formed that is relatively immobile. At larger relaxation time (\( K = 1000000 \)), the breathers become quite mobile. Large sized breathers take longer time to relax. Initially, for short time durations, it shows a larger pressure fluctuation and as time increases, the fluctuation becomes less, which owes its origin to significant reduction in the internal pressure over the period of time. In our experimental observation, the value of relaxation time (\( K = 1000000 \)) is well matched which is depicted in the Figure 7.3. The behavior of \( \frac{dV}{dt} \) versus time is also shown in the same figure for comparison. The relaxation time constant \( K \) in our picture is similar to the coupling constant \( k \) that describes the energy landscape in nonlinear lattices induced by breathers [1]. In rheology experiments reported earlier, it was found that the length scale (viscoelastic length) in coacervate showed a linear decay with time which was fitted to a scaling relation, \( r = r_o - a t \) reproduced in Figure 7.1 (inset). The data fitting yielded a high \( \chi^2 \sim 0.95 \), and the value obtained for constant \( r_o = 14 \) and slope, \( a = 0.002 \).
Figure 7.2: Variation of internal pressure with time plotted for different values of using Eq. 7.17.

It can be argued that the value of $r$ goes to a minimum value $r_m$ as $P_{\text{int}}(r, t) = 0$ at $t \rightarrow \infty$. Physically, it is clear that the internal pressure inside the coacervate will reduce until $P^i = 0$, and thereafter it will shrink in order to maintain zero pressure [9]. So, Thus the total internal pressure ($P_{\text{int}}$) will comprise of three independent contributions as discussed earlier. Viscoelastic length scale can account for such shrinking of the coacervate (see Figure 7.1). Due to experimental limitations we could not produce the viscoelastic length scale data beyond three decades in Figure 7.1 (inset).
Figure 7.3: Variation of internal pressure with time plotted with the corresponding release of supernatant through syneresis. Error associated with the release data is between 5-10% which was lost during measurement. The inset pictures reveal how the coacervate sample changes from an opaque phase (presence of supernatant as submicron sized droplets) to a transparent phase (similar sized islands of coacervate droplets) with respect to time through syneresis. Fitting parameters used were \( A = 0.02 \), \( B = 0.02 \), \( C = 1.0 \), \( \lambda^2 = 1 \), \( T = 300.0 \), \( K^* = 1.0 \), \( K = 1000000.0 \), \( r_* = 14.0 \), and \( a = 0.002 \) (Eq. 7.17). Rate of release of supernatant (\( \text{d}V/\text{d}t \)) deduced from the data presented in Figure 7.2 by assuming density of supernatant liquid ~1.

The inset shown in Figure 7.3 reveals how the coacervate sample changes from an opaque phase (length scale was comparable to wavelength of visible light ~500nm) to a transparent phase (length scale shrinking to much less than wavelength of light) with respect to time through syneresis. The initial turbidity of the coacervate owes its origin to the presence of supernatant as submicron sized droplets inside the coacervate, and to the presence of similar sized islands of coacervate droplets which are still not part of the bulk matter. This process is very similar to the Ostwald ripening, where the growth of larger droplets at the expense of smaller ones (Laplace pressure effect, \( \Delta P = 2\gamma / R \)), \( R \) is size of smaller droplets and \( \gamma \) is the surface tension. The decrease in concentration of smaller
droplet species can offset decrease in $\Delta P$. The formation of coacervate droplets is well studied by Bungenberg de Jong and Oparin [8,24]. With time the excess internal pressure squeezes the supernatant out, and the coacervate droplets coalesce with the bulk to minimize interfacial energy which in turn makes the sample transparent. Figure 7.3 also depicts the theoretical plot of excess internal pressure (Eq. 7.17) obtained by using the above mentioned values for $K$ in numerical calculations. This is compared with the release kinetics of supernatant from the coacervate phase in the same figure. Thus, we do find one to one correspondence between the internal pressure inside the coacervate and its effect on syneresis. This corroborates our earlier claim that these two physical parameters mirror identical time dependence. Envelop of the damped oscillation will be given by the exponential term of Eq. 7.17. In addition, qualitatively, one observes a much slower relaxation and the model proposed adequately describes this feature. The calculation presented is still much idealized. The important point, however, is that a direct demonstration of how internal pressure produces syneresis has been given, amounting to a translation into mathematics of the simplest intuitive picture of the phenomenon.

In passing, it is possible to workout the entropy associated with such a process

$$\frac{dV}{dt} = \nabla \cdot \nabla P^{\text{int}} \quad \text{and} \quad \text{TdS} = P^{\text{int}} dV \Rightarrow T \frac{dS}{dt} = P^{\text{int}} \left( \frac{dV}{dt} \right).$$

So

$$\frac{T}{P^{\text{int}}} \frac{dS}{dt} = -\nabla \cdot J \quad \text{(by Eq. 7.7)}$$

gives

$$T \frac{dS}{dt} = -P^{\text{int}} \nabla \cdot J,$$

and consequently

$$T \frac{dS}{dt} = -\nabla \cdot (P^{\text{int}} J) + \nabla P^{\text{int}} \cdot J.$$ Here, $P^{\text{int}} J$ is a reversible entropy flow (resulting in the entropy transfer through the boundaries of the system) and $\nabla P^{\text{int}} \cdot J$ is the rate of entropy production in the bulk. The second term indicates the entropy, $\nabla P^{\text{int}} \cdot J \geq 0$ inside the bulk. But if we consider two entropic terms as well, the entropy of the system decreased, because the flows are possible in the presence of thermodynamical forces, without applying external work.

Ilya Prigogine noted that self-organization [25] can only be occurring far away from thermodynamic equilibrium. It would appear that, since isolated systems cannot decrease their entropy, only open systems could exhibit self-organization. However, a closed system can gain macroscopic order while increasing its overall entropy. Specifically, a few of the system’s macroscopic degree of freedom can become more ordered at the expense of microscopic disorder. In many cases of the biological self-assembly, for
instance metabolism, the increasing organization of large molecules is more than 
compensated for by increasing entropy of small molecules, especially water. Self-
assembly is the fundamental principle, which generates structural organization on all 
scales from molecules to galaxies. Self-assembly can be classified as either static or 
dynamic. Static self-assembly is when the ordered state occurs when the system is in 
equilibrium and does not dissipate energy. Dynamic self-assembly is when the ordered 
state requires dissipation of energy. The syneresis is a good example of dynamic self-
assembly. When production of entropy flux $\sigma = 0$, i.e. equilibrium state. When production 
of entropy flux $\sigma > 0$, i.e. steady state and it organize itself and goes to equilibrium state.

The idea of self organization challenges an earlier paradigm of ever decreasing order 
which was based on a philosophical generalization from the second law of 
thermodynamics. However, at the microscopic level, the two need not be in contradiction: 
it is possible for the system to reduce its entropy by transferring it to its surrounding or 
environment. In over system it is flow of matter and energy through the system that 
allows the systems to self organize, and to exchange entropy to the environment. This is 
the basis of the energy of dissipative structures.

There may be other reasons of syneresis which can not be avoided; (i) In a non-solvent 
system, the monomer of proteins excludes water and the interaction is very strong i.e. 
excluded volume decreases as system decreases, (ii) When monomer-monomer overlap 
occurs, the solvent in the depletion region goes out and the entropy increases as the 
solvent get more volume. In other language, we can say that the polymer entropy 
decreases and the entropy of water increases and the overall entropy of the system 
increases, which reduces the energy of the system, and the syneresis occurs and the 
system goes to a equilibrium state. As the water expelled from the overlap volume 
($V_{\text{overlap}}$), this results in an osmotic pressure differences ($\Delta \Pi$), between overlap volume 
and bulk phase. This osmotic pressure results in an effective attraction of the polymer 
chains. Due to this attraction of the polymer chains, the volume, which is available for the 
water, increases with $V_{\text{overlap}}$. This increases of the volume by $V_{\text{overlap}}$ results in a lowering 
of the free energy of the system by $- \Pi V_{\text{overlap}}$ (depletion effect).
7.3 Conclusions

Syneresis exhibited by a heterogeneous polyampholyte coacervate (polymer-rich phase) is discussed through non-equilibrium statistical thermodynamics. It has been shown that the coacervate phase is associated with fluctuating excess internal pressure that gives rise to syneresis. The coacervate system will contract upon cross linking until the pressure, caused by the restriction of a chain by entanglement with its neighbours, balances the negative pressure due to the cross links. It is proposed that energy is dissipated to the environment only by the surface of coacervate, whereas in the bulk, gelatin chains only exchange energy with each other with negligible or no dissipation. Consequently, the internal pressure inside the coacervate follows a damped oscillatory behaviour that relaxes slowly with time, independently of amplitude. The connection of volume of the supernatant released with time (exponential relaxation behavior) with the presence of long-lived nonlinear localized modes (the existence of breathers) is highly stressed. The calculation presented is still very idealized. The important point, however, is that a direct demonstration of how internal pressure produces syneresis has been given, amounting to a translation into mathematics of the simplest intuitive picture of the phenomenon.
7.4 References