

TABLE II. Pseudo-Gruneisen parameter for binary molten alkali chlorides.

System	x_{NaCl}	T (K)	Γ_{cal}	Γ_{expt}	Average % deviation
(Li-Na)Cl	0.5	1073	0.82	0.83	-1.2
(Na-K)Cl	0.207	1073	0.96	1.03	-12.6
	0.512	1073	0.87	0.99	
	0.729	1073	0.83	0.97	
(Na-Rb)Cl	0.25	1073	0.99	1.05	-16.97
	0.50	1073	0.86	1.00	
	0.75	1073	0.77	0.98	
(Na-Cs)Cl	0.25	1073	0.67	0.96	-25.8
	0.50	1073	0.79	0.88	
	0.75	1073	0.68	0.85	

$$\theta_2 = 1 - \theta_1 = \frac{\psi_2}{\psi_2 + \psi_1 (V_2^*/V_1^*)^{1/3}} \quad (11)$$

The interaction parameter X_{12} has been evaluated following Berthelot's approximation for monopolar species and is expressed as

$$X_{12} = P_1^* \left[1 - \left(\frac{V_2^*}{V_1^*} \right)^{1/6} \left(\frac{P_2^*}{P_1^*} \right)^{1/2} \right]^2 \quad (12)$$

The experimental values of the pseudo-Gruneisen parameter were calculated using Eq. (2). The values of γ and α used were taken from literature.⁸⁻¹¹

The results of the pure components are given in Table I. On a perusal of the table, we find an excellent agreement of the calculated and experimental values.

The results of binary alkali chlorides (Table II) although within range of error show greater deviation. This deviation increases with increase in the size of the second component. The reason for the deviation could be explained on account of the variation of the expansiv-

ities and compressibilities with increase in the concentration of the second (heavier) component.

The free spaces between the molecules are gradually occupied, resulting in changes of α and β_T which give rise to deviations. Another reason for the discrepancies could be the assumption incorporated in the formulation of the interaction parameter, the shortcomings of which are discussed in Flory's original paper.⁵

The expansivities and compressibilities remain unaffected at a single temperature in the case of pure molten salts, thus minimising the deviations between experimental and calculated values in these systems.

We can also arrive at the conclusive juncture that Flory's theory has universal applicability, and need not be restricted to molecular liquids.

We extend our united thanks to the University Grants Commission, New Delhi, India for financial aid.

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Transverse modes in polymer gels^{a)}

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(Received 22 January 1982; accepted 30 March 1982)

Two recent articles^{1,2} have addressed the dynamics of polymer gels on the basis of a coupled elastic (for the polymer network) and hydrodynamic (for the solvent) model. Such a description bears a close resemblance to models that have been developed for flow in porous media.³ Earlier, less complete forms of the model have been employed to describe polarized light scattering⁴ and sound attenuation⁵ in polymer gels which depend upon *longitudinal modes*. Relatively less attention^{1,4} has been given to the *transverse modes* which are impor-

tant for various phenomena such as depolarized light scattering.^{4,6} Whereas a previous article² focused on the propagation wave vectors of the elastodynamic modes, considered as a complex function of a real valued frequency $k(\omega)$, the purpose of this note is to summarize the behavior of those modes in a form appropriate to light scattering experiments; the frequency is considered to be a complex valued function of the real valued scattering wave vector $\omega(k)$. This is done in the limits of both strong and weak frictional coupling be-

tween network and solvent.

The model equations of motion for a two-component solid/fluid system are²

$$(\rho_{11} + \rho_{12}) \frac{\partial^2 \mathbf{s}}{\partial t^2} + \rho_{12} \left(\frac{\partial^2 \mathbf{d}}{\partial t^2} - \frac{\partial^2 \mathbf{s}}{\partial t^2} \right) = P \nabla (\nabla \cdot \mathbf{s}) + Q \nabla (\nabla \cdot \mathbf{d}) - \mu \nabla \times \nabla \times \mathbf{s} + f \left[\frac{\partial \mathbf{d}}{\partial t} - \frac{\partial \mathbf{s}}{\partial t} \right], \quad (1a)$$

$$(\rho_{22} + \rho_{12}) \frac{\partial^2 \mathbf{d}}{\partial t^2} + \rho_{12} \left(\frac{\partial^2 \mathbf{s}}{\partial t^2} - \frac{\partial^2 \mathbf{d}}{\partial t^2} \right) = R \nabla (\nabla \cdot \mathbf{d}) + Q \nabla (\nabla \cdot \mathbf{s}) + (\eta_v + \frac{4}{3} \eta_s) \nabla \left(\nabla \cdot \frac{\partial \mathbf{d}}{\partial t} \right) - \eta_s \nabla \times \nabla \times \frac{\partial \mathbf{d}}{\partial t} - f \left[\frac{\partial \mathbf{d}}{\partial t} - \frac{\partial \mathbf{s}}{\partial t} \right], \quad (1b)$$

where $\mathbf{s}[\mathbf{d}]$ is the displacement and ρ_{ij} combinations of the density $\rho_n[\rho_o]$ of the network [solvent]; f is the friction coefficient between the two. $\eta_s[\eta_v]$ is the macroscopic shear [bulk] viscosity of the solvent component. The quantities P , Q , R , μ are known functions of the various elastic constants; in Ref. 2 it is shown that for low frequency (so that the viscous skin depth is large compared to pore dimensions) and dilute gel concentration, y , the model may be reduced to

$$\rho_n \frac{\partial^2 \mathbf{s}}{\partial t^2} = -\mu \nabla \times \nabla \times \mathbf{s} + (\kappa + 4\mu/3) \nabla (\nabla \cdot \mathbf{s}) + y c_0^2 \rho_o \nabla (\nabla \cdot \mathbf{d}) - f \left[\frac{\partial \mathbf{s}}{\partial t} - \frac{\partial \mathbf{d}}{\partial t} \right], \quad (2a)$$

$$\rho_o \frac{\partial^2 \mathbf{d}}{\partial t^2} = c_0^2 \rho_o \nabla (\nabla \cdot \mathbf{d}) - \eta_s \nabla \times \nabla \times \frac{\partial \mathbf{d}}{\partial t} + \left(\eta_v + \frac{4\eta_s}{3} \right) \nabla \left(\nabla \cdot \frac{\partial \mathbf{d}}{\partial t} \right) + y c_0^2 \rho_o \nabla (\nabla \cdot \mathbf{s}) - f \left[\frac{\partial \mathbf{d}}{\partial t} - \frac{\partial \mathbf{s}}{\partial t} \right]. \quad (2b)$$

Here, c_0 is the speed of sound in the solvent. As indicated in Ref. 2, these equations are the same as those presented in Ref. 1.

The transverse modes are determined by substituting Fourier coefficients $\exp[-i\mathbf{k} \cdot \mathbf{r} + i\omega t]$ for \mathbf{s} and \mathbf{d} and setting the longitudinal components equal to zero. The resulting dispersion equation is

$$\omega \left[\left(\omega^2 - \frac{\mu k^2}{\rho_n} \right) \left(\omega - \frac{i\eta_s k^2}{\rho_o} \right) - (if/\rho_o \rho_n) (\omega^2 \rho_T - \mu k^2 - i\omega \eta_s k^2) \right] = 0, \quad (3)$$

where $\rho_T = \rho_o + \rho_n$. We ignore the mode $\omega = 0$ and assume viscosity is "small" so that $\sqrt{\rho_n} \eta_s k / \rho_T \sqrt{\mu} \ll 1$.

In the limit of no coupling [$f = 0$] we recover three modes; $\omega_{\pm}^0 = \pm (\mu k^2 / \rho_n)^{1/2}$ that describe the propagating shear waves in the network and $\omega_3^0 = i\eta_s k^2 / \rho_o$ that describes the diffusive transverse mode. For small friction [i.e., $f/\rho_n \ll (\omega_{\pm}^0, \omega_3^0)$] there will be corrections to these modes. One finds

$$\omega_{\pm} = \omega_{\pm}^0 + (if/2\rho_n) \quad \text{and} \quad \omega_3 = \omega_3^0 + if/\rho_o.$$

The more interesting case is for large friction which causes the network and the solvent to tend to move together as an average medium.^{1,2} In the limit $f \rightarrow \infty$ one finds

$$\omega_{\pm}^{\infty} = \frac{i\eta_s k^2}{2\rho_T} \pm \frac{1}{2} \left[\left(\frac{i\eta_s k^2}{\rho_T} \right)^2 + \frac{4k^2 \mu}{\rho_T} \right]^{1/2} - \pm \sqrt{\frac{\mu k^2}{\rho_T}} \quad (4)$$

for the propagating shear modes and a "fast" mode $\omega_3^{\infty} = if\rho_T/\rho_o\rho_n$. Corrections to this limit are $\omega_{\pm} = \omega_{\pm}^{\infty} + i\Gamma k^2$ where $\Gamma = [(\eta_s/2\rho_T) + (\mu\rho_o^2/2f\rho_T^2)]$ for the propagating modes and $\omega_3 = \omega_3^{\infty} + i(\eta_s k^2/\rho_o)$ for the fast mode. Thus for large friction ($f/\rho_o \gg \omega_{\pm}^{\infty}$), one predicts the light scattering spectrum to consist of a broad central peak of width $|\omega_3|$, and two sidebands of width Γk^2 which are split by amounts ω_{\pm}^{∞} from the central peak. As noted previously,² this is in sharp contrast to the previous prediction⁴ which follows from the uncoupled network dispersion equation.

The transverse modes $\omega_{\pm}(k)$ as derived here are identical to the low frequency limit shear modes derived previously,² $\lim_{\omega \rightarrow 0} k(\omega) = \pm \sqrt{(\rho_T/\mu)} \omega$. The mode $\omega_3(k)$ is the small wave vector limit of the mode whose low frequency behavior was derived previously,² $\lim_{\omega \rightarrow 0} k(\omega) = i\sqrt{f/\eta}$ signifying the inability of this transverse mode to penetrate the gel below a certain frequency.

Our model does not include rotational diffusion; if this mechanism is important the spectrum discussed here will be obscured by a broad central component. Moreover, if the assumption of small viscosity does not hold the spectrum will be modified, but presumably it is still described by Eq. (3). We believe further depolarized light scattering and transverse mechanical relaxation measurements are required to confirm this model and its several predictions presented here.

^aSupported in part by a National Science Foundation grant to John M. Deutch.

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