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RESEARCH ARTICLE

Swelling of ferrogels in uniform magnetic field – A theoretical approach

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Abstract

Magnetic field sensitive gels (ferrogels or magnetoelasts) are three-dimensional cross-linked networks of flexible polymers swollen by ferrofluids or magnetic fluids. The influence of external magnetic field on the equilibrium swelling degree is the subject of this study. Using thermodynamic arguments it is shown that uniform external field may result in deswelling of the ferrogels at high field intensities.

Keywords

Ferrogel · magnetoelast · magnetic nanoparticles · ferrofluid

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1 Introduction

A new type of magnetoelastic or magnetostrictive materials has been developed recently by introducing finely distributed colloidal particles into chemically cross-linked swollen polymer network [1-22]. Magnetic field sensitive gels, generally referred as ferrogels are soft composite systems consisting of a rubbery polymer matrix (chemically cross-linked network) loaded with finely dispersed ferro- ferri- or superparamegnetic particles having Langevin type magnetisation. The magnetic particles are fixed to the network chains by strong adsorptive forces. Their motion is due to the fluctuation of network chains. No macroscopic migration can occur.

A comprehensive study of the effect of uniform field on the swelling behaviour is still missing. It is therefore a major objective of this work to build a significant understanding of the swelling behaviour of ferrogels under the action of uniform external magnetic field. We consider here a highly swollen chemically crosslinked network swollen in charge free organic liquid under good solvent condition. The gel contains randomly distributed magnetic particles showing superparamagnetic behaviour.

2 The swelling equilibrium under uniform magnetic field

In the absence of an external magnetic field, a ferrogel presents a swelling behaviour very close to that of a swollen filler-loaded network. The chemical potential of the swelling agent (denoted by index 1), $\Delta\mu_1$ can be expressed as the sum of mixing-,$\Delta\mu_{1,mix}$ elastic, $\Delta\mu_{1,el}$ contributions:

$$\Delta\mu_1 = \Delta\mu_{1,mix} + \Delta\mu_{1,el} \tag{1}$$

These quantities can be derived from free energy of the elastic- and mixing interactions [23].

$$\Delta\mu_{1,mix} = RT\left[\ln\left(1-\Phi_P\right) + \Phi_P + \chi_H\Phi_P^2\right] \tag{2}$$

$$\Delta\mu_{1,el} = RTA\nu^* q_o^{-2/3}\Phi_P^{1/3} \tag{3}$$

where $\Phi_P$represents the volume fraction of the polymer in the gel, $\chi_H$stands for the Huggins interaction parameter, q_0 is the so called memory term, which is often identified as concentration of the polymer solution during cross-linking and ν^* means the concentration of the elastically active network chains in the dry state. A is used as a model parameter with a value of 1 or 1/2. R and T is the gas constant and temperature, respectively.

Fig. 1 shows the dependence of chemical potentials $\Delta\mu_{1,mix}$, $\Delta\mu_{1,el}$ and $\Delta\mu_1$on the volume fraction of the polymer. In equilibrium with pure solvent Eq.1 can be written as $\Delta\mu_1 = 0$.Thus

$$\begin{aligned} &RT\left[\ln\left(1-\Phi_e\right)+\Phi_e+\chi_H\Phi_e^2\right]+ \\ &+RTA\nu^* q_o^{-2/3}\Phi_e^{1/3}=0 \end{aligned} \tag{4}$$

where Φ_e denotes the volume fraction of the polymer in swelling equilibrium. The solution of Eq.4 for Φ_e gives the dependence of swelling degree ($q_V = 1/\Phi_e$) on different quantities, like $\chi_H\left(T\right)$ and ν^*.

A description of the effect of magnetic field on the thermodynamic properties requires the adoption of the magnetic energy as additional interaction energy. We consider here a piece of ferrogel under the action of a homogeneous magnetic field. The magnetic induction B, the magnetic field strength H and the magnetic moment per unit volume m are all parallel. The Gibbs free energy can be expressed as:

$$dG = Vdp - SdT + \sum_i \mu_i dn_i + \mu_o H dM \tag{5}$$

where $M = V \cdot m$ is the total magnetic moment in the gel of volume V.

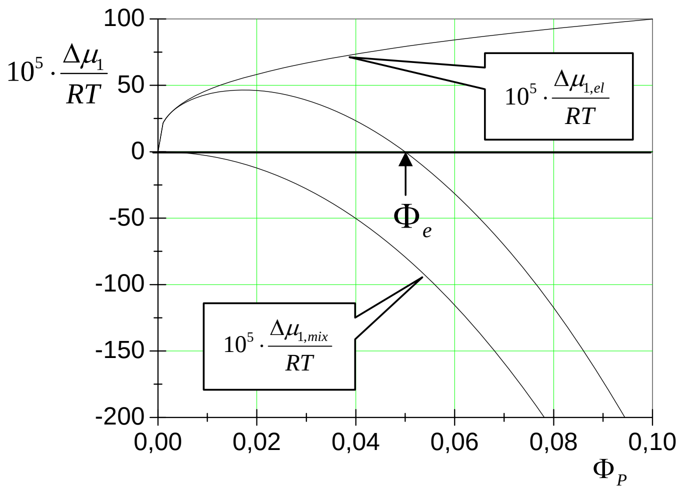

Fig. 1. Components of the chemical potential of the swelling agent as a function of volume fraction of the polymer. For the calculation $\chi_H = 0.3$ and $A\nu^* q_o^{-2/3} = 2.15 \cdot 10^{-3}$ was used.

In order to study the effect of the external magnetic field on the swelling equilibrium we rewrite Eq.5 by introducing a new function $G - \mu_o HM$, which is a Legendre transformation of the Gibbs free energy function of G.

$$d\left(G - \mu_o HM\right) = Vdp - SdT + \sum_i \mu_i dn_i - \mu_o M dH \tag{6}$$

We also assume that the saturation magnetization occurs at very high magnetic field intensities. Taking into account Eq.6.

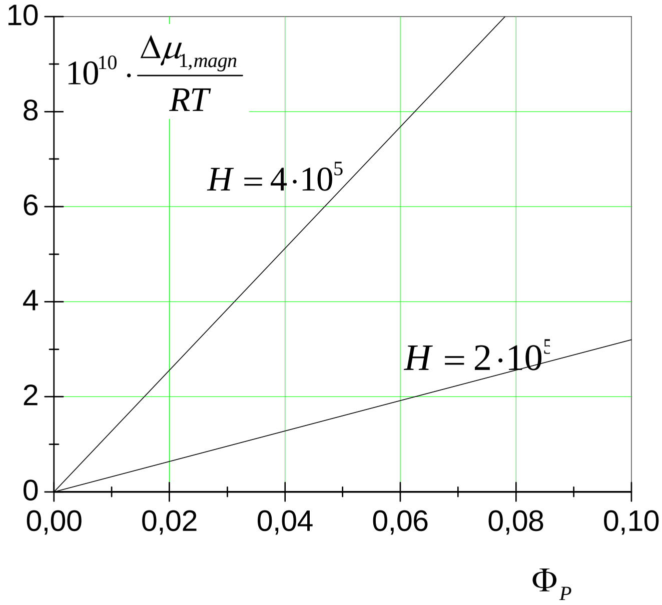

Fig. 2. Dependence of magnetic chemical potential on the volume fraction of the polymer at two field intensities given in the Figure in A/m unit. For the calculation $\frac{\mu_o k_\chi V_1 v_m}{2RT v_p} = 8 \cdot 10^{-10}$ was used.

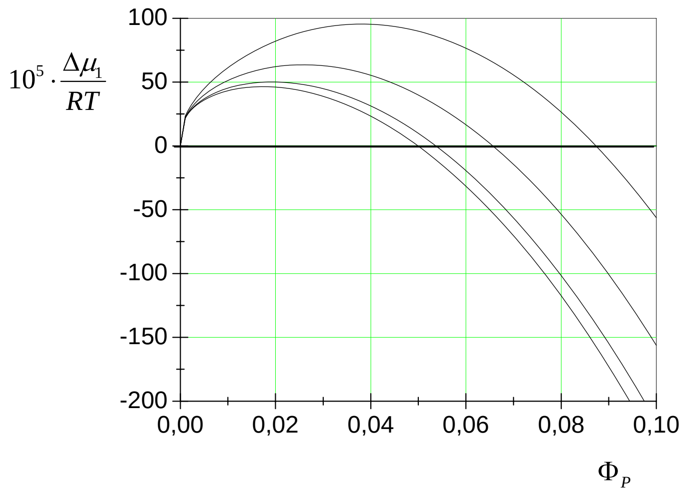

Fig. 3. The influence of magnetic field on the chemical potential. The magnetic field strength varies from left to right as $10^{-5} \cdot H$=0, 5, 10 and 15 A/m.

with constant temperature and pressure, a Maxwell relation gives

$$\left(\frac{\partial\mu_1}{\partial H}\right)_{T,P,n_2} = -\mu_o V H \left(\frac{\partial\chi_m}{\partial n_1}\right)_{T,P,H,n_2} \tag{7}$$

where χ_m represents the molar magnetic susceptibility and the subcript 1 stands for the swelling agent. The magnetic susceptibility of ferrogel samples was found to be linearly dependent on the concentration of magnetic particles [9].

$$\chi_m = k_\chi \Phi_m = k_\chi \frac{v_m}{v_p}\Phi_P \tag{8}$$

where Φ_m stands for the volume fraction of the magnetite in the whole gel, v_m and v_p denotes the volume of the magnetic material and the polymer in the gel, respectively. The quantity k_χ was found to be 0.338 for magnetite loaded hydrogels [9].

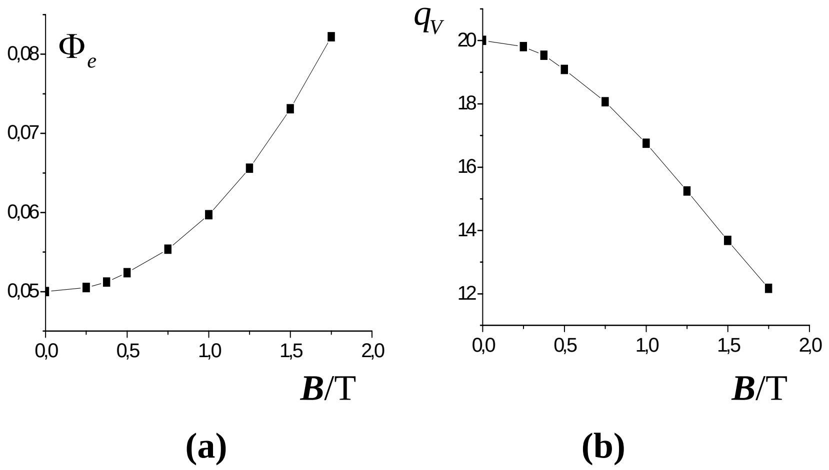

Fig. 4. The influence of magnetic induction on the equilibrium volume fraction (a), as well as the equilibrium swelling degree (b) of the ferrogel.

The quantities in Eq. (7) (V, n_1 and χ_m) can be related to the volume fraction Φ_P of the polymer in the gel.

$$V\left(\frac{\partial \chi_m}{\partial n_1}\right)_{T,P,H,n_2} = -k_\chi V_1 \frac{v_m}{v_p}\Phi_P \tag{9}$$

where V_1 denotes the partial molar volume of the solvent which is considered to be constant.

Combination of Eqs. (7) and (9) results in

$$\left(\frac{\partial \mu_1}{\partial H}\right)_{T,P,n_2} = \mu_o k_\chi V_1 \frac{v_m}{v_p}\Phi_P H \tag{10}$$

where μ_1 represents the magnetic contribution of the chemical potential of ferro fluid. After integration we have for the magnetic contribution of the swelling agent:

$$\Delta\mu_{1,magn}\left(\Phi_P, H\right) = \frac{1}{2}\mu_o k_\chi V_1 \frac{v_m}{v_p}\Phi_P \cdot H^2 \tag{11}$$

This equation says that the magnetic interaction increases the chemical potential of the swelling agent. A linear dependence of $\Delta\mu_{1,magn}$ on the volume fraction of the polymer has been obtained, as shown in Fig. 2.

The dependence of the chemical potential of the swelling agent on the network parameter and on the magnetic field strength can be expressed as:

$$\begin{aligned} \tfrac{\Delta\mu_1}{RT} &= \left[\ln\left(1-\Phi_P\right) + \Phi_P + \chi_H \Phi_P^2\right] + \\ &+ A\nu^* q_o^{-2/3}\Phi_P^{1/3} + \tfrac{\mu_o k_\chi V_1}{2RT}\tfrac{v_m}{v_p}\Phi_P \cdot H^2 \end{aligned} \tag{12}$$

Fig. 3 shows the effect of magnetic field intensity on the dependence of $\Delta\mu_1$ on the polymer concentration.

The condition of swelling equilibrium under uniform magnetic field can be expressed as follows:

$$\Delta\mu_1 = \Delta\mu_{1,mix} + \Delta\mu_{1,el} + \Delta\mu_{1,magn} = 0 \tag{13}$$

$$\begin{aligned} &\ln\left(1-\Phi_e\right) + \Phi_e + \chi_H \Phi_e^2 + \\ &+ A\nu^* q_o^{-2/3}\Phi_e^{1/3} + \frac{\mu_o k_\chi V_1}{2RT}\frac{v_m}{v_p}\Phi_e \cdot H^2 = 0 \end{aligned} \tag{14}$$

Numerical solution of the above equation provides the equilibrium concentration as a function of magnetic field intensity. This is shown in Fig. 4. Not only the equilibrium volume fraction, Φ_e but also the swelling degree defined as $q_V = 1/\Phi_e$ is shown in the figure.

On the basis of these figures it can be concluded that significant effect of magnetic field on the equilibrium swelling degree can be expected at high field intensities. At small field intensities ($0 \le B \le 300mT$) the change in the equilibrium swelling degree is comparable with the experimental accuracy. As the field intensity increases ($B \ge 300mT$), significant decrease of the swelling degree is expected. Swelling experiments have shown that in the range of ($0 \le B \le 300mT$), no volume change was detected.

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