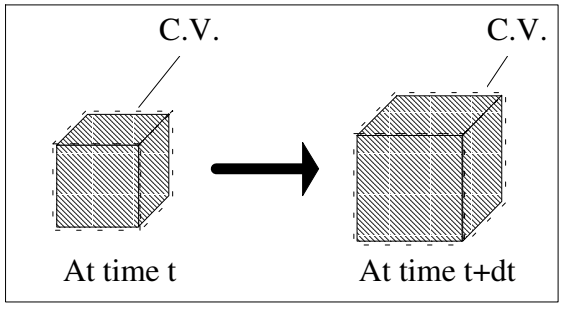
Bond Graph Modeling of Non-Electrolyte Gel



System: (Polymer gel network + solvent inside) inside the control volume (c.v.)., i.e., the control volume is changing as the get network is expanding due to absorbing the surrounding solvent fluid.

Modeling Assumptions:

- Process is relatively slow, and the inertial effects of fluid flow and polymer network are negligible.
- Process is solvent diffusion-limited into the gel network, and the effects of surrounding fluid convection is negligible.
- Process is quasistatic; i.e., the properties inside the c.v. is uniform at any instant of time.
- Process is isothermal (constant temperature), isobaric (constant pressure), which is typical in laboratory setting.
- Process consists of two sub-processes: mixing/diffusion and elastic expansion of the polymer-solvent network (Flory).
- The polymer and solvent are incompressible.

Mixing/Diffusion Process: Entropy generating process

Consider the polymer gel network inside the c.v. as shown above. The c.v. is surrounded by the solvent fluid at constant temperature, T_O, and constant pressure, P_O. As the solvent fluid enters the c.v., the c.v. expands, and the state of the system inside the control volume at an instant of time can be themodynamically described by

$$dU_{cv} = T_o dS_{cv} - P_o dV_{cv} + \mu_P dn_P + \mu_S dn_S \qquad (1)$$

where U_{CV} is the internal energy of the system inside the c.v.,

S_{CV} is the entropy of the system inside the c.v.,

V_{CV} is the volume of the c.v.,

T_O is the temperature the system inside the c.v. experiences,

P_O is the pressure the system inside the c.v. experiences,

μ_p is the chemical potential of polymer inside the c.v.,

μ_s is the chemical potential of solvent inside the c.v.,

n_p is the number of mole of polymer inside the c.v.,

n_s is the number of mole of solvent inside the c.v.

Since the number of mole of polymer inside the c.v. is fixed, the third term on the right hand side (RHS) is zero, i.e., $\mu_p dn_p = 0$. In addition, the second term on the RHS, $P_o dV_{cv}$, represents the differential expansion work done by the c.v.. Assuming both the polymer and the solvent to be incompressible, then $P_o dV_{cv} = 0$ since the expansion of c.v. alone is exactly cancelled by the flow work done by the solvent flowing into the c.v.. The Equation (1) then simplies to

$$dU_{cv} = T_o dS_{cv} + \mu_S dn_S \tag{2}$$

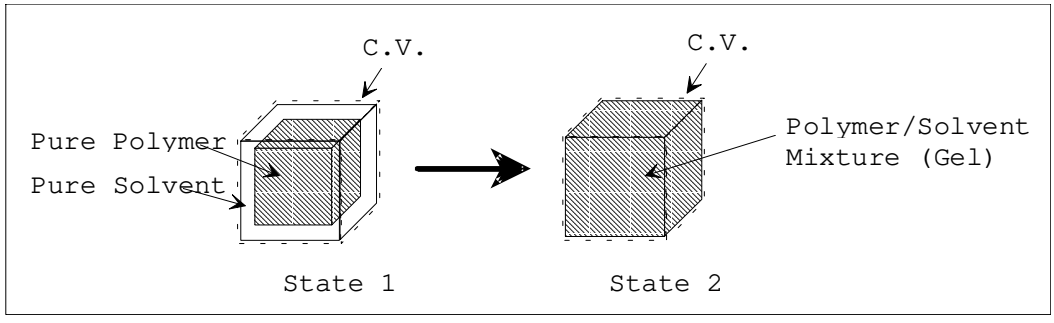
With the assumption of quasi-staticity of the process, then the system inside the c.v. may be treated as the lumped parameter multiport capacitance with the relation

$$\frac{dU_{cv}}{dt} = T_o \frac{dS_{cv}}{dt} + \mu_S \frac{dn_S}{dt} \tag{3}$$

The first term on RHS represents the effects of heat transfer, entropy transfer due to convection and the entropy generation due to irreversibility. The second term on RHS represents the chemical energy brought in by the incoming surrounding solvent. The bond graph representation of the system is

The constitutive relations describing the equilibrium state of the polymer-solvent gel network system has been derived by Flory, and it will be base of the multiport capacitance model.

Flory's model:



State 1: The pure polymer network and pure solvent inside the control volume (c.v.) are completely separated.

State 2: The polymer network and the solvent inside the control volume mix and form homogeneous polymer solution, while maintaining constant volume of c.v.

The process from state 1 to state 2 is therefore entropy generating run-down mixing process, and the changes in thermodynamic properties of control volume due to such mixing process are described by Flory.

$$\Delta G_M = \left(G_{cv2} - G_{cv1}\right) = \left\{G_{cv2} - \left(G_s^o + G_p^o\right)\right\}$$

where ΔG_M is the change in Gibbs free energy of c.v. due to mixing,

G_{cv1} is the Gibbs free energy of c.v. at state 1,

G_{cv2} is the Gibbs free energy of c.v. at state 2,

$G_s{}^o$ is the standard Gibbs free energy of solvent,

$G_p{}^o$ is the standard Gibbs free energy of polymer.

Similarly,

$$\Delta S_M = \left(S_{cv2} - S_{cv1}\right) = \left\{S_{cv2} - \left(S_s^o + S_p^o\right)\right\}$$

where S denotes entropy.

The Gibbs free energy change of c.v. by mixing of polymer and solvent is considered to be due to two effects; combinatorial effect, $\Delta G_M{}^{comb}$, and polymer-solvent contact effect, $\Delta G_M{}^{cont}$. $\Delta G_M{}^{comb}$ accounts for the many different conformations the amorphous polymer may adopt, and $\Delta G_M{}^{cont}$ accounts for the effects of non-randomness induced by intermolecular interactions.

$$\Delta S_M{}^{comb} = -R(n_s \ln \phi_s + n_p \ln \phi_p)$$

$$\Delta G_M{}^{comb} = -T\Delta S_M{}^{comb} = RT(n_s \ln \phi_s + n_p \ln \phi_p)$$

$$\phi_s = \frac{n_s}{n_s + xn_p} \qquad \phi_p = \frac{xn_p}{n_s + xn_p}$$

where R is the universal gas constant,

n_s is the number of mole of solvent,

n_p is the number of mole of polymer,

ϕ_s is the volume fraction of solvent,

ϕ_p is the volume fraction of polymer,

x is the number of chain segments of a polymer molecule such that the volume of a polymer molecule is equal to x time the volume of a solute molecule, i.e., $V_p = x\, V_s$.

The intermolecular interaction also involves enthalpy change.

$$\Delta G_M^{cont} = \Delta H_M^{cont} - T\Delta S_M^{cont} = RTn_s\phi_p\chi$$

where χ is the Flory-Huggins polymer-solvent interaction paramter. χ is a temperature dependent dimensionless quantity which characterizes polymer-solvent interactions, and can be expressed in the form

$$\chi = a + b/T$$

where a and b are temperature independent quantities. Then, $\Delta G_M{}^{cont}$ can be written as

$$\Delta G_M^{cont} = RTn_s\phi_p\left(a + b/T\right) = RTn_s\phi_p a + Rn_s\phi_p b$$

Since

$$\left(\frac{\partial \Delta G_M^{cont}}{\partial T}\right)_{p,n_s,n_p} = -\Delta S_M^{cont} = Rn_s\phi_p a$$

then,

$$\Delta H_M^{cont} = Rn_s\phi_p b$$

Note that $\Delta H_M{}^{cont}$ represents the thermal energy generated due to the mixing process, and thus can be modelled as the heat transferred to the surrounding solvent environment while maintaining isothermal condition.

Combining both the combinatorial and polymer-solvent contact effects, we have

$$\Delta G_M = \Delta H_M - T\Delta S_M$$

$$\Delta H_M = \Delta H_M{}^{cont} = Rn_s\phi_p b$$

$$\Delta S_M = \Delta S_M{}^{comb} + \Delta S_M{}^{cont} = -R\left(n_s \ln\phi_s + n_p \ln\phi_p + n_s \ln\phi_p a\right)$$

The change in Gibbs energy can be viewed as the energy lost due to entropy generating process, and for quasistatic mixing/diffusion process, the rate of change of ΔG_M can be written as

$$\Delta \dot{G}_M = -T\dot{S}_{gen} = \Delta \dot{H}_M - T\Delta \dot{S}_M$$

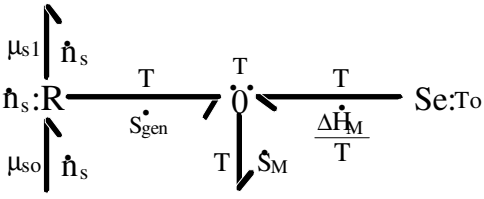
Also,

$$\Delta\dot{G}_M = \left(\frac{\partial \Delta G_M}{\partial n_s}\right)_{p,n_p,T} \frac{dn_s}{dt} + \left(\frac{\partial \Delta G_M}{\partial n_p}\right)_{p,n_s,T} \frac{dn_p}{dt} + \left(\frac{\partial \Delta G_M}{\partial T}\right)_{p,n_p,n_s} \frac{dT}{dt} + \left(\frac{\partial \Delta G_M}{\partial P}\right)_{n_s,n_p,T} \frac{dP}{dt}$$

Since $\left(\frac{\partial \Delta G_M}{\partial n_s}\right)_{p,n_p,T} = \Delta\mu_{s,M}, \ \frac{dn_p}{dt} = 0, \ \frac{dT}{dt} = 0, \ \frac{dP}{dt} = 0$

it simplifies to $\Delta\dot{G}_M = \Delta\mu_{s,M}\dot{n}_s = -T\dot{S}_{gen} = \Delta\dot{H}_M - T\Delta\dot{S}_M$

This entropy generation process can be modelled as a 3-port resistance field driven by the chemical potentials of solvents across the gel's control volume boundary.



Since the entropy and Gibbs free energy of gel system inside the control volume at are

$$S_{cv} = \Delta S_M + n_s s_s^o + n_p s_p^o, \ \ G_{cv} = \Delta G_M + n_s \mu_s^o + n_p \mu_p^o$$

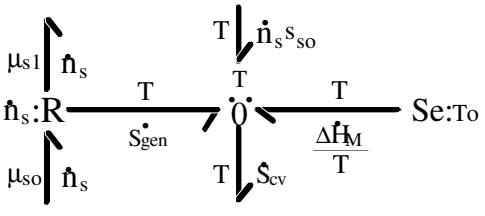
and s_s^o, n_p, s_p^o, μ_s^o, μ_p^o are constant during the process, the rate of change of S_{CV}, and G_{CV} with respect to time are

$$\dot{S}_{cv} = \Delta\dot{S}_M + \dot{n}_s s_s^o, \ \ \dot{G}_{cv} = \Delta\dot{G}_M + \dot{n}_s \mu_s^o$$

Combining the above results, we then have

$$\Delta\mu_{s,M}\dot{n}_s = -T\dot{S}_{gen} = \Delta\dot{H}_M - T\dot{S}_{cv} + T\dot{n}_s s_s^o$$

The bond graph structure of the polymer-solvent mixing/diffusion model is therefore



Note that the resistive R field in the bond graph is presented such that the kinetics of the solvent flow may depend on both the chemical potentials of solvent outside and inside the gel rather than just the net difference in chemical potential across the gel boundary. The phenomenological description of diffusion/mixing process is also needed here to relate the rate of solvent flow into the control volume to the chemical potentials of solvent. For initial investigation, a simple description of non-electrolyte solvent diffusion is employed;

$$\dot{n}_s = P(\mu_s^o - \mu_{s,M})$$

where P represents the permeability coefficient.

Rubber Elasticity

Flory's model

According to Flory's work, deformation of polymer gel network may be modelled as consisting of two step processes; first, expansion due to free swelling and second, stretching at constant volume, without changing the enthalpy of the gel system. Based on statistical theory of rubber elasticity where the end-to-end distances of the polymer chains can be described by the Gaussian distribution, the Gibb's free energy change, ΔG_{el}, and the entropy change, ΔS_{el}, due to elastic deformation are described by

$$\Delta G_{el} = -T\Delta S_{el}$$

$$\Delta S_{el} = -\left(\frac{k\nu_e}{2}\right)\left(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - \ln(\alpha_x\alpha_y\alpha_z)\right)$$

where k is the Boltzmann's constant,

ν_e is the effective number of chains in the gel,

α_x represents the elongation factor in x-axis; α_x = length/free length in x-axis

α_y represents the elongation factor in y-axis

α_z represents the elongation factor in z-axis.

Assume that the network formed at volume V_O is subsequently swollen isotropically by a diluent to a volume V such that the volume fraction of polymer is $\nu_2 = V_o / V$. In the subsequent deformation due to stretching, the volume is assumed constant. Letting α_x, α_y, and α_z represent the changes in dimensions resulting from the combination of swelling and elongation, we have therefore that $\alpha_x\alpha_y\alpha_z = 1/\nu_2$ is constant during the elongation. Considering only a simple elongation in the x-direction, let α represent the length in this direction relative to the swollen, unstretched length $L_{O,S} = (V/V_O)^{1/3} L_O$, since the swelling is isotropic, i.e.,

$$\alpha = L / L_{o,s}$$

Then

$$\alpha_x = \alpha\left(V/V_o\right)^{\frac{1}{3}} = \alpha / \nu_2^{1/3}$$

$$\alpha_y = \alpha_z = 1 / \left(\alpha^{1/2}\nu_2^{1/3}\right)$$

Substituting the above results, then

$$\Delta S_{el} = - \frac{k\, v_e}{2\, v_2^{2/3}} \left[\alpha^2 + 2/\alpha - 3 v_2^{2/3} + v_2^{2/3} \ln v_2 \right]$$

For the deformation process during swelling and stretching, the heat of deformation ΔH_{el} is considered negligible, and therefore the Gibbs free energy is then

$$\Delta G_{el} = -T\Delta S_{el} = \frac{Tk\, v_e}{2\, v_2^{2/3}} \left[\alpha^2 + 2/\alpha - 3 v_2^{2/3} + v_2^{2/3} \ln v_2 \right]$$

At contant temperature as assumed previously, ΔG_{el} is a function of the number of mole of solvent in the c.v. and the elongation, i.e., $\Delta G_{el} = \Delta G_{el}(n_s, \alpha)$. Taking the above result by Flory, then the rate of change of Gibb's free energy with respect to time can be represented as

$$\frac{d\Delta G_{el}}{dt} = \left(\frac{\partial \Delta G_{el}}{\partial n_s} \right)_{\alpha, T} \frac{dn_s}{dt} + \left(\frac{\partial \Delta G_{el}}{\partial \alpha} \right)_{n_s, T} \frac{d\alpha}{dt}$$

In addition,

$$\left(\frac{\partial \Delta G_{el}}{\partial n_s} \right)_{\alpha, T} = \Delta \mu_s, \quad \left(\frac{\partial \Delta G_{el}}{\partial \alpha} \right)_{n_s, T} = -T \left(\frac{\partial \Delta S_{el}}{\partial \alpha} \right)_{n_s}$$

and,

$$F = -T \left(\frac{\partial \Delta S_{el}}{\partial L_x} \right)_{n_s, T}, \quad \alpha = \frac{L_x}{L_{o,s,x}}$$

After combining the above result and little algebraic manipulations, we have

$$\frac{dG_{el}}{dt} = \frac{d\Delta G_{el}}{dt} = \Delta \mu_{s,el} \frac{dn_s}{dt} + F \frac{dL_x}{dt}$$

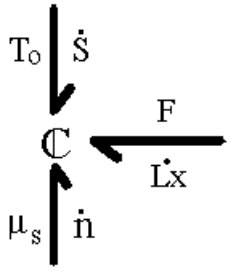
and

$$\frac{dS_{el}}{dt} = -\frac{1}{T} \left(\Delta \mu_{s,el} \frac{dn_s}{dt} + F \frac{dL_x}{dt} \right)$$

Since

$$\frac{dU_{el}}{dt} = \frac{dG_{el}}{dt} + T \frac{dS_{el}}{dt} = \Delta \mu_{s,el} \frac{dn_s}{dt} + F \frac{dL_x}{dt} + T \frac{dS_{el}}{dt}$$

the bondgraph structure for multiport capacitance due to rubber elasticity is



The validity of the Flory's assumption of modelling the deformation process as two step process should be checked. Specificially, researchers have observed that elongation of elastomeric polymer gel increases the swelling degree of the gel. In other words, stretching decreases the osmotic pressure of solvent inside the gel whereas compressing has reverse effect. Similarly, it also implies that the chemical potential of the solvent inside the gel should decrease when stretched and increase when compressed. However, it is found that the Flory's model does not predict such behavior according to the our preliminary results, but in fact predicts reverse effect. The validity of our results as well as the Flory's model of deformation effect need to be investigated further.

Simple Mechanical Model of the Rubber Elasticity Effect

The above theory on rubber elasticity of swelling gel by Flory is based on the complex statistical theory which remarkably relates how the molecular structure of elastomer responds to an applied strain to the macroscopic deformation behavior. However, this theory still offers only qualitative approximation to the actual behavior of elastomer, mainly due to the assumption that end-to-end distances of the chains can be described by the Gaussian distribution. Given such deficiency of statistical model, the purpose of this section is to describe the gel's elasticitic behavior with simpler mechanical analog; the springs.

Let's consider a unit cube of the isotropic gel where the opposite faces of the cube are linked by a mechanical spring in all three axes. These mechanical springs represents the rubber elasticity of the gel elastomer, and therefore their rest lengths are the linear dimensions of gel when it is fully contracted and free of external stress. In addition, the elastomer itself occupies a constant finite volume. Defining the control volume as the space occupied by the solvent only, the mechanical springs inside the control volume then may be treated as volume-less pure mechanical spring elements, and let's assume such control volume is still an isotropic cube for simplicity. Then, static force balance at each face of the control volume relates the pressures of solvent to the tensile force as

$$
\begin{aligned}
P_x A_x &= P_o A_x + F_x \\
P_y A_y &= P_o A_y + F_y \\
P_z A_z &= P_o A_z + F_z \\
A_x &= L_y L_z \\
A_y &= L_x L_z \\
A_z &= L_x L_y
\end{aligned}
$$

where A_x is the surface area of the face pointing in x-axis,

A_y is the surface area of the face pointing in y-axis,

A_z is the surface area of the face pointing in z-axis,

P_x is the pressure exerted on A_x by solvent inside c.v.,

P_y is the pressure exerted on A_y by solvent inside c.v.,
P_z is the pressure exerted on A_z by solvent inside c.v.,
P_o is the external solvent bath pressure,
F_x is the tensile force in x-axis,
F_y is the tensile force in y-axis,
F_z is the tensile force in z-axis,
L_x is the elongation is x-axis,
L_y is the elongation is y-axis,
L_z is the elongation is z-axis.

Assuming the uniform pressure P inside the control volume,

$$P_x = P_y = P_z = P$$

and modeling the mechanical spring as simple Hookean spring, the spring forces are then

$$F_x = K L_x$$
$$F_y = K L_y$$
$$F_z = K L_z$$

where K is the spring stiffness which may be linear or nonlinear.

For the simple case of uniaxial tension in x-axis, $L_y = L_z$ due to isotropy of gel, and thus

$$V = L_x L_y L_z = L_x L_y^2$$

where V is the volume of the solvent inside the control volume.

Combining above results, we get

$$\left(P - P_o\right)^3 + \frac{KF_x}{V}\left(P - P_o\right) - \frac{K^3}{V} = 0$$

where the solvent pressure P can be solved as a function of F_x and V.

Modeling the effect of rubber elasticity as purely mechanical, the change in chemical potential of solvent due to the rubber elasticity is then

$$\Delta\mu_{s,el} = \mu^o(T_o, P) - \mu^o(T_o, P_o)$$

In addition,

$$\Delta\mu^o = v_1^o \Delta P$$

where v_1^o is molar volume of pure solvent. Combining above two results, we get

$$\Delta\mu_{s,el} = v_1^o(P - P_o)$$

For the case of free swelling, the effect of rubber elasticity is

$$\Delta\mu_{s,el} = v_1^o K / V^{1/3}$$

and this result is consistent with Flory and Treloar.

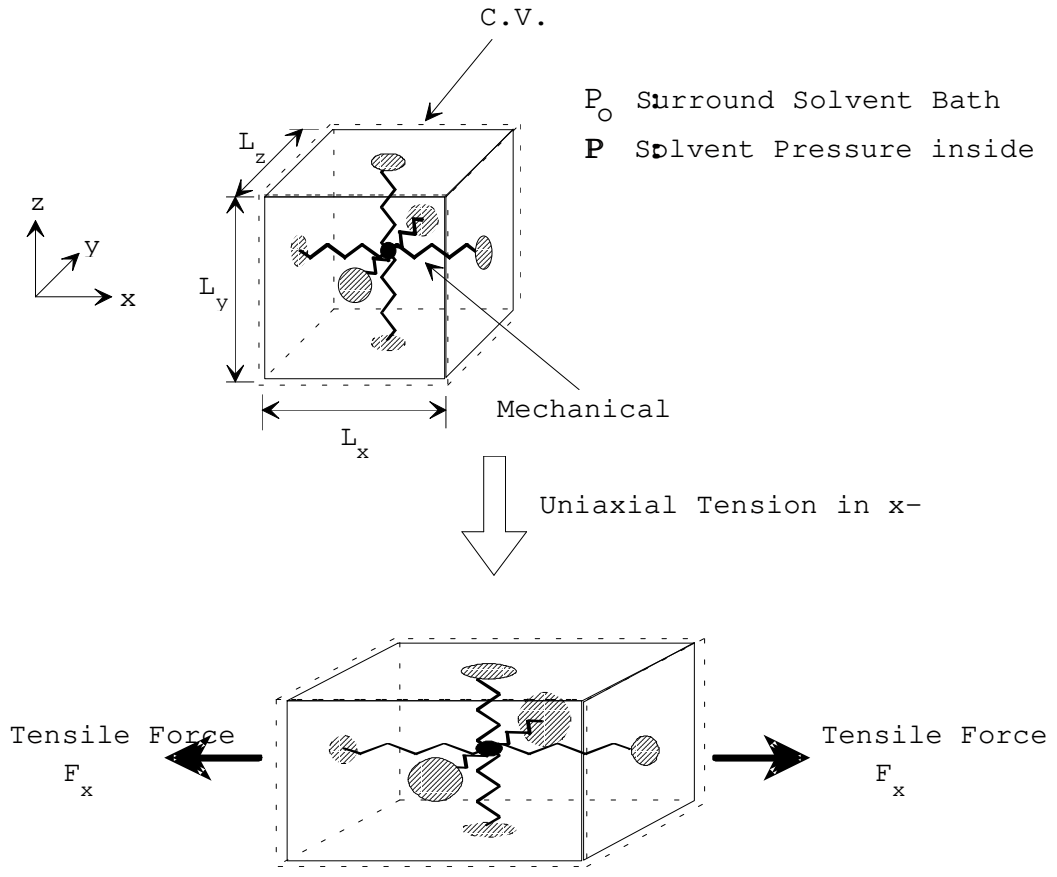


Figure: Mechanical model of isotropic gel elastomer under uniaxial tension.

According to above results based on simple mechanical spring, the effect of elongation/compression on the swelling degree of gel is in agreement with the observed behavior. The change in chemical potential of solvent inside the gel is directly proportional to the osmotic pressure, and both the solvent's chemical potential and osmotic pressure is decreased when elongated and increased when compressed. Before proceeding, however, one should note the limitations of this simple mechanical model, namely the lack of coupling between the mechanics and thermodynamics of the mechanical spring. With real elastomer, there is thermal-mechanical energy conversion, as Flory's model describes in terms of entropy change due to deformation. For instance, when the

elastomer is stretched, it is observed to grow warmer. Such energy coupling behavior is neglected in this simple pure mechanical spring model, and the importance of this coupling effect needs to be investigated further in order to validate this simple model.

Overall Process: Mixing/Diffusion and Deformation

Combining the previous results on mixing/diffusion process and the deformation process, we then have

$$\dot{S}_{cv} = \dot{S}_M + \dot{S}_{el}$$

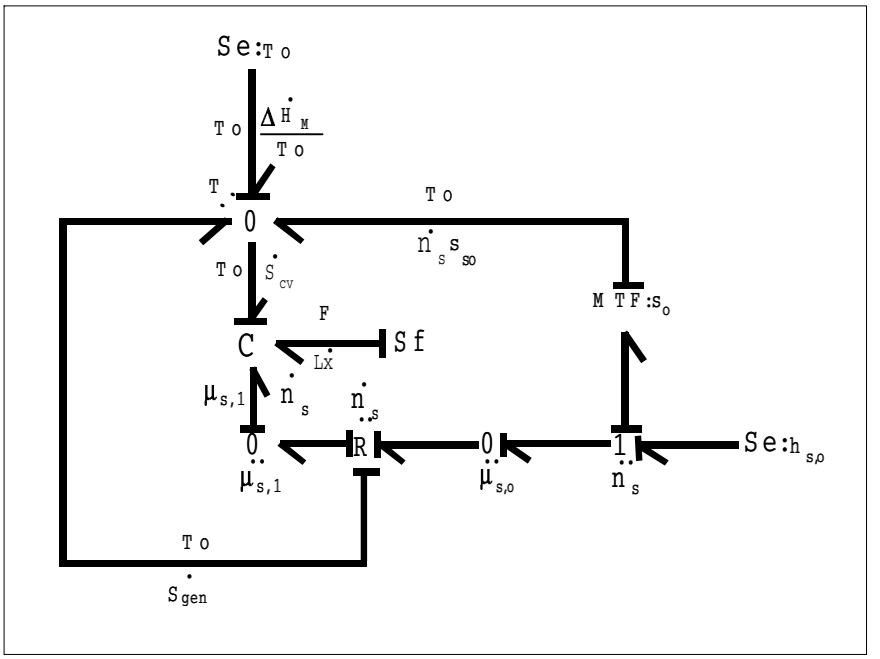
and, therefore

$$T\dot{S}_{cv} = \Delta\dot{H}_M + T\dot{n}_s s_s^o - \Delta\mu_s \dot{n}_s - F\dot{L}_x$$

where

$$\Delta\mu_s = (\Delta\mu_{s,M} + \Delta\mu_{s,el})$$

One should note that the mechanical force contribution in above equation is based on Flory's rubber elasticity model, and it does not show up explicitly in junction structure since it is embedded in the nature of multiport capacitance. Applying the integral causality to chemical and mechanical ports to the multiport capacitance field, the bond graph representation of the overall system is then



Note that for the surrounding solvent

$$h_s^{\,o} = \mu_s^{\,o} + Ts_s^o$$