CONTEMPORARY TOPICS IN ADVANCED POLYMER SCIENCE AND TECHNOLOGY
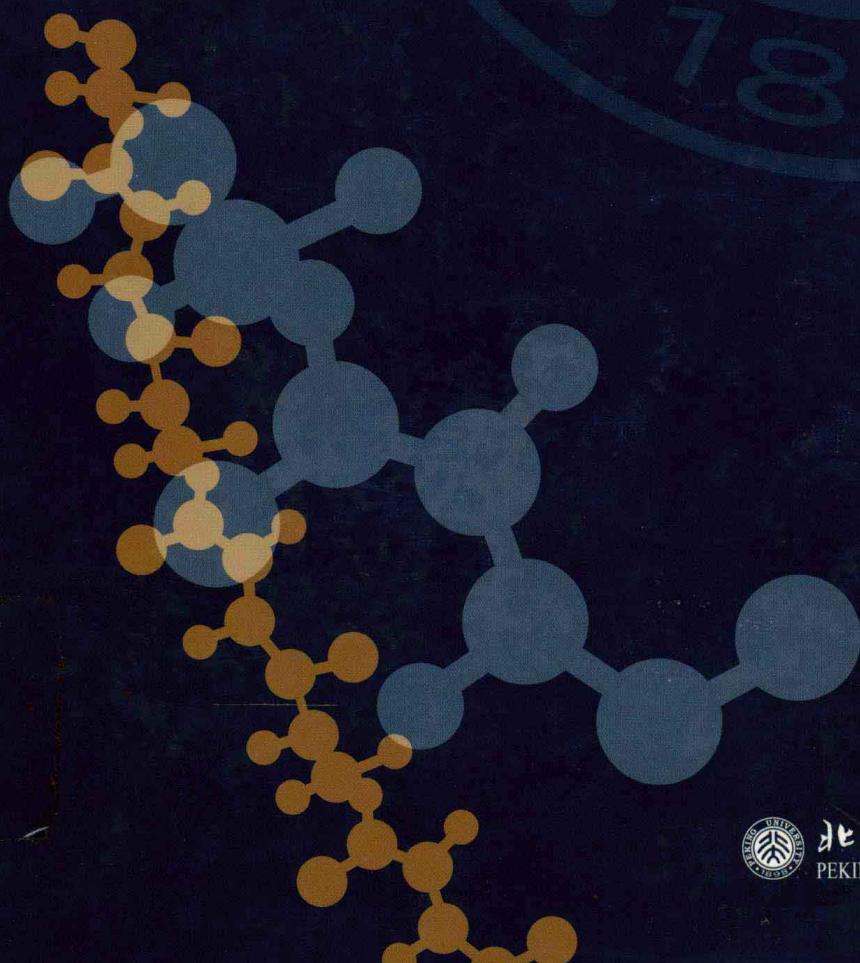
高分子科学与技术前沿课题

Edited by

Qi-Feng Zhou
Stephen Z.D.Cheng

CONTEMPORARY TOPICS IN ADVANCED POLYMER SCIENCE AND TECHNOLOGY

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QI-Feng Zhou（周其凤）
Stephen Z.D. Cheng（程正迪）

Preface

This book presents a collection of articles by a group of renowned polymer scientists from around the world who participated in the May 29 ~ 31, 2004 conference celebrating 50 years of polymer education and research at Peking University. About fifty years ago when Dr. Xin-De Feng, an early student of Professor C. C. Price at the University of Notre Dame, started to teach polymer courses at Peking University, he described polymer science as being "young and beautiful". Fully living up to the expectations expressed by Dr. Xin-De Feng, the field of polymer science and engineering has quickly developed into the newest and most active area in chemistry, materials science, and engineering during the second half of the 20th century.

Today, a new and very exciting interdisciplinary macromolecular science and engineering is rapidly emerging: a field at the crossroads of chemistry, physics, biology, materials science, polymer science and engineering. This field will have a profound impact in the 21st century improving chemical, pharmaceutical, biomedical, manufacturing, infrastructure, electronic, optical, and information technologies. The origin of this field is in an area of polymer science and engineering encompassing plastic technologies, and it has been explosively expanding into new interdisciplinary research areas such as biomaterials, macromolecular biology, novel macromolecular structures, and environmental macromolecular science while tirelessly translating new discoveries into technologies through the innovative engineering and nano-fabrication of products.

Reading this collection of advanced topics in polymer science and engineering, brings one in touch with the fervent living world of polymers which has and will continue to have an immediate impact on our present life, while laying the foundation for the future humankind is entering; It is a new era that is centered on information, bio- and life sciences and technologies. Polymer scientists and engineers have played an essential role in innovating new materi-

als and new technologies to meet present and upcoming needs. Therefore, the design and controlled synthesis of desired polymers, the fabrication of environmental friendly and smart materials, the controlled assembly and micro-fabrication of 2D and 3D nano-structures, the chemical and biological synthesis of naturally existing and non-existing proteins and bio-materials, the study and fundamental understanding of molecular and supra-molecular structures, their dynamics, and the properties of both synthetic and biological macromolecules, have become essential research and development themes in modern science, engineering, and technology.

Our heartfelt thanks are due to all the authors who make this a most interesting, knowledgeable, and edifying book. Gratitude is also due to our friends Dr. Jun-Fei Liu (柳军飞博士) from Sinosoft Co, Ltd. and Mr. Hao-Wei Chen (陈豪伟先生) from Hongchang Paints Co., to China Academic Degrees and Graduate Education Development Center as well as Peking University and the PRC Ministry of Education (with the project for promoting postgraduate education) for their generous support which was essential to make this event such a success.

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Stephen Z. D. Cheng
Qi-Feng Zhou

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The Packing of Polymers in the Cold Glassy State

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Abstract: We offer a simple theory which derives the fine structure of a cooled polymer melt cooperatively approaching glassy state at the transition temperature T_G(Vogel-Fulcher-Dolittle). It is argued that the crudest view of the cooling of a glass is found if one divides its degrees of freedom into slow, configurational degrees of freedom, and fast such as vibrations and electronic excitations if appropriate. The latter can be regarded as in thermal equilibrium defining the temperature, whereas the former have a distribution which is not in equilibrium and could relax for example to an earlier temperature in the cooling. The crudest view of the configurational modes is to view the atoms as if they are grains in a granular material and the glass as the mode mixture where the slow try to catch up with the fast. The argument leads to the definition of three temperatures: T_G the glass transition temperature for infinitely slow cooling, T_g for cooling rate $\dot{\tau}$ and T_0 for the temperature at which cooling starts, and their relation is $T_g = T_0 - \dfrac{T_0 - T_G}{1 + \mu\dot{\tau}(T_0 - T_G)}$ where μ is the constant of the material.

1. The Model of Glass Transition

Liquids based on spheres (atoms) are difficult because of the N body problem[1]. Polymers are just as difficult in compression, but easy in shear. Because polymers are connected and so within a self-consistent view is a 1 body problem. Tube models seem to work for polymers as has been confirmed by

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simulations. Polymer glasses are simpler than atomic or small molecule glasses because

(1) The T_G is very high, so we can get many experiments.

(2) We hope to show models can be made.

(3) There are several simple laws to be deduced:

a) length dependence

$$T_G = T_\infty - \frac{\alpha}{N} \tag{1}$$

b) harmonic mean

$$\frac{1}{T_G} = \frac{\alpha_2}{T_{G_2}} + \frac{\alpha_1}{T_{G_1}} \tag{2}$$

where proportions $\alpha_1 + \alpha_2 = 1$.

Model of reptation in a tube with pinch points which block the motion so that diffusion D_G

$$D_G = D_0\left(1 - \frac{\tau}{T}\right) \tag{3}$$

where τ is the life-time of a pinched point which leads to

$$T_G \sim T_{g\infty}\left(1 - \frac{\alpha}{N}\right) \tag{4}$$

A polymer chain trapped inside a tube is pinched at entanglement points. The friction coefficient ζ is

$$\zeta(s) = \zeta^{(0)} + \sum_n \zeta^{(1)}(\delta(\mathbf{R}(s,t) - \mathbf{R}(s_n, t_0))) \tag{5}$$

The dynamics are governed by the motion of the pinch points when $\zeta^{(1)} \gg \zeta^{(0)}$. The probability distribution of L_n is given by

$$\Phi(L_n) \sim \exp\left[-\frac{3}{2\overline{N}_n b^2}(L_n - \overline{L}_n)^2\right] \tag{6}$$

The motion of s_n is characterised by the potential

$$U(s_n) = \frac{k_n}{2}\sum_{n=1}^{z}(L_n - \overline{L}_n)^2 \tag{7}$$

The dynamics of s_n are described by

$$\zeta_n(t)\frac{\partial s_n}{\partial t} = -k_n\frac{\partial U(s_n)}{\partial s_n} + f_n \simeq k\frac{\partial^2 s_n}{\partial n^2} + f_n \tag{8}$$

The friction coefficient $\zeta_n(t)$ is replaced by an average value $\overline{\zeta}$, which is determined self-consistently

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$$\bar{\zeta}\frac{\partial s_n}{\partial t} = k\frac{\partial^2 s_n}{\partial n^2} + f_n \qquad (9)$$

The diffusion coefficient D_c of the center of mass for the 1D motion along the tube

$$D_c = \frac{k_B T}{Z\bar{\zeta}} \qquad (10)$$

The diffusion coefficient for the 3D motion is

$$D_G = \frac{D_c}{3Z} \qquad (11)$$

$\bar{\mu} \equiv \frac{1}{\bar{\zeta}}$ is estimated by the time average

$$\bar{\mu} \simeq \langle \mu_n(t) \rangle_t = \frac{1}{t}\int_0^t \mu_n(t')dt' \simeq \mu^{(0)}(1-\alpha) \qquad (12)$$

where $\alpha \simeq \frac{\tau_1}{\tau_1 + \tau_2}$ and hence $D_G = D_0(1-\alpha)$. The life-time τ_1 of a pinch point is given by the disentanglement time τ_d such that:

$$\tau_1 \simeq \tau_d \simeq \frac{L^2}{D_c} \qquad (13)$$

The time for finding a new pinched point is

$$\tau_2 \simeq \frac{a^2}{D_G} \qquad (14)$$

hence

$$\alpha \simeq 1 - \frac{\text{const}}{Z} \simeq 1 - \frac{\text{const}}{N} \qquad (15)$$

If α is proportional to the glass transition temperature $\frac{T_g}{T}$

$$T_g = T_{g\infty}\left(1 - \frac{\text{const}}{N}\right) \leftrightarrow \text{Flory-Fox law} \qquad (16)$$

2. The Packing Problem and Glass Transition

The volume problem is of special interest in dealing with threads or fibres as the analogue of grains and the related problem of polymers as the analogue of compressible particles which can sustain a thermal temperature. The glass transition of polymerized material can happen at quite high temperature, often way above room temperature. This means that we have a system which ex-

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hibits properties at convenient temperatures for experiments which have the nature of very low temperatures in small molecular i. e. non-polymeric glasses.

2.1 Analogy with Granular Packings

There have been advances in our knowledge of granular materials which seem to us to o. er some new ideas on glasses. The simplest granular system is that of perfectly rough grains which are incompressible and form contacts with their nearest neighbours. In general the configuration of such packing depends on how the material has been created i. e. how it was deposited, how it was stressed, whether there are any other phases like pore fluid and gas are present, all questions which a civil engineer knows are critical in applications. However recent experiments by Nagel and co-workers[2,3] show that granular systems can behave under the appropriate conditions in a way showing them amenable to the laws of statistical mechanics. The crucial experiments show that external vibrations lead to a slow approach of the packing density to a final steady-state value. Depending on the initial conditions and the magnitude of the vibration acceleration, the system can either reversibly move between steady-state densities, or can become irreversibly trapped into metastable states; that is, the rate of compaction and the final density depend sensitively on the history of vibration intensities that the system experiences (see Figure 1).
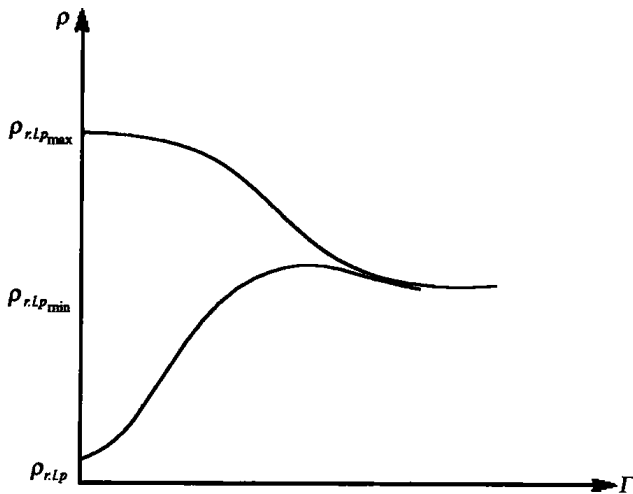

Figure 1 Dependence of the packing fraction on the history of tapping amplitude. The parameter $\Gamma = \dfrac{A}{g}$ is the ratio of the recorded peak acceleration during a single tap A to the gravitational acceleration g. In the Chicago experiments, Γ was varied by changing the amplitude of excitation A at fixed frequency $\omega = 30\,\mathrm{Hz}$.

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This suggests that one might imagine a crude model of a glass in which the heavy atoms are like a granular material and the shaking or tapping of the above-mentioned experiment is provided by the vibrations and any other fast degrees of freedom are present. Papers are now appearing in the literature to develop such concepts[5~9] and we give a brief outline of one of them here. Although it is not necessary a "visual aid" comes from the analysis of solvability of Newton's equations for static packings of hard rough grain analysis[12]. One finds (within certain provisos) that each grain has $d + 1$ contacts, where d is the dimension of the system (see Figure 2). The 2D picture then looks like a three-fold coordinated elemental glass (see Figure 3). We now need a formulation for the glass.
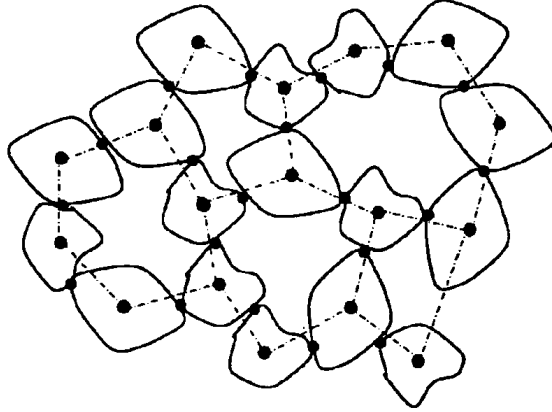

Figure 2　Two-dimensional continuous random network: a sketch of a packing of three-fold coordinated grains of irregular shape. Black circles denote the contact points and dashed lines joining the centroids of contacts, form the continuous random network.

2.2　Compactivity

We argue that subject to N grains of the Chicago experiment filling a volume V, and when at rest (i. e. after tapping has finished) have contacts which fix their positions in space, all configurations are equally likely[4]. This is just as energy possessing ergodic systems have a probability distribution

$$P = e^{-\frac{S}{k}}\delta(E - H) \tag{17}$$

grains have

$$P = e^{-\frac{S}{\lambda}}\delta(V - W\{\mathcal{R}\})\Theta\{\mathcal{R}\} \tag{18}$$

where $W\{\mathcal{R}\}$ is the function of contact points $\{R\}$ which leads to the volume
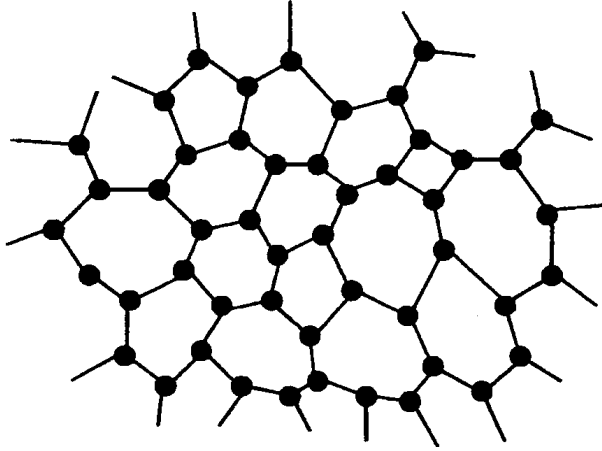
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Figure 3 Two-dimensional continuous random network: a sketch of a threefold coordinated elemental glass, where the continuous random network is formed by lines joining the centres of atoms.

V and $\Theta \{\mathscr{R}\}$ means all the grains are in contact. Expressions for W are given in ref. [8]. Such distributions are in overall agreement with the Chicago experiment, and with simulations by Kurchan and co-workers[9] which contain more detailed analysis than experiment can at present. Just as in thermodynamics

$$T = \frac{\partial E}{\partial S} \tag{19}$$

in the granular system the key quantity is the compactivity

$$X = \frac{\partial V}{\partial S} \tag{20}$$

A formal connection with thermal physics has

$$\frac{1}{X} = \left. \left(\frac{\partial P}{\partial T} \right)_V \right|_{T \to 0} \tag{21}$$

which we use in the next section.

The volume problem is of special interest in dealing with threads or fibres as the analogue of grains and the related problem of polymers as the analogue of compressible particles which can sustain a thermal temperature. The glass transition of polymerized material can happen at quite high temperature, often way above room temperature. This means that we have a system which exhibits properties at convenient temperatures for experiments which have the nature of very low temperatures in small molecular i.e. non-polymeric glasses.

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It is interesting to think of the behaviour of glasses at low temperatures in terms of analogy with granular media. Although it is certainly an oversimplification to assume that volume formation governs the behaviour of polymer glasses, in our view, it does o. er a new insight. The problem is to estimate the volume of a system which is a packing of polymer chains (see Figures 4 and 5). A slowly cooled polymer melt of an atactic (random, hence uncrystallizable) structure will look more like the structure of Figure 5 whereas a rapidly quenched melt will look like a "spaghetti" globule of Figure 4.
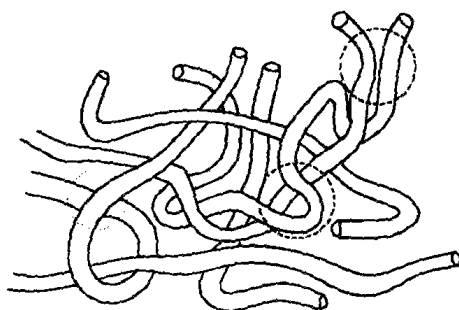

Figure 4   A rapidly quenched polymer melt with characteristic one- and two-chain configurations. (dashed circles)
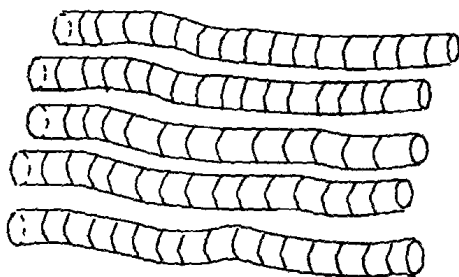

Figure 5   Aligned chains of the slowly cooled polymer melt.

We think of Figure 4 as a smallest volume, a "ground state" and for a given configuration we argue that the volume formation can be classified in terms of "one-body", "two-body" etc. contributions. Examples of polymer chain configurations corresponding to "one-body" and "two-body" terms are presented by Figures 6 and 7.
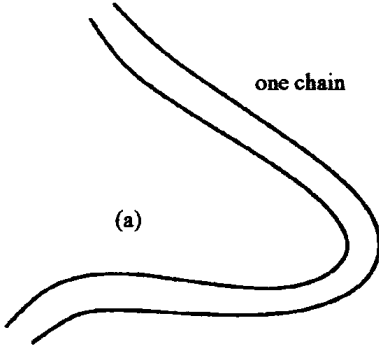
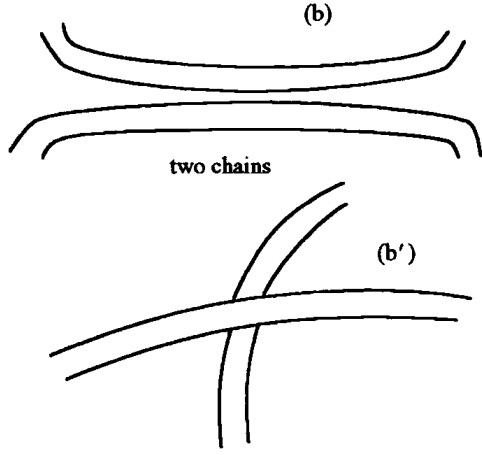**Figure 6**   One-chain configuration in the "spaghetti" globule.

Figure 7   Two-chain configurations in the "spaghetti" globule.

If the polymer is characterized by $\mathbf{R}(s)$ such that $\left(\dfrac{\partial \mathbf{R}}{\partial s}\right)^2 = 1$ then

• the "one-body" contribution to the volume function corresponding to the chain configuration in Figure 6 is given by $\epsilon \displaystyle\int \left(\dfrac{\partial^2 \mathbf{R}}{\partial s^2}\right)^2 ds$.

• the "two-body" term corresponding to the chain configurations in Figure 7 is

$$\eta \int \left[\left(\frac{\partial \mathbf{R}(s_1)}{\partial s_1} \times \frac{\partial \mathbf{R}(s_2)}{\partial s_2} \right)^2 - 1 \right] ds_1 ds_2$$

These expressions may look complicated but can be handled since they are still quadratic forms. Result of a calculation is

$$\int \prod d\mathbf{R} \exp\left(-\frac{1}{X} \left(V_0 + \epsilon \int \left(\frac{\partial^2 \mathbf{R}}{\partial s^2} \right)^2 ds \right.\right.$$
$$\left.\left. - \eta \int \left[\left(\frac{\partial \mathbf{R}(s_1)}{\partial s^1} \times \frac{\partial \mathbf{R}(s_2)}{\partial s^2} \right)^2 - 1 \right] ds_1 ds_2 \right) \right) \tag{22}$$

$$V = V_1 + aX + bX^2 \tag{23}$$

We have commented that polymeric glasses have features in common with granular materials. The long molecules jam by having "pinch" points hold them at points along the defacto tube which is formed by their neighbours. Between pinches they can have motion hence energy, but when the pinches hold the molecule one has reached the glass transition. There is an analogue here with jammed deformable spheres where there is still heat capacity even though

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there is no transport. The configuration shown in Figures 4 and 5 tell us that the entropy of the jammed system depends on the cooling rate. If we ignore the residual thermal motion only X is available to characterise the system *provided* there is some analogue of the tapping of the Chicago experiments. Pulsed heating and cooling could provide this. Thus we argue that the cooling into the glass phase should take us to the analogue of point $\rho_{r.l.p}$ of Figure 1, and a pattern of heating and cooling take the glass to $\rho_{r.l.p_{min}}$ and thereafter to a reversible curve. Polymers allow one to visualize what is happening and we believe this to be the system which will be the first one to give a consistent glass theory at low temperatures.

3. Cooling of a Glass

We aim to develop a theory shown in Figure 8 where we plot the inverse viscosity as a function of temperature in terms of the rate of cooling $\dot{\tau}$ the temperature T_0 at which cooling starts and which is equal to the glass transition temperature if $\dot{\tau} \to \infty$, the glass temperature at $\dot{\tau}$ T_g and the glass temperature for $\dot{\tau} = 0$ T_G.
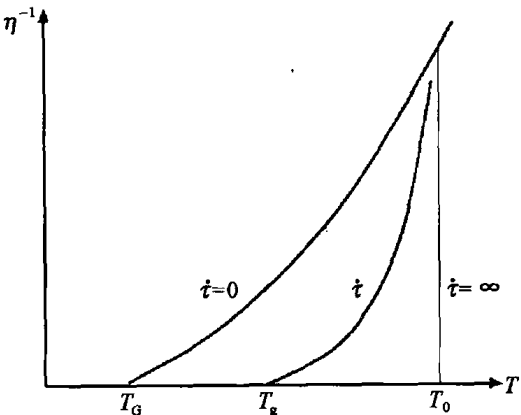
To derive such a diagram, we make what is probably far too crude an approximation but one that leads to quite reasonably looking curves.

Figure 8　The inverse viscosity η^{-1} as a function of temperature T given for different values of the cooling rate asymptotically approaching infinity.

We argue that when the slow configurational and fast modes are in equilibrium

$$\frac{1}{X} = \left(\frac{\partial P}{\partial T} \right)_V \tag{24}$$

but in general there is a non-vanishing value

$$Z = X - \left(\frac{\partial P}{\partial T} \right)_V^{-1} \tag{25}$$

We can expect Z to look like (see Figure 9) and a simple derivation leads to

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