The University Of Sheffield.

DEPARTMENT OF PHYSICS & ASTRONOMY

Autumn Semester 2006-2007

PHYSICS OF SOFT CONDENSED MATTER **2 Hours**

Answer THREE QUESTIONS.

A formula sheet and table of physical constants is attached to this paper.

All questions are marked out of ten. The breakdown on the right-hand side of the paper is meant as a guide to the marks that can be obtained from each part.

1 (a) Consider a viscoelastic liquid with a single relaxation time, τ, to which a unit shear strain is applied at time = 0 and then held constant. Sketch a graph showing the strain in the liquid as a function of time. Indicate on your graph the high frequency shear modulus, $G(\infty)$, and the viscosity, η. **[3]**

(b) Use the graph to deduce a scaling relationship between τ, $G(\infty)$ and η. **[1]**

(c) Explain why the temperature dependence of viscosity in many fluids has the form

$$\eta \propto \exp\left(\frac{\varepsilon}{k_B T}\right) .$$

How can the activation energy, ε, be related to another physically measurable property of the liquid? **[3]**

(d) Describe how and why the temperature dependence of the viscosity of glass-forming liquid differs from this behaviour. **[3]**

2 (a) Using the Regular Solution model of the mixing of two liquids, A and B, the free energy of mixing, F, is given by

$$\frac{F}{k_B T} = \phi_A \ln\phi_A + \phi_B \ln\phi_B + \chi\phi_A\phi_B ,$$

where ϕ_A and ϕ_B are the volume fractions of A and B respectively. Explain the physical significance of the parameter χ. **[2]**

(b) Sketch the curves of the free energy for the following conditions:

(i) $0 < \chi < 2$;

(ii) $\chi \geq 2$.

Explain why in case (ii) some compositions are unstable and will phase separate. **[3]**

(c) Explain, using sketches of the free energy, what the critical point is. Demonstrate that, for a mixture described by the relation in part (a), the critical point occurs at $\phi_A = \phi_B = 1/2$, for $\chi = 2$.. **[2]**

(d) In another mixture of liquids, A and C, the molecular volumes of the two components are different. This complication can be accounted for using a modification of the expression for the free energy given above:

$$\frac{F}{k_B T} = \phi_A \ln\phi_A + \frac{\phi_C}{N}\ln \phi_C + \chi\phi_A\phi_C ,$$

where N is a constant. Calculate the critical composition for the case $N = 2$. **[3]**

3 Write an essay describing how scattering techniques can be used to measure the sizes of polymer chains. You should include the types of scattering radiation that can be used and discuss their various benefits and shortcomings. **[10]**

4 (a) Show that the freely jointed chain model of a polymer predicts a root-mean-squared end-to-end distance for a polymer chain with N segments given by

$$\left\langle \mathbf{r}^2 \right\rangle^{1/2} = aN^{1/2} \quad .$$

[2]

(b) The probability distribution function, $P(\mathbf{r},N)$, that gives the probability that a freely jointed chain with N segments, one end of which is at the origin, ends at position $\mathbf{r}$ is

$$P(\mathbf{r},N) \propto \exp\left(-\frac{3\mathbf{r}^2}{2Na^2}\right).$$

Use this relation to write down an expression for the part of the entropy of the chain that depends on $\mathbf{r}$. **[2]**

(c) Show that a single polymer chain can act as a spring and how the spring constant can be calculated. What is the origin of the restoring force when a freely jointed chain is extended? **[3]**

(d) Explain with the use of diagrams why a polymer chain in the melt obeys ideal random walk statistics. **[3]**

5 (a) Rubber gets stiffer when it is warmed up. Referring to the fundamental physics underlying rubber elasticity and using qualitative arguments, explain why this is so. **[2]**

(b) A piece of rubber is subject to an affine deformation, such that the point at coordinates (x,y,z) moves to $\left(\lambda x,\ y/\sqrt{\lambda}, z/\sqrt{\lambda}\right)$, where the extension ratio λ is related to the tensile strain e by $\lambda = 1+e$.

The entropy of a single polymer strand of degree of polymerization N and statistical step length a, with end-to-end distance $\mathbf{r}$, is given by

$$S(\mathbf{r}) = -\frac{3}{2}k_B\frac{|\mathbf{r}|^2}{Na^2} \ .$$

By considering the change in entropy on deformation of a strand starting at the origin and ending at (x,y,z) show that the change in the entropy per unit volume is

$$\Delta S = -\frac{k_B}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right).$$

[2]

(c) A certain rubber has n strands per unit volume. Using the expression for ΔS given in part (b) show that the relationship between tensile stress, τ, and strain is

$$\tau = nk_BT\left[(1+e) - \frac{1}{(1+e)^2}\right] \ .$$

[3]

(d) Use the expression for τ given in (c) to show that Young's modulus (in the limit of small deformation) is given by $E = 3nk_BT$. **[1]**

(e) Show that the shear modulus of rubber, G, is given by

$$G = \frac{\rho RT}{M_x} \ ,$$

where M_x is the density of cross links and ρ is the physical density. **[2]**

END OF EXAMINATION PAPER