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# On polymer network rupture in gels in the limit of very slow straining or a very slow crack propagation rate

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Abstract

The *J*-integral is formulated in a direct manner for a gel consisting of a cross-linked polymer network and a mobile solvent. The form of the *J*-integral is given for a formulation that exploits the Helmholtz energy density of the gel and expressions are provided for it in both the unswollen reference configuration of the polymer network and in the current swollen configuration of the gel when small strains are superimposed on the swollen state. Similarly, the form of the *J*-integral is developed for an approach that exploits the Landau energy density of the gel and its reference and current configuration expressions are also developed. The Flory-Rehner model of the gel is used to obtain expressions for both the densities of Helmholtz energy and the Landau energy, with the chemical potential of the solvent derived from the Helmholtz energy used in the Legendre transformation that generates the Landau energy. Both the Helmholtz and Landau energies are expanded asymptotically for small strains superimposed on the swollen state of the gel. The results for the various forms of the energies are then used to obtain the elasticity law and the incompressibility constraint for the gel, each derived from both the Helmholtz and the Landau energies. The results are then inserted into the *J*-integral and fracture mechanics insights obtained for the rapid and slow loading of a gel body with a stationary crack and for a gel body with a crack that is experiencing slow, steady propagation. It is found that the Landau energy form of the *J*-integral is particularly useful for the slow loading of stationary cracks and for the slow steady propagation of the crack. It is noted that solvent flux during crack growth can cause an increase in the effective fracture toughness of the gel. However, it is found that there is an absence of such diffusional toughening in the rapidly loaded stationary crack case, the very slowly loaded stationary crack case and for the crack experiencing extremely slow but steady propagation. It is further found that, for cracks propagating very slowly, diffusional toughening rises linearly with crack propagation rate up to a critical crack growth rate, above which the diffusional toughening becomes insensitive to the crack propagation rate. The critical crack propagation rate for this transition is found to be dependent on the linear dimension of the gel body and on constitutive parameters for the gel elasticity and solvent diffusion.

Dedication

This paper is dedicated to Professor Davide Bigoni on the occasion of his 60th birthday. RMM acknowledges many fruitful and helpful discussions and interactions with Professor Bigoni and

notes that RMM has learned much and enjoyed reading many of Professor Bigoni's papers, hearing his presentations at conferences and symposia, and from interactions in other fora such as doctoral examinations. RMM also looks forward to many more years of learning from and enjoying Professor Bigoni's elegant and enthusiastic approach to his subject, and also to his delightful company and friendship.

## Introduction

Gels are cross-linked polymer networks swollen by a solvent. As noted by Bouklas, Landis and Huang (2015), they have many uses that range from biomedical devices through actuators for soft robotics to switchable valves and permanent seals in fluidic systems. In these and other applications the rupture of the system by propagation of tears and cracks in the polymer network can undermine the material's utility. On the other hand, gels that are very tough can be synthesized and exploited. Bouklas *et al*. (2015) cite several papers in which the rupture and toughness of gels are considered. We note also the very high toughness of double and triple network polymer gel systems, such as those developed by Gong *et al*. (2003) and discussed by Gong (2010).

The free energy model of Flory and Rehner (1943) enables the analysis of gel swelling, and has been augmented by Hong *et al*. (2008) to address the elastic deformation of the polymer network and the gel's poroelastic response when the solvent diffuses through the network. Those developments were the foundation upon which Bouklas *et al*. (2015) constructed a model for crack propagation in gels, including the effect of dissipation associated with the necessary flux of the solvent when a rupture extends. The resulting theory has similarities to that used for poroelastic fracture mechanics often utilized in geomechanics (Kishimoto, Aoki and Sakata, 1980; Chien and Herrmann, 1996; Yang, Wang and Cheng, 2006). Similar models have also been exploited in the context of fracture when diffusing species are present (Gao and Zhou, 2013; Haftbaradaran and Qu, 2014). Noselli *et al*. (2016) developed their model of fracture by extending the preceding concepts to provide an approach in which small deformations are superimposed on a large degree of swelling. In that work, steady state crack propagation was considered and a cohesive zone model introduced to characterize rupture propagation in gels. Simulations were carried with and without the presence of the cohesive zone model, and it was found that in the absence of the cohesive zone model poroelastic toughening is independent of the crack propagation velocity under the small scale process zone assumption. Yu, Landis and Huang (2018b) carried out analysis of steady state crack propagation in a confined, strained strip of thick polymer gel, using both asymptotic analysis and the finite element method to obtain results. Similarly, Yu *et al*. (2018a) analyzed the time dependent crack tip fields for a center cracked specimen of polymer gel subject to step function boundary conditions in time by which the component was either subjected to a fixed strain or a fixed stress after their sudden application.

The purpose of the present paper is to provide derivations of conservation integrals relevant to fracture that have been introduced in the preceding contributions, but we develop them in a more straightforward and direct manner that elucidates more clearly their utility. In addition, we present some solutions for rupture propagation in gels that rely on limiting cases of relatively rapid and very slow straining of a gel body with a stationary crack, and very slow steady

extension of the polymer network crack. These cases are of some importance as they represent the conditions of greatest vulnerability of the polymer network in regard to fracture, as they are the states in which solvent diffusion dissipates the least energy per unit extension of the crack, and thus contributes the minimum in regard to resistance to propagation of the rupture.

Derivation of the *J*-integral for a gel

We first introduce the Helmholtz energy per unit reference volume of the gel as

$$\psi_o = \psi_o\left(F_{ij}, C, T\right) \tag{1}$$

where

$$F_{ij} = \frac{\partial x_i}{\partial X_j} \tag{2}$$

is the deformation gradient, $x_i$ is the position of a polymer element in the current configuration that has position $X_i$ in the reference state, with the reference state defined as the dry, unswollen polymer. The solvent concentration is $C$, defined as the number of moles of solvent per unit volume of the dry, unswollen polymer. The temperature is $T$. We note that the functional dependencies in Eq. (1) render it a special case as the Helmholtz energy density can, in general, be more complicated, such as where electrostatics contributes to the system behavior or chemical reactions take place in the material. However, Eq. (1) is sufficient for the analysis we carry out below.

We can now write

$$\frac{d\psi_o}{dt} = t_{ij}\frac{dF_{ji}}{dt} + \mu\frac{dC}{dt} - s\frac{dT}{dt} \tag{3}$$

where $t$ is time, $t_{ij}$ is the 1st Piola-Kirchhoff stress, $\mu$ is the chemical potential of the solvent and $s$ is the entropy per unit reference volume. As we will focus on isothermal conditions of a body at uniform temperature, we will take $dT/dt$ to be zero, and consider heat to be withdrawn from or injected into the body sufficiently fast that the isothermal condition can be maintained.

With $dT/dt = 0$, we integrate Eq. (3) over the body to obtain

$$\frac{d\Psi}{dt} = \int_{V_o}\frac{d\psi_o}{dt}dV_o = \int_{V_o} t_{ij}\frac{dF_{ji}}{dt}dV_o + \int_{V_o}\mu\frac{dC}{dt}dV_o \tag{4}$$

where $\Psi$ is the total Helmholtz energy of the body and $V_o$ is the reference volume of the body.

Next, we use the principle of virtual work to obtain

$$\frac{d\Psi}{dt} = \int_{A_o} T_i^o\frac{dx_i}{dt}dA_o + \int_{V_o}\mu\frac{dC}{dt}dV_o \tag{5}$$

where $A_o$ is the surface of the body in the reference state, and $T_i^o$ is the nominal surface traction.

Based on the approach of Rice (1968a), with further details given in Rice (1968b), we write the energy release rate, $G$, for a crack in the form

$$G\dot{a} = \int_{\Gamma_o} T_i^o \frac{dx_i}{dt} d\Gamma_o + \int_{A_o^\Gamma} \mu \frac{dC}{dt} dA_o - \frac{d}{dt}\int_{A_o^\Gamma} \psi_o dA_o \tag{6}$$

where $\dot{a}$ is the crack length extension rate, $\Gamma_o$ is a contour around the crack tip from one crack surface to another and $A_o^\Gamma$ is the area inside the contour. This setup is shown in Figure 1. The interpretation of the result in Eq. (6) is straightforward. The 1st two terms on the right hand side of Eq. (6) is the rate at which the material inside the contour can acquire an increase in its Helmholtz energy and the 3rd term is the actual rate of increase. The difference is the flux of Helmholtz energy to the crack tip. We note that such an energy balance can be constructed for any form of energy (*e.g.* internal energy, enthalpy, Helmholtz, Gibbs, or Landau energy or any other form that is consistently defined).

To calculate the desired result we introduce

$$\frac{d}{dt} = \frac{\partial}{\partial t} - \dot{a}\frac{\partial}{\partial X_1} \tag{7}$$

where, as usual, $d/dt$ is the material derivative with respect to time, $\partial/\partial t$ is the spatial derivative in a coordinate system convected with propagation of the crack (*i.e.* a coordinate system whose origin is at the current location of the crack tip) and $X_1$ is the coordinate parallel to the crack as shown in Figure 1.

Based on the approach of Rice (1968a, 1968b) we observe that

$$\frac{d}{dt}\int_{A_o^\Gamma} \psi_o dA_o = \int_{A_o^\Gamma} \frac{\partial \psi_o}{\partial t} dA_o - \dot{a}\int_{\Gamma_o} \psi_o N_1 d\Gamma_o \tag{8}$$

where $N_i$ is the outward unit normal to the contour in the reference configuration as shown in Figure 1. As a consequence, Eq. (6) becomes

$$G\dot{a} = \int_{\Gamma_o} T_i^o \frac{\partial x_i}{\partial t} d\Gamma_o + \int_{A_o^\Gamma} \mu \frac{\partial C}{\partial t} dA_o - \int_{A_o^\Gamma} \frac{\partial \psi_o}{\partial t} dA_o + \dot{a}\left[\int_{\Gamma_o}\left(\psi_o N_1 - T_i^o \frac{\partial x_i}{\partial X_1}\right) d\Gamma_o - \int_{A_o^\Gamma} \mu \frac{\partial C}{\partial X_1} dA_o\right] \tag{9}$$

By Eq. (5) the first 3 integrals sum to zero and we obtain

$$J = G = \int_{\Gamma_o}\left(\psi_o N_1 - T_i^o \frac{\partial x_i}{\partial X_1}\right) d\Gamma_o - \int_{A_o^\Gamma} \mu \frac{\partial C}{\partial X_1} dA_o \tag{10}$$

in agreement with Bouklas *et al*. (2015).

We repeat the derivation in the current, swollen configuration on the assumption that superimposed strains and displacements are small. The swollen configuration is a fixed one in equilibrium with the surrounding solvent pressure. The Helmholtz energy per unit swollen volume of the body is

$$\psi = \psi(\varepsilon_{ij}, c) \tag{11}$$

where we have assumed isothermal conditions. The strain beyond the purely swollen condition is

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \tag{12}$$

where $x_i$ is the position of a polymer element in the swollen configuration, $u_i$ is its displacement from that position and $c$ is the solvent concentration in moles per unit swollen volume. Note that we will treat $\psi$ as an increment of energy added to the Helmholtz energy in the purely swollen configuration. Therefore, in the purely swollen state before it is augmented by further deformation and concentration changes, $\psi = 0$. The Helmholtz energy density, $\psi$ , could be written as $\Delta\psi$ to emphasize this point, but for simplicity we omit the letter delta.

We can then write

$$\frac{d\psi}{dt} = \sigma_{ij}\frac{d\varepsilon_{ij}}{dt} + \mu\frac{dc}{dt} \tag{13}$$

where $\sigma_{ij}$ is the stress measured as force per unit swollen area.

We integrate Eq. (13) over the body to obtain

$$\frac{d\Psi}{dt} = \int_V \frac{d\psi}{dt}dV = \int_V \sigma_{ij}\frac{d\varepsilon_{ij}}{dt}dV + \int_V \mu\frac{dc}{dt}dV = \int_A T_i\frac{du_i}{dt}dA + \int_V \mu\frac{dc}{dt}dV \tag{14}$$

where $V$ is the volume of the body in the purely swollen state, $A$ is its surface and $T_i$ is the traction in equilibrium with $\sigma_{ij}$.

These results allow us to write the energy release rate, $G$, for a crack in the form

$$G\dot{a} = \int_\Gamma T_i\frac{du_i}{dt}d\Gamma + \int_{A^\Gamma}\mu\frac{dc}{dt}dA - \frac{d}{dt}\int_{A^\Gamma}\psi dA \tag{15}$$

where $\Gamma$ is a contour around the crack tip in the swollen configuration and $A^\Gamma$ is the area inside the contour. The configuration of the contour is analogous to that shown in Figure 1, but is in the swollen state of the gel. To calculate the desired result we introduce

$$\frac{d}{dt} = \frac{\partial}{\partial t} - \dot{a}\frac{\partial}{\partial x_1} \tag{16}$$

and observe that

$$\frac{d}{dt}\int_{A^\Gamma}\psi dA = \int_{A^\Gamma}\frac{\partial\psi}{\partial t}dA - \dot{a}\int_\Gamma \psi n_1 d\Gamma \tag{17}$$

where $n_i$ is the outward unit normal to the contour in the swollen configuration. As a consequence, Eq. (15) becomes

$$G\dot{a} = \int_\Gamma T_i\frac{\partial u_i}{\partial t}d\Gamma + \int_{A^\Gamma}\mu\frac{\partial c}{\partial t}dA - \int_{A^\Gamma}\frac{\partial\psi}{\partial t}dA + \dot{a}\left[\int_\Gamma\left(\psi n_1 - T_i\frac{\partial u_i}{\partial x_1}\right)d\Gamma - \int_{A^\Gamma}\mu\frac{\partial c}{\partial x_1}dA\right] \tag{18}$$

As noticed before, the first 3 integrals sum to zero and we obtain the *J*-integral in the swollen configuration as

$$J = G = \int_\Gamma\left(\psi n_1 - T_i\frac{\partial u_i}{\partial x_1}\right)d\Gamma - \int_{A^\Gamma}\mu\frac{\partial c}{\partial x_1}dA \tag{19}$$

as derived by Noselli *et al*. (2016).

To complete the set of *J*-integrals of interest, we introduce the Landau energy per unit reference volume as

$$L_o(F_{ij},\mu,T) = \psi_o - \mu C \tag{20}$$

from which we infer that, when temperature is allowed to change,

$$\frac{dL_o}{dt} = t_{ij}\frac{dF_{ji}}{dt} - C\frac{d\mu}{dt} - s\frac{dT}{dt} \tag{21}$$

By analogy to our derivation above, and due to the fact that the energy flux to the crack tip can be computed in terms of any consistent energy, in isothermal conditions of uniform temperature of the gel we obtain the *J*-integral in the reference configuration as

$$J = G = \int_{\Gamma_o}\left(L_o N_1 - T_i^o\frac{\partial x_i}{\partial X_1}\right)d\Gamma_o + \int_{A_o^\Gamma} C\frac{\partial\mu}{\partial X_1}dA_o \tag{22}$$

also in agreement with Bouklas *et al*. [1]. The result in the swollen configuration is

$$J = G = \int_\Gamma\left(L n_1 - T_i\frac{\partial u_i}{\partial x_1}\right)d\Gamma + \int_{A^\Gamma} c\frac{\partial\mu}{\partial x_1}dA \tag{23}$$

where *L* is the increment of Landau energy per unit swollen volume and will be used as an increment beyond the value in the purely swollen state. That is, in the purely swollen state before it is augmented by deformation and further changes to the solvent chemical potential, $L = 0$. A *J*-integral derived as a linearization of Eq. (22) and essentially identical to that in Eq. (23) was previously used by Yu *et al*. (2018a, 2018b).

<u>Helmholtz energy model for the gel</u>

Following Hong *et al*. (2008), Bouklas *et al*. (2015) and Noselli *et al*. (2016) we adopt the following version of the Flory-Rehner model for the Helmholtz energy:

$$\psi_o = \frac{1}{2}\tilde{G}_o\left(F_{ij}F_{ij} - 3\right) + RT\left[C\log\frac{\Omega C}{1+\Omega C} - \frac{\chi}{\Omega(1+\Omega C)}\right] + \Pi(\Omega C + 1 - J) \tag{24}$$

where $\tilde{G}_o$ is the shear modulus of the dry, unswollen polymer, $\Omega$ is the molar volume of the solvent, $\chi$ is a parameter, a constant, associated with the enthalpy of mixing of the solvent and the polymer network, $J$ is the determinant of $F_{ij}$ and $\Pi$ is a Lagrange multiplier enforcing the incompressibility constraint, $\Omega C + 1 = J$, on the solvent and the molecules of the polymer network combined. That is, the polymer network expands by increasing the space between chains but the exact volume occupied by the monomers of the polymer network remains unchanged. The solvent is assumed incompressible. Obviously, the logarithmic term arises from the entropy of mixing and the term quadratic in the deformation gradient arises from the entropy of the deformed polymer network. The form in the parenthesis with coefficient $\tilde{G}_o/2$ in Eq. (24) can be derived directly from Gaussian statistics of freely-jointed polymer chains subjected to deformation $F_{ij}$ (Treloar, 1975). For that reason we adopt the form in Eq. (24) as the simplest free energy model for the deformation of the polymer network. However, other models can be used, including the very similar one used by Hong *et al*. (2008), Bouklas *et al*. (2015) and Yu *et al*. (2018a, 2018b) and the more complicated one utilized by Cohen and McMeeking (2019).

In the reference configuration, which, as noted above, is the dry, unswollen polymer network, $F_{ij} = \delta_{ij}$, $J = 1$ and $C = 0$, where $\delta_{ij}$ is the Kronecker delta. When the dry polymer network is placed in the solvent, it swells to $J > 1$. The 1st Piola-Kirchhoff stress is then, in general, including response to any deformation imposed on the system,

$$t_{ij} = \frac{\partial\psi_o}{\partial F_{ji}} = \tilde{G}_o F_{ji} - \Pi J F_{ij}^{-1} \tag{25}$$

and the chemical potential of the solvent is

$$\mu = \frac{\partial\psi_o}{\partial C} = RT\left[\log\frac{\Omega C}{1+\Omega C} + \frac{1+\Omega C+\chi}{(1+\Omega C)^2}\right] + \Pi\Omega \tag{26}$$

In equilibrium, the chemical potential is equal to that of the solvent external to the gel.

*Pure swelling of the gel*

Now consider the polymer network swollen uniformly to $J = J_o$ without distortion and to be in equilibrium with a liquid external solvent. Therefore,

$$F_{ij} = F_{ij}^o = J_o^{1/3}\delta_{ij} \tag{27}$$

The incompressibility constraint provides

$$\Omega C = \Omega C_o = J_o - 1 \tag{28}$$

and the chemical potential of the solvent satisfies

$$\mu = RT\left[\log\frac{\Omega C_o}{1+\Omega C_o} + \frac{1+\Omega C_o+\chi}{(1+\Omega C_o)^2}\right] + \Pi_o\Omega = p_e\Omega \tag{29}$$

where $p_e$ is the pressure in the external solvent. The stress must be in equilibrium with this pressure so that

$$\tilde{G}_o J_o^{-1/3} - \Pi_o = -p_e \tag{30}$$

We eliminate the external pressure and the Lagrange multiplier and substitute using Eq. (28) and obtain

$$\Omega\tilde{G}_o J_o^{-1/3} + RT\left[\log\frac{J_o-1}{J_o} + \frac{J_o+\chi}{J_o^2}\right] = 0 \tag{31}$$

which can then be solved to compute the degree of swelling. Once that is done, the solvent concentration is computed from Eq. (28) and the Lagrange multiplier is

$$\begin{aligned}\Pi_o = p_e + \frac{\tilde{G}_o}{J_o^{1/3}} = p_e + \frac{\tilde{G}_o}{(1+\Omega C_o)^{1/3}} &= p_e - \frac{RT}{\Omega}\left[\log\frac{J_o-1}{J_o} + \frac{J_o+\chi}{J_o^2}\right] \\ &= p_e - \frac{RT}{\Omega}\left[\log\frac{\Omega C_o}{1+\Omega C_o} + \frac{1+\Omega C_o+\chi}{(1+\Omega C_o)^2}\right]\end{aligned} \tag{32}$$

where we have identified the 4 equivalent expressions that arise from the equilibrium conditions.

*Small deformations of a swollen gel*

Now, following Lucantonio and Nardinocchi (2012), superimpose a small deformation on the swollen state of the gel with the external pressure in the solvent held fixed. As a result, the deformation gradient becomes

$$F_{ij} = F^1_{ik}F^o_{kj} = \left(\delta_{ik} + \frac{\partial u_i}{\partial x_k}\right)J_o^{1/3}\delta_{kj} = J_o^{1/3}\left(\delta_{ij} + \frac{\partial u_i}{\partial x_j}\right) \tag{33}$$

where $F^1_{ik} = \left(\delta_{ik} + \frac{\partial u_i}{\partial x_k}\right)$ is the small deformation. From Eq. (25) we obtain the Cauchy stress as

$$\sigma_{ij} = \frac{\tilde{G}_o}{J_o^{1/3}}\left(\delta_{ij} + \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \varepsilon_V\delta_{ij}\right) - \Pi\delta_{ij} \tag{34}$$

where $\varepsilon_V = \varepsilon_{kk}$ is the volumetric strain superimposed on the swollen configuration and we have neglected higher order terms. This allows us to conclude that the shear modulus for the swollen gel is $\tilde{G}_o/J_o^{1/3}$.

To proceed further, we return to Eq. (24) and specialize it to purely dilatant conditions, to obtain

$$\psi_o = \frac{1}{2}\tilde{G}_o\left(3J^{2/3} - 3\right) + RT\left[C\log\frac{\Omega C}{1+\Omega C} - \frac{\chi}{\Omega(1+\Omega C)}\right] + \Pi(\Omega C + 1 - J) \tag{35}$$

We expand this around the purely swollen configuration and obtain, to 2nd order, with the contribution from deviatoric strain, $\varepsilon_{ij}^d$, added,

$$\psi_o\left(F_{ij}, C, \Pi\right) = \psi_o\left(F_{ij}^o, C_o, \Pi_o\right) + (\Pi - \Pi_o + p_e)[\Omega(C - C_o) - J_o\varepsilon_V] + J_o^{2/3}\tilde{G}_o\varepsilon_{ij}^d\varepsilon_{ij}^d - \frac{1}{6}\tilde{G}_o J_o^{2/3}\varepsilon_V^2 + \frac{1}{2}RT\left[\frac{1 + \Omega C_o - 2\chi\Omega C_o}{C_o(1 + \Omega C_o)^3}\right](C - C_o)^2 \tag{36}$$

We then convert the result in Eq. (36) to give the change of energy per unit swollen volume to obtain

$$\psi = (\Pi - \Pi_o + p_e)[\Omega(c - c_o) - \varepsilon_V] + \frac{\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d\varepsilon_{ij}^d - \frac{\tilde{G}_o}{6J_o^{1/3}}\varepsilon_V^2 + \frac{RT\Omega}{2}\left[\frac{J_o - 2\chi(J_o - 1)}{(J_o - 1)J_o^2}\right](c - c_o)^2 \tag{37}$$

where $c_o$ is the concentration per unit swollen volume that is equivalent to $C_o$. The constitutive behavior is then

$$\sigma_{ij} = \frac{\partial\psi}{\partial\varepsilon_{ij}} = -(\Pi - \Pi_o + p_e)\delta_{ij} + \frac{2\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d - \frac{\tilde{G}_o}{3J_o^{1/3}}\varepsilon_V\delta_{ij} \tag{38}$$

$$\mu = \frac{\partial\psi}{\partial c} = (\Pi - \Pi_o + p_e)\Omega + RT\Omega\left[\frac{J_o - 2\chi(J_o - 1)}{(J_o - 1)J_o^2}\right](c - c_o) \tag{39}$$

complemented by the incompressibility constraint

$$0 = \frac{\partial\psi}{\partial\Pi} = \Omega(c - c_o) - \varepsilon_V \tag{40}$$

Note that $p_e - \Pi_o$ in these equations may be rewritten using the 1st of Eq. (32) to read

$$p_e - \Pi_o = -\frac{\tilde{G}_o}{J_o^{1/3}} \tag{41}$$

However, for the following manipulations we find it more convenient to leave the equations in the form given. We now enforce the constraint in Eq. (40), and evaluate $\Pi - \Pi_o$ in terms of other variables to obtain

$$\Pi - \Pi_o + p_e = \frac{\mu}{\Omega} - \frac{RT}{\Omega}\left[\frac{J_o - 2\chi(J_o - 1)}{(J_o - 1)J_o^2}\right]\varepsilon_V \tag{42}$$

We substitute this into the expression for the stress and find

$$\sigma_{ij} = \frac{2\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d + \left\{\frac{RT}{\Omega}\left[\frac{J_o - 2\chi(J_o-1)}{(J_o-1)J_o^2}\right]\varepsilon_V - \frac{\tilde{G}_o}{3J_o^{1/3}}\varepsilon_V - \frac{\mu}{\Omega}\right\}\delta_{ij} \tag{43}$$

This can be rewritten as

$$\sigma_{ij} = 2\tilde{G}\varepsilon_{ij}^d + \left(\kappa\varepsilon_V - \frac{\mu}{\Omega}\right)\delta_{ij} \tag{44}$$

where

$$\tilde{G} = \frac{\tilde{G}_o}{J_o^{1/3}} \tag{45}$$

$$\kappa = \frac{RT}{\Omega}\left[\frac{J_o - 2\chi(J_o-1)}{(J_o-1)J_o^2}\right] - \frac{\tilde{G}}{3} \tag{46}$$

as given by Noselli *et al*. (2016). Furthermore, with the constraint of Eq. (40) enforced, Eq. (37) becomes

$$\psi = \frac{\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d\varepsilon_{ij}^d - \frac{\tilde{G}_o}{6J_o^{1/3}}\varepsilon_V^2 + \frac{RT}{2\Omega}\left[\frac{J_o - 2\chi(J_o-1)}{(J_o-1)J_o^2}\right]\varepsilon_V^2 = \tilde{G}\varepsilon_{ij}^d\varepsilon_{ij}^d + \frac{1}{2}\kappa\varepsilon_V^2 \tag{47}$$

as given by Noselli *et al*. (2016).

Now return to Eq. (37) & (39). The latter result allows us to compute the Landau energy per unit swollen volume as

$$L = -(\Pi - \Pi_o + p_e)\varepsilon_V + \frac{\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d\varepsilon_{ij}^d - \frac{\tilde{G}_o}{6J_o^{1/3}}\varepsilon_V^2 - \frac{[\mu - (\Pi - \Pi_o + p_e)\Omega]^2}{2RT\Omega\left[\frac{J_o - 2\chi(J_o-1)}{(J_o-1)J_o^2}\right]} - (\mu - p_e\Omega)c_o \tag{48}$$

The constitutive response is then

$$\sigma_{ij} = \frac{\partial L}{\partial \varepsilon_{ij}} = -(\Pi - \Pi_o + p_e)\delta_{ij} + \frac{2\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d - \frac{\tilde{G}_o}{3J_o^{1/3}}\varepsilon_V\delta_{ij} \tag{49}$$

$$c = -\frac{\partial L}{\partial \mu} = c_o + \frac{\mu - (\Pi - \Pi_o + p_e)\Omega}{RT\Omega\left[\frac{J_o - 2\chi(J_o-1)}{(J_o-1)J_o^2}\right]} \tag{50}$$

along with the constraint of

$$0 = \frac{\partial L}{\partial \Pi} = \frac{\mu - (\Pi - \Pi_o + p_e)\Omega}{RT\left[\frac{J_o - 2\chi(J_o-1)}{(J_o-1)J_o^2}\right]} - \varepsilon_V \tag{51}$$

If we combine Eq. (50) & (51), we find that the result is consistent with Eq. (40), ensuring that the kinematic constraint is satisfied.

Now rearrange Eq. (51) to read

$$\Pi - \Pi_o + p_e = \frac{\mu}{\Omega} - \frac{RT}{\Omega}\left[\frac{J_o - 2\chi(J_o - 1)}{(J_o - 1)J_o^2}\right]\varepsilon_V \tag{52}$$

We substitute this into Eq. (49) to find

$$\sigma_{ij} = \frac{2\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d + \left(\frac{RT}{\Omega}\left[\frac{J_o - 2\chi(J_o - 1)}{(J_o - 1)J_o^2}\right]\varepsilon_V - \frac{\tilde{G}_o}{3J_o^{1/3}}\varepsilon_V - \frac{\mu}{\Omega}\right)\delta_{ij} \tag{53}$$

identical to Eq. (43). Therefore, Eq. (44) to (46) are valid for this setting.

The Landau energy from Eq. (48) is

$$\begin{aligned} L &= \frac{\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d\varepsilon_{ij}^d - \frac{\tilde{G}_o}{6J_o^{1/3}}\varepsilon_V^2 + \frac{RT}{2\Omega}\left[\frac{J_o - 2\chi(J_o - 1)}{(J_o - 1)J_o^2}\right]\varepsilon_V^2 - \frac{\mu}{\Omega}\varepsilon_V - (\mu - p_e\Omega)c_o \\ &= \tilde{G}\varepsilon_{ij}^d\varepsilon_{ij}^d + \frac{1}{2}\kappa\varepsilon_V^2 - \frac{\mu}{\Omega}\varepsilon_V - (\mu - p_e\Omega)c_o \end{aligned} \tag{54}$$

<u>Application to a crack</u>

*Rapid strain limit when small strains are superimposed on the swollen state*

For relatively rapid straining there is negligible time for diffusion to reconfigure the solvent distribution, and thus, to leading order, $c = c_o$; Eq. (40) then requires that $\varepsilon_V = 0$, so that incompressible conditions determine the response. As can be inferred from Eq. (44), with $\varepsilon_V = 0$ the chemical potential of the solvent divided by its molar volume responds as a pressure to enable satisfaction of the equations that govern stress and deviatoric strain. Therefore, the solution for stress and strain around the crack tip is that which prevails for an isotropic, incompressible, linear elastic material. As in any incompressible material, only the deviatoric strains contribute to the strain energy, in this case via the Helmholtz energy density as given in Eq. (47) with $\varepsilon_V = 0$.

Because the solvent concentration is uniform, the result in Eq. (19) is purely a line integral. The integral is path independent, and its form is exactly that which applies to an isotropic, incompressible, linear elastic material. As a result, the crack tip stress field has a square root singularity and conforms to the usual linear elastic, isotropic stress field at a crack tip.

We assume that the fracture toughness of the gel is due to the polymer network alone and is such that

$$G = G_c \tag{55}$$

Therefore, in plane strain Mode I the crack will propagate when

$$K_I = K_C^u = 2\sqrt{\tilde{G}G_c} \tag{56}$$

as determined by the incompressible response, where $K_I$ is the Mode I stress intensity factor and $K_c^u$ is its critical value for rupture propagation with undrained response (*i.e.* at a relatively high rate of loading).

We note that in this situation there is no toughening arising from solvent diffusion as that does not occur. As a consequence, the stress intensity factor computed from stress and strain results far from the crack tip will give the same value as that which arises from stress and strains close to the crack tip. This is an obvious consequence of the path independence of the integral in Eq. (19) and the fact that it is purely a line integral.

We note that Yu *et al*. (2018a) have carried out a numerical solution of the crack tip field after instantaneous, step loading of a center cracked panel of a polymer gel and provided results at a time immediately after the cessation of the rapid increase in load; as done by Yu *et al*. (2018a) we will designate that solution to prevail at time $t = 0^+$ where $t = 0$ is the time at which the step function of load is applied. As an outcome of their analysis they found that the stress intensity factor at time $t = 0^+$, through immediate poroelastic toughening due to solvent diffusion, falls to a value $K_{I0}/[2(1-\nu)]^{0.735}$ where $K_{I0}$ is the value of $K_I$ produced by the step loading, *i.e.* at $t = 0$ and $\nu = \left(3\kappa - 2\tilde{G}\right)/\left(6\kappa + 2\tilde{G}\right)$ is the effective Poisson ratio of the polymer gel. This result found by Yu *et al*. (2018a) is consistent with analysis by Atkinson and Craster (1991). Thus it appears that the stress intensity factor, after rising instantaneously to $K_{I0}$, immediately falls to the lower value. As a consequence, continued crack growth would appear to require a higher value of the stress intensity factor than given in Eq. (56) to allow for this sudden drop. We do not explore this aspect of the behavior of the system.

*Slow strain limit when small strains are superimposed on the swollen state*

We assume that the polymer network is in the fully immersed condition with all of its surfaces free to exchange solvent with the surrounding bath. In that case, for relatively slow straining the solvent, to 1st order, remains in equilibrium with the surrounding environment, *i.e.* $\mu = p_e\Omega$, and does so by diffusing through the polymer network while it strains. This condition implies that the diffusion lengthscale has exceeded all dimensions of the polymer gel body. We note that this diffusion length scale, effectively determining the size of the crack tip process zone, is inversely proportional to the crack propagation velocity as given below in Eq. (74) (Bouklas *et al*., 2015; Noselli *et al*., 2016; Yu *et al*., 2018b).

As a consequence of this condition, Eq. (53) & (54) become

$$\sigma_{ij} = -p_e\delta_{ij} + \frac{2\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d + \left(\frac{RT}{\Omega}\left[\frac{J_o - 2\chi(J_o-1)}{(J_o-1)J_o^2}\right] - \frac{\tilde{G}_o}{3J_o^{1/3}}\right)\varepsilon_V\delta_{ij} = -p_e\delta_{ij} + 2\tilde{G}\varepsilon_{ij}^d + \kappa\varepsilon_V\delta_{ij} \tag{57}$$

$$L = \frac{\tilde{G}_o}{J_o^{1/3}}\varepsilon_{ij}^d\varepsilon_{ij}^d + \frac{1}{2}\left(\frac{RT}{\Omega}\left[\frac{J_o - 2\chi(J_o - 1)}{(J_o - 1)J_o^2}\right] - \frac{\tilde{G}_o}{3J_o^{1/3}}\right)\varepsilon_V^2 - p_e\varepsilon_V$$
$$= \tilde{G}\varepsilon_{ij}^d\varepsilon_{ij}^d + \frac{1}{2}\kappa\varepsilon_V^2 - p_e\varepsilon_V \tag{58}$$

Because the solvent chemical potential is uniform, the result in Eq. (23) is purely a line integral. For its computation, we use the results in Eq. (57) & (58) with $p_e = 0$ as the terms containing it, by the divergence theorem, contribute zero to the integral. As the integral is path independent, and its form is exactly that which prevails for an isotropic, compressible, linear elastic material, the crack tip stress field has a square root singularity and conforms to the usual linear elastic, isotropic stress field at a crack tip. This result was also obtained by Yu *et al*. (2018a) for the long term limit for a center cracked panel under constant applied load.

We assume, as before, that the fracture toughness of the gel is due to the polymer network alone and is such that

$$G = G_c \tag{59}$$

Therefore, in Mode I the crack will propagate when

$$K_I = K_C^d = \sqrt{\frac{4\tilde{G}(\tilde{G}+3\kappa)G_c}{4\tilde{G}+3\kappa}} = K_C^u\sqrt{\frac{\tilde{G}+3\kappa}{4\tilde{G}+3\kappa}} \tag{60}$$

where $K_C^d$ is the critical value of the Mode I stress intensity factor in the drained condition (*i.e.* for low rates of loading, straining and crack propagation). From Eq. (44) to (46) we find that this result provides

$$K_C^d = \sqrt{\frac{\frac{RT}{\Omega}\left[\frac{J_o-2\chi(J_o-1)}{(J_o-1)J_o^2}\right]}{\frac{RT}{\Omega}\left[\frac{J_o-2\chi(J_o-1)}{(J_o-1)J_o^2}\right]+\frac{\tilde{G}_o}{J_o^{1/3}}}}\,2\sqrt{\tilde{G}G_c} = \sqrt{\frac{\left[\frac{J_o-2\chi(J_o-1)}{(J_o-1)J_o^2}\right]}{\left[\frac{J_o-2\chi(J_o-1)}{(J_o-1)J_o^2}\right]-\left[\log\frac{J_o-1}{J_o}+\frac{J_o+\chi}{J_o^2}\right]}}\,2\sqrt{\tilde{G}G_c} \tag{61}$$

The coefficient in the form of the square root of a quotient on the RHS of Eq. (60) is less than unity. These results point to delayed fracture where a gel is loaded at a high rate to $K_I$ such that $K_C^d < K_I < K_C^u$ and, then, $K_I$ is held constant. If crack growth does not immediately occur, it will eventually set in.

For example, consider a through crack of length $2a$ in a large plane strain sample of swollen gel. Assume that such a sample is rapidly loaded by an in-plane biaxial stress $\sigma_a$ that is superimposed on the solvent pressure by being applied directly to the polymer network. Upon such loading of the gel, the stress intensity factor for the crack will be

$$K_I = K_{I0} = \sigma_a\sqrt{\pi a} \tag{62}$$

We choose the value of this stress intensity factor to be infinitesimally higher than $K_C^d$ but lower than $K_C^u$. Therefore, the crack will not propagate to begin with, as the value of $K_I$ that is finally imposed is less than $K_C^u$, the value that has to be reached if the crack is to propagate without solvent diffusion taking place. Now consider the applied stress $\sigma_a$ to be held constant and stipulate that the crack does not propagate until the chemical potential of the solvent is uniform. At first, the stress intensity factor and the value of the *J*-integral will fall suddenly to their values relevant at time $t = 0^+$(Yu *et al*., 2018a). The solvent will diffuse to equalize its chemical potential, after which the stress field will satisfy Eq. (57), *i.e*. linear elasticity, and the result in Eq. (23) will be purely a line integral. As a result, the crack tip field will have a square root singularity, the stress intensity factor will be given by Eq. (62) once more and it will lie infinitesimally above $K_C^d$. This will allow the crack to propagate, but its growth rate will be slow as solvent diffusion must occur to enable the chemical potential of the solvent to remain equalized so that the fracture propagation criterion continues to be met.

The previous paragraph demonstrates that, in the circumstances described, delayed crack propagation must eventually occur. Furthermore, Yu *et al*. (2018a) have shown through numerical results that a center cracked panel of polymer gel with the applied tractions held fixed will experience a monotonically increasing value of the *J*-integral from its magnitude at time $t = 0^+$ to the value that is consistent with the chemical potential at equilibrium. Therefore, crack propagation will only occur in such circumstances after enough time has elapsed for the solvent chemical potential to equalize. Furthermore, this outcome demonstrates that, for conditions in which the applied load is instantaneously imposed and then held steady, the fracture toughness of the gel in terms of stress intensity factor is given by Eq. (60) and (61) and that it controls crack propagation such that it occurs in a delayed manner.

We note that in the situation of very slow straining of the pre-swollen gel there is no toughening arising from solvent diffusion, even though such diffusion is taking place while the gel strains. This situation prevails because the straining is very slow and the resulting dissipation associated with solvent diffusion is negligible. As a consequence, the stress intensity factor computed from stress and strain results far from the crack tip will give the same result as that which arises from stress and strains close to the crack tip. This is an obvious consequence of the path independence of the integral in Eq. (23) and the fact that it is purely a line integral.

The comment of the previous paragraph is also applicable to a crack that is growing very slowly in steady state and for which the stress intensity factor is held constant at $K_C^d$. This observation is in contrast to results given by Noselli *et al*. (2016) in their Figure 5 for steady state crack propagation. The results appear to show diffusional toughening associated with the solvent even for very slow crack propagation, as the figure indicates that the stress intensity factor computed in the far field is then greater than that computed at the crack tip. This implies that energy is dissipated by solvent diffusion around the crack tip. However, we interpret those results to arise when crack propagation is relatively rapid, but in a gel for which the network toughness approaches zero. This condition arises because of the constraint used by Noselli *et al*. (2016) that the strain response in the far field is incompressible. In contrast, for a crack that is truly propagating slowly, solvent diffusion would allow volumetric straining in the far field.

In addition, Yu *et al*. (2018b) have provided asymptotic and numerical results for steady state propagation of a crack in a thick, plane strain, confined strip of polymer gel of infinite length. They find that there will be poroelastic toughening even in the case of a crack that is growing extremely slowly. This result seems to contradict our conclusions for cracks that are growing extremely slowly. However, we note that in the problem tackled by Yu *et al*. (2018b) the diffusion length scale can never exceed the length of the strip as the latter is infinite. Therefore, even as the diffusion length scale diverges towards extreme magnitudes as the crack velocity is reduced, the process zone size for the crack is always less than the half-length of the strip. As a consequence, there will always be poroelastic toughening in the solutions obtained by Yu *et al*. (2018b) even as crack velocities are approached that are extremely slow. Thus, there is no contradiction with our results for fully immersed polymer gels when the crack velocity is extremely slow.

*Estimate of diffusional toughening for cracks that are growing slowly in steady state*
We have demonstrated that there is no diffusional toughening for cracks that are growing extremely slowly in fully immersed polymer gels, but have observed that diffusional flux of the solvent does occur in that case in the near tip field. To estimate how much toughening this flux may cause for cracks that are growing slowly rather than extremely slowly, we consider the near tip strain field for a crack that is growing slowly at a constant Mode I crack tip stress intensity factor $K_I = K_C^d$. The relevant infinitesimal strain is the dilatation given by

$$\varepsilon_V = \frac{K_C^d}{\left(\kappa+\frac{\tilde{G}}{3}\right)\sqrt{2\pi r}}\cos\frac{\theta}{2} \tag{63}$$

which corresponds to Eq. (17) of Noselli *et al*. (2016). As the crack grows at a steady rate $\dot{a}$, the material dilatational strain rate is, from Eq. (7),

$$\frac{d\varepsilon_V}{dt} = -\dot{a}\frac{\partial\varepsilon_V}{\partial x_1} = \frac{\dot{a}K_C^d}{2\left(\kappa+\frac{\tilde{G}}{3}\right)\sqrt{2\pi}r^{3/2}}\cos\frac{3\theta}{2} \tag{64}$$

Conservation of mass for the solvent provides

$$\frac{d\varepsilon_V}{dt} + \Omega\frac{\partial h_i}{\partial x_i} = 0 \tag{65}$$

where $h_i$ is the solvent flux and the diffusion law is of the Darcy form

$$h_i = -M\frac{\partial\mu}{\partial x_i} \tag{66}$$

where $M$ is the solvent mobility. As a result, the governing equation for the solvent chemical potential is

$$\frac{\partial^2\mu}{\partial x_i\partial x_i} = \frac{\dot{a}K_C^d}{2M\Omega\left(\kappa+\frac{\tilde{G}}{3}\right)\sqrt{2\pi}r^{3/2}}\cos\frac{3\theta}{2} \tag{67}$$

The boundary conditions in terms of $\theta$ are $\mu(\pm\pi) = 0$. As noted by Noselli *et al*. (2016), based on a work by Atkinson and Craster (1991), the solution to leading order at the crack tip is

$$\mu = p_e\Omega - \left[\frac{\dot{a}K_C^d}{4M\Omega\left(\kappa+\frac{\tilde{G}}{3}\right)}\sqrt{\frac{r}{2\pi}}\cos\frac{3\theta}{2} - K_2\sqrt{r}\cos\frac{\theta}{2}\right] \tag{68}$$

where the term containing $K_2$ is the homogeneous solution and we have included the uniform term $p_e\Omega$ for completeness. We disregard $K_2$ as it has no influence on our subsequent results and regard the term in brackets in Eq. (68) to be a small perturbation of the otherwise uniform solvent chemical potential, $p_e\Omega$, when the crack is growing slowly.

Now consider Eq. (19) in the form

$$\int_\Gamma \left(\psi n_1 - T_i\frac{\partial u_i}{\partial x_1}\right) d\Gamma = G_C + \int_{A^\Gamma} \mu\frac{\partial c}{\partial x_1} dA \tag{69}$$

and define

$$G_C^A = \int_{\tilde{\Gamma}} \left(\psi n_1 - T_i\frac{\partial u_i}{\partial x_1}\right) d\Gamma \tag{70}$$

where $\tilde{\Gamma}$ is a contour far from the crack tip. The integral in Eq. (70) is computed from stresses that are controlled by elasticity; to infer this see Eqs. (47) & (44) but recall that the dominant term in the chemical potential in Eq. (44) is the uniform value $p_e\Omega$ so that $\mu/\Omega$ is dominated by the uniform pressure $p_e$. Thus, $G_C^A$ is the apparent energy release rate computed in the far field, and is related to the near tip value of the energy release rate by

$$G_C^A = G_C + \int_{A^{\tilde{\Gamma}}} \mu\frac{\partial c}{\partial x_1} dA \tag{71}$$

The difference between $G_C^A$ and $G_C$ is thus the dissipation due to solvent flux.

From Eq. (40) we observe that $\varepsilon_V = \Omega(c - c_o)$ and therefore

$$G_C^A - G_C = \int_{A^{\tilde{\Gamma}}} \frac{\mu}{\Omega}\frac{\partial \varepsilon_V}{\partial x_1} dA = \frac{\dot{a}\left(K_C^d\right)^2}{16\pi M\Omega^2\left(\kappa+\frac{\tilde{G}}{3}\right)^2}\int_0^R dr\int_{-\pi}^{\pi}\cos^2\frac{3\theta}{2}d\theta = \frac{\dot{a}\left(K_C^d\right)^2 R}{16M\Omega^2\left(\kappa+\frac{\tilde{G}}{3}\right)^2} \tag{72}$$

where the upper limit of the radial integral, $R$, a value to be determined, is considered to be representative of the size of the near tip region within which solvent flux is significant.

As noted by Noselli *et al*. (2016), in an infinite body the crack problem is characterized by two length scales. A diffusional length scale in the gel is given by

$$l_d = \sqrt{M\Omega^2\left(\kappa + \frac{4\tilde{G}}{3}\right)t} \tag{73}$$

and is relevant before crack propagation occurs. The other length scale in an infinite body relates to the crack growth rate once crack propagation begins, and is given by

$$l_g = \frac{M\Omega^2\left(\kappa+\frac{4\tilde{G}}{3}\right)}{\dot{a}} \tag{74}$$

The significance of $l_g$ can be understood as follows. As observed in the numerical results of Noselli *et al*. (2016), a crack steadily growing in a large, essentially infinite body perturbs the solvent distribution by causing it to diffuse around the crack tip and does so to a significant extent out to a distance of $\gamma l_g$ from the crack tip. Here $\gamma$ is a constant of order one that in general may depend upon the Poisson ratio of the gel. Beyond a radius equal to $\gamma l_g$ there is negligible solvent flux.

Now consider a fully immersed gel body of finite size, characterized by $L$. There are now 2 length scales of significance during crack growth, $l_g$ and $L$. From the results of Noselli *et al*. (2016) we conclude that if $L >> \gamma\, l_g$, the gel body is essentially infinite in size as far as diffusion is concerned when solvent flux is driven by crack growth; the upper limit $R$ in Eq. (72) should then be chosen to be $\gamma l_g$, as selected by Noselli *et al*. (2016). If $L < \gamma\, l_g$, solvent flux during crack growth extends out to $r = L$, and so the entire body is engaged in the dissipation associated with solvent flux. In this situation, the upper limit $R$ in Eq. (72) should be chosen to be $L$.

First consider the case of $L < \gamma l_g$ so that $R = L$. In that case, Eq. (72) becomes

$$G_C^A = G_C + \frac{\dot{a}\left(K_C^d\right)^2 L}{16M\Omega^2\left(\kappa+\frac{\tilde{G}}{3}\right)^2} \tag{75}$$

an expression that provides an estimate for $G_C^A$ as based on the asymptotic fields of Eqs. (63) & (68). We conclude therefore that the diffusional toughening for slowly growing cracks is proportional to the rate of growth. Note also from Eq. (60) that Eq. (75) can be rewritten as

$$G_C^A = \left[1 + \frac{\dot{a}L\tilde{G}}{4M\Omega^2\left(\kappa+\frac{\tilde{G}}{3}\right)\left(\kappa+\frac{4\tilde{G}}{3}\right)}\right] G_C \tag{76}$$

We infer that this result is valid for gel bodies with sizes, $L$, up to approximately $\gamma l_g$ and note that when $L = \gamma l_g$ Eq. (76) leads to

$$G_C^A = \left(1 + \frac{\gamma}{4}\frac{\tilde{G}}{\kappa+\frac{\tilde{G}}{3}}\right) G_C \tag{77}$$

Now consider the case of $L >> \gamma l_g$ such that $R = \gamma l_g$. Of course, also in this case Eq. (72) leads to Eq. (77)

$$G_C^A = G_C + \frac{\gamma}{16}\frac{\dot{a}\left(K_C^d\right)^2 l_g}{M\Omega^2\left(\kappa+\frac{\tilde{G}}{3}\right)^2} = G_C + \frac{\gamma}{16}\frac{\left(K_C^d\right)^2\left(\kappa+\frac{4\tilde{G}}{3}\right)}{\left(\kappa+\frac{\tilde{G}}{3}\right)^2} \tag{78}$$

When we use Eq. (60), Eq. (78) converts to be Eq. (77).

Thus our picture is that, for crack growth rates $\dot{a}$ less than $M\Omega^2\left(\kappa + 4\tilde{G}/3\right)/L$, the effective toughness of the gel rises linearly with $\dot{a}$, obeying Eq. (76), but above that crack growth rate the effective toughness plateaus at the value given in Eq. (77).

We note again that there is no contradiction between our results as stated in Eq. (76) and those of Yu *et al*. (2018b) for crack growth in an infinitely long polymer gel strip. In the case of the work of Yu *et al*. (2018b), the characteristic size of the strip is always infinite and in all cases $L > l_g$. Therefore, the solutions of Yu *et al*. (2018b) are never in the limit where $L < l_g$ that we have considered to obtain our slow crack propagation result.

## Conclusions

For stationary cracks that are loaded very rapidly, there is no toughening associated with the presence of the solvent in a gel and the toughness for crack propagation in terms of energy release rate is that of the polymer network. For stationary cracks that are loaded extremely slowly, the situation is the same because solvent diffusion is then so sluggish that the dissipation it causes upon crack extension is negligible. Therefore, the toughness, when measured in terms of energy release rate, for very rapid loading and very slow loading of the gel is the same. However, due to the incompressibility constraint that prevails during rapid loading and the dilatational relaxation that occurs in the gel during very slow straining, the toughness of the gel, when measured in terms of stress intensity factor, is lower during extremely slow straining compared to that which prevails during very rapid straining. This suggests that delayed fracture can occur in a gel with a crack when it is rapidly loaded to a stress level that is subcritical for propagation upon rapid loading, but above the critical level for extremely slow loading.

We also find that toughening due to the dissipation associated with solvent flux occurs for steady state crack propagation. In particular, the energy release rate decreases linearly with crack propagation rate, when such a rate is very low. Above a critical rate of crack propagation, the magnitude of diffusional toughening becomes independent of the crack growth rate. The critical rate of crack propagation for this transition is determined by the size of the gel body in combination with constitutive parameters for both the elasticity of the gel and the solvent diffusion.

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**Figures**

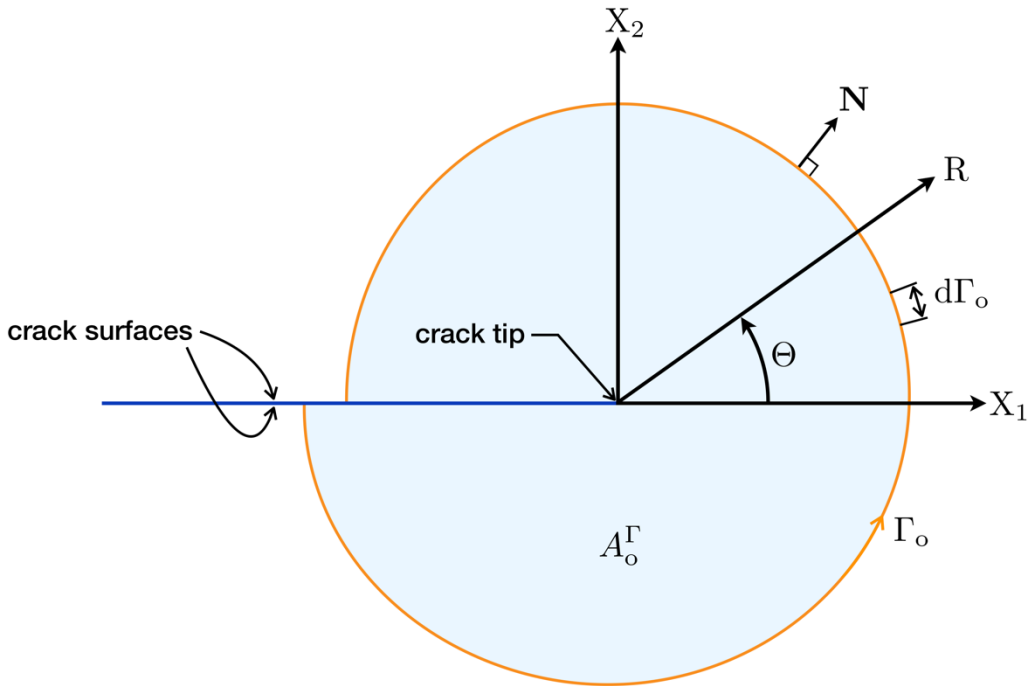


**Figure 1**. Contour around the crack trip for the *J*-integral shown in the reference configuration.