

EXPERIMENTAL STUDY OF FLUCTUATIONS IN MATERIALS

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ABSTRACT

Spontaneous fluctuations of dynamic variables in materials are related to their macroscopic properties. One can sample the correlation functions of fluctuations via scattering experiments. In this paper a brief review of these aspects is presented with suitable examples taken from X-ray and neutron scattering studies. Material scientists can throw light on mechanical behaviour by a study of microscopic fluctuations by devising suitable experiments.

INTRODUCTION

MECCHANICAL behaviour is decided by the role of defects—be they point defects, precipitates, dislocations etc. Deformation of materials, in particular, is decided by how the defects move, multiply, annihilate etc under external forces. This kinetics of defects is random in character and the process is generally referred to as a stochastic process.

The system response to any impressed force depends on the magnitude of the force. When the force is 'small', the system response is linear and one can relate this response to fluctuations in the system. In the region of plastic deformation, nonlinear effects begin to play their role; highly nonlinear effects lead to instabilities like the yield drop.

While the physicists are content with the study of the linear response of the system, real-life situations affecting the lifetime of the various mechanical components pertain to the nonlinear regimes. Mechanical engineers and metallurgists carry out a variety of tests like the creep test, rupture test, tensile test, hardness test, fatigue test etc to determine essentially the limits of stresses to which a material can be subjected to during its life-time. Physicists have studied ideal solids from the microscopic point of view for a long time now. There is a gap to be bridged between the world of the physicist and that of the engineer.

In this paper we point out the relation of fluctuations in defects to the mechanical properties and how one can study these fluctuations

by tools of the physicist. Some of the recent experimental studies using radiation scattering techniques would also be discussed.

STOCHASTIC THEORY OF FLUCTUATIONS

It is well recognized now that defect kinetics is governed by intrinsic random fluctuations of defects. As mentioned in the introduction, what we are concerned here is investigation of materials via scattering techniques. In this section, we present the basic concepts that illustrate how fluctuations are related to macroscopic properties. In the next section we discuss how information from scattering techniques is related to fluctuations; so finally a unifying picture of intrinsic fluctuations with macroscopic properties should emerge via scattering experiments.

Statistical mechanics tell us that random processes are governed by various probability functions like the joint probability function $W_2(x_1, t_1, x_2, t_2)$ or the conditional probability function $P(x_1, t_1, x_2, t_2)$ for occurrence of certain variables. With the help of these functions one can evaluate the average values of various dynamical variables of the system under study. One of the specific averages denoted by $\langle x_1(t_1) x_2(t_2) \rangle$, referred to as the autocorrelation function, is given by

$$\begin{aligned} \phi_{x_1, x_2}(t_1, t_2) &= \langle x_1(t_1) x_2(t_2) \rangle \\ &= \iint dx_1 dx_2 x_1 x_2 W_2(x_1, t_1, x_2, t_2). \end{aligned} \quad (1)$$

It is a measure of how the variable x_2 at t_2 is correlated to the variable x_1 at t_1 . This correlation function is related to the intensity of scattered radiation in any experiment as will be discussed later. The spectral density of fluctuations of a variable x , $S_x(\omega)$ is given by

$$S_x(\omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle x(0)x(t) \rangle_{\text{eq}}. \quad (2)$$

This is known as the Wiener-Kinchin theorem. The spectral density is what is sampled in scattering experiments.

When a certain external force, say F , is applied on a system, it can couple to a conjugate variable B of the system. As an example, if F corresponds to a magnetic field, it couples to B , the magnetization. The force affects not only the conjugate variable B , but can affect any other variable of the system, say A , linked to this conjugate variable of our interest via different experiments. We have implied here that fluctuations in A can arise because of certain impressed forces. However fluctuations in A can arise spontaneously too as the system itself is a heat bath. The question, we have to answer is, how does the system respond as far as A is concerned when a certain force is impressed on the system? Is it linear, is it nonlinear and how to measure this? It is here that we take recourse to another famous theorem of statistical mechanics namely the fluctuation-dissipation theorem which states that the *average response* of A to an external applied force can be got from *spontaneous fluctuations of A* . This arises because the system, as such, does not distinguish between random forces originating in the system itself which drive the 'spontaneous' fluctuations of A and the external force. So if $\chi_{AA}(\omega)$ is the susceptibility of the system (a measure of the response) the imaginary part of this susceptibility $\chi''_{AA}(\omega)$ is related to the spectral density of the intrinsic fluctuations.

$$S_{AA}(\omega) = -\frac{2\hbar}{1 - \exp(\beta\hbar\omega)} \chi''_{AA}(\omega), \quad (3)$$

$\chi''_{AA}(\omega)$ is, a direct measure of the energy dissipation and $S_{AA}(\omega)$ is as already said, the spectral density of the fluctuations and hence (3) is the mathematical statement of the fluctuation-dissipation theorem. $\chi''_{AA}(\omega)$ is also referred to as compliance sometimes.

Fluctuations of intrinsic variables occur in all systems spontaneously. For example, we have fluctuations of particle velocity in a liquid, current in a resistor or strain in a metal. These fluctuations occur irrespective of whether external forces are applied or not, because certain stochastic forces always operate in the system. A mathematical description of time dependence of variables can be written in the form,

$$p\dot{x}(t) + qx(t) = F_r(t) + F_{\text{ext}}, \quad (4)$$

where $x(t)$ is the fluctuating variable and $F_r(t)$ is the stochastic force: p and q are constants of the system. This equation is the famous Langevin equation. From this equation one can determine $\langle x(0)x(t) \rangle$ and hence the power density in the absence of F_{ext} . If a certain force F_{ext} is impressed on the system the average behaviour of the system is governed by the equation,

$$p \frac{d}{dt} \langle x(t) \rangle + q \langle x(t) \rangle = F_{\text{ext}}. \quad (5)$$

Note that the stochastic forces do not appear in this equation as $\langle F_r(t) \rangle = 0$ in a purely random system. One can obtain relations connecting the compliance and spectral densities by means of (2) and (3). Interested reader may see reference¹ for details concerning the specific cases mentioned above.

The above discussion shows that for a mechanical system, one can calculate, for example, the creep function for a linear anelastic material in terms of fluctuations from equilibrium of the strain in the absence of any applied stress.

Balakrishnan *et al*² recently analysed the nature of viscoelasticity and anelasticity of

materials by taking into account fluctuations of certain properties on the microscopic scale. This approach is possible because anelasticity is due to relaxation processes associated with point defects, defect pairs and defect clusters. Even in the absence of external forces, the defects assume different configurations continuously due to the 'heat bath', that is, they fluctuate. In the presence of external force, there is a coupling with the defects but different defects couple differently with the applied nature of force and results in various kinds of relaxation phenomena.

Neelakantan³ has built electrical analogues of various 'machine equations' and has mimicked the material undergoing various tests. Although there may be questions relating to what one studies in an electrical system and that pertaining to what occurs in a mechanical system, the 'synergetic' approach has merits in the sense that it is not unlikely that similar behaviour occurs in apparently widely dissimilar fields. A system undergoing plastic flow and yield serrations is non-monotonic. It has built-in negative resistance features. This is another aspect that can be studied by a synergetic approach.

EXPERIMENTAL STUDY OF FLUCTUATIONS VIA SCATTERING EXPERIMENTS

Fluctuations are usually studied by experimental measurements of their transforms. If $x(t, \omega, \Delta\omega)$ is that portion of $x(t)$ in the frequency range $(\omega, \omega + \Delta\omega)$ one can define a measure of random power in unit frequency range as

$$G_x(\omega) = S_x(\omega) = \lim_{\Delta\omega \rightarrow 0} \frac{\psi_x^2}{\Delta\omega}$$

$$= 2 \int_0^t dt \exp(i\omega t) \langle x(0)x(t) \rangle_{eq}, \quad (6(a))$$

$$\psi_x^2(\omega, \Delta\omega) = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt x^2(t, \omega, \Delta\omega). \quad (6(b))$$

So in conventional spectroscopy the scheme given in figure 1 is followed. Signal $x(t)$ is sampled over a certain time period T . This signal passes through a filter centred at ω_0 . The filtered signal is fed to a square law detector followed by time-averaging system. The measurement, therefore, gives an estimate of the power at a certain frequency of filter ω within a band width $\Delta\omega$. By tuning this frequency, power is measured as a function of frequency, provided T is large enough to sample all frequencies.

TECHNIQUES USEFUL FOR STUDYING MECHANICAL PROPERTIES INVOLVING FLUCTUATIONS I.E. WITH DEFECT KINETICS

For a stationary system, resistance fluctuation spectroscopy, light scattering, ultrasonic attenuation and small angle neutron scattering techniques have been used and for non-stationary processes acoustic emission and ultrasonic attenuation have been used.

The resistance fluctuation spectroscopy deals with measurements of fluctuations of voltage across a specimen through which a current is passing. This technique was suggested by Venkataraman *et al*⁴ and one set of experiments in Al is reported by an Italian group⁵ results of which are analysed by Balakrishnan and Bansal⁶ based on a theory that takes into account birth and death of vacancies

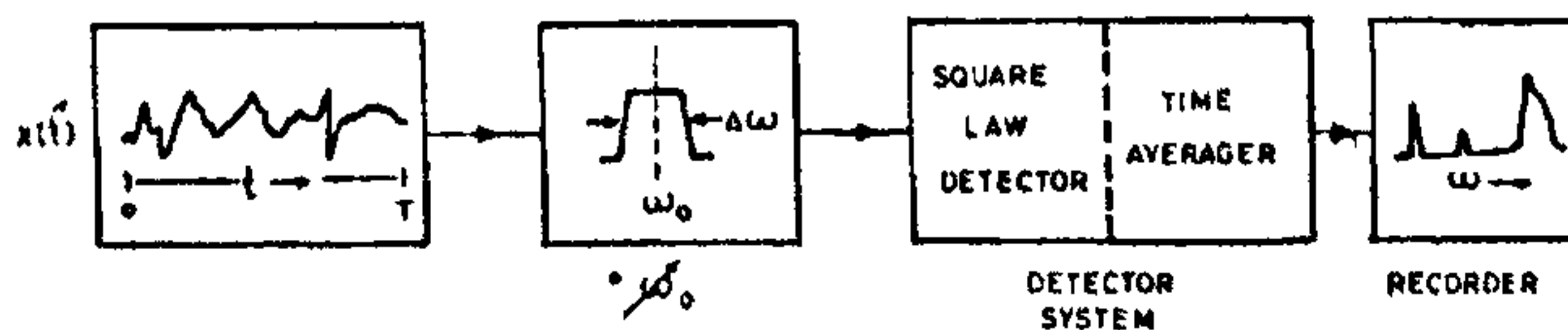


Figure 1. Scheme of conventional spectroscopy.

stochastically. Similarly voltage fluctuation studies are common in superconductors.

There is one light intensity fluctuation experiment reported in literature on NaCl and KCl system which is alluded to the motion of dislocation and that correlation time is related to reaction rate of Schottky defect creation, diffusion of vacancies and glide of dislocations. Light intensity fluctuation spectroscopy is restricted to non-metals.

NUCLEATION, DIFFUSION AND SPINODAL DECOMPOSITION

The so-called Master equation describes evolution of a statistical system as a function of time. Thermodynamically unstable situations like nucleation, atomic diffusion and spinodal decomposition that are relevant to mechanical behaviour are described ultimately by a well-known equation, the Cahn's equation⁷,

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = M \nabla^2 \left[\frac{\partial f(c_0)}{\partial c_0} - k \nabla^2 c \right], \quad (7)$$

where $c(\mathbf{r}, t)$ is the concentration of one species of atoms at position \mathbf{r} at time t . Equation (7) given above is akin to the Langevin equation discussed earlier.

If one were to define the departures from average concentration C_0 by $u(\mathbf{r}, t)$,

$$u(\mathbf{r}, t) = C(\mathbf{r}, t) - C_0, \quad (8(a))$$

$$u(\mathbf{Q}, t) = \int d\mathbf{r} \exp(i\mathbf{Q} \cdot \mathbf{r}) u(\mathbf{r}, t), \quad (8(b))$$

one can analyse the situation through a perturbative analysis. Taking into account a stochastic term $R(\mathbf{r}, t)$ one can write

$$\begin{aligned} \frac{\partial u(\mathbf{Q}, t)}{\partial t} &= -\alpha(\mathbf{Q})u(\mathbf{Q}, t) + R(\mathbf{Q}, t) \\ &+ \sum_{n=0}^{\infty} (n-1)! \frac{\partial^n f(C_0)}{\partial C_0^n} u^{n-1}(\mathbf{Q}, t). \end{aligned} \quad (9)$$

This equation describes various situations depending on the importance of various terms.

The first term on the right side describes the diffusion phenomenon if

$$\alpha(\mathbf{Q}) = Q^2 D(\mathbf{Q}) = M Q^2 \left[\frac{\partial^2 f(C_0)}{\partial C_0^2} + Q^2 K \right]. \quad (10)$$

Addition of the second term brings in thermal fluctuations and $U(\mathbf{Q}, t)$ the Q th. Fourier component of concentration fluctuation evolves independently. The rest of the terms correspond to a nonlinear situation similar to the introduction of anharmonicity in lattice vibration theories.

One can use (9) to discuss the nature of evolution of a system. The first order solution of (9) is given by

$$u^{(1)}(\mathbf{Q}, t) = \int_0^t dt' \exp[-\alpha(\mathbf{Q})(t-t')] R(\mathbf{Q}, t'). \quad (11)$$

In the case of spinodal decomposition, one is dealing with the process of unmixing, this is, of phase separation under quenching. In figure 2 we have shown the free energy at the temperatures of quench, $\partial^2 f / \partial c^2$ and variation of composition as a function of temperature. We shall discuss the behaviour of the system as a function of the state of the system.

Point (a) corresponds to the phase point (T_0, C_0) being outside the coexistence curve. $D(\mathbf{Q})$ defined in (10), is positive: As $Q \rightarrow 0$ $D(\mathbf{Q}) \rightarrow D(0)$. $U^{(1)}(\mathbf{Q}, t)$ behaves as

$$u^{(1)}(\mathbf{Q}, t) = \exp[-Q^2 D_0(t-t_0)] \rho(\mathbf{Q}); \quad (12)$$

that is, the disturbance dies exponentially. If one were to define a correlation function $C_2(\mathbf{Q}, t)$ as

$$C_2(\mathbf{Q}, t) = \int d^3\mathbf{r} \exp(-i\mathbf{Q} \cdot \mathbf{r}) \langle u(\mathbf{r}, t) u(\mathbf{0}, t) \rangle \quad (13)$$

one can show that the first order solution to $C_2(\mathbf{Q}, t)$ is

$$C_2^{(1)}(\mathbf{Q}, t) = \frac{1 - \exp\{-2Q^2 D(\mathbf{Q})t\}}{D(\mathbf{Q})} \quad (14)$$

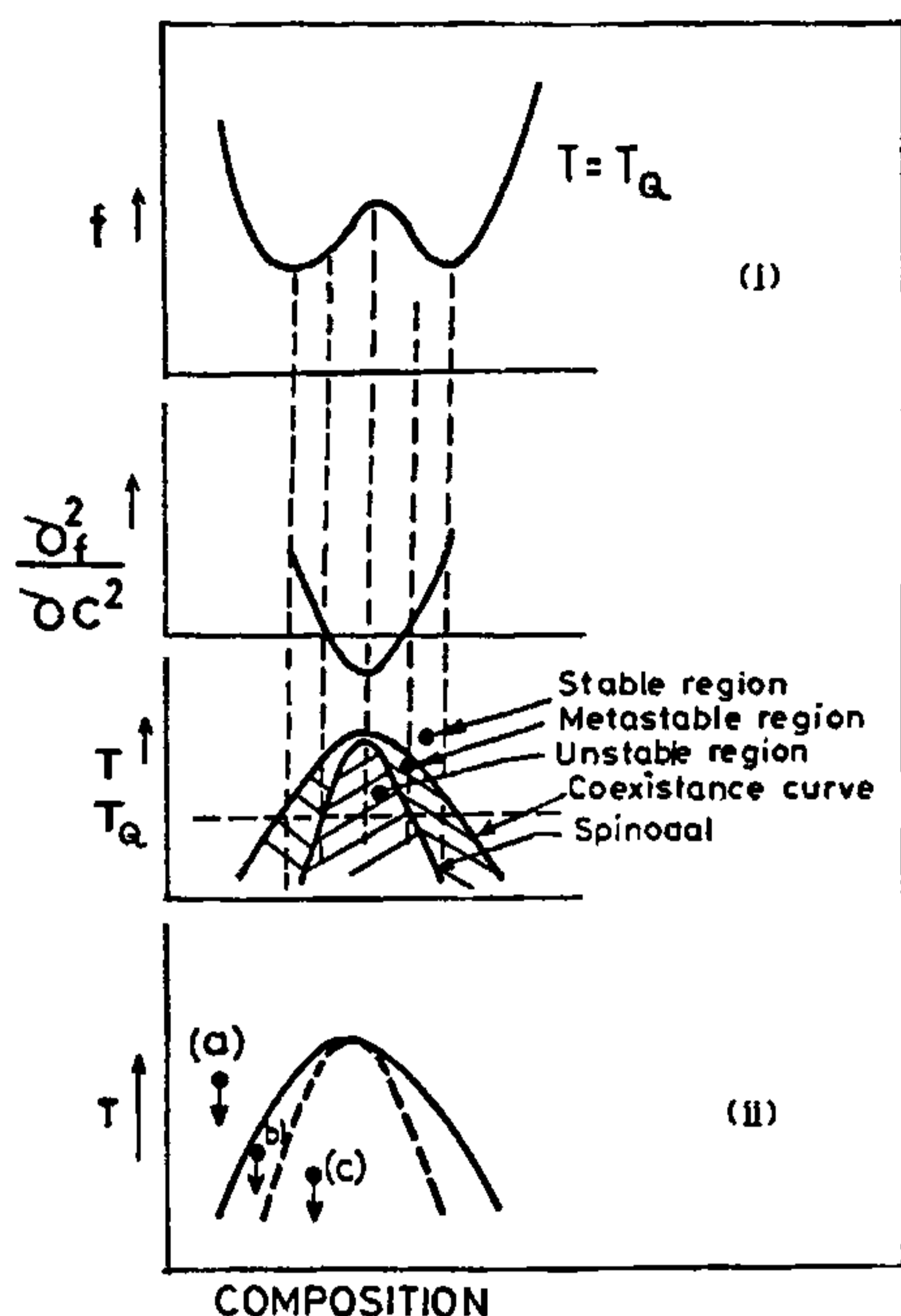


Figure 2. (i) Variation of free energy f , $\partial^2 F/\partial c^2$ as a function of composition and variation of concentration as a function of temperature relevant to study of spinodal decomposition. (ii) The points (a), (b) and (c) correspond to quenches from the stable, metastable and unstable equilibrium situations.

which is observable in light scattering experiments. For the case under consideration.

$$C_2^{(1)}(Q,t) = \frac{1}{D(Q)} \text{ after } t \geq \tau$$

$$\tau = 2D(Q)Q^2 \tag{15}$$

We note two facts: (i) that τ depends on Q and (ii) the light scattering intensity can grow and level off after some time.

In the region of (b), nothing much happens to differentiate between stable and unstable situations.

Region (c), within the spinodal, is the most interesting region. Here $\partial^2 f/\partial c^2$ is negative;

however $D(Q)$ is positive for Q greater than a critical value Q_c and negative for Q less than Q_c . Q_c is given by

$$Q_c = K/(\partial^2 f/\partial c^2). \tag{16}$$

From this we observe that those components in $u(Q,t)$ for which $Q < Q_c$ will grow and those for $Q > Q_c$ will decay. The nonlinear terms that occur in (9) essentially help to stabilize the growing modes.

EXPERIMENTAL STUDY OF SPINODAL DECOMPOSITION

Light, X-rays and neutrons couple weakly to the scattering medium, say, an alloy or a binary liquid mixture. Hence the scattered intensity of these radiations can be used to study the correlation function pertaining to density. Experiments have been conducted to study light scattering from polymers, liquids undergoing crystallization and binary liquids separating into liquid phases. X-ray scattering studies have been directed at study of a few alloys, the most notable of them being that related to Al + 5% Zn. Amongst liquid mixtures studied are those of methanol-cyclohexane and 2-6 butadiene-water. These studies have already shown that experimentally one finds departures from those discussed in the previous paragraph.

NEUTRON SMALL ANGLE SCATTERING (NSAS) EXPTS

One of the earliest experiments to study spinodal decomposition of alloys by NSAS technique related to the study of $^{65}\text{Cu}_{0.45}\text{Ni}_{0.56}$. By measuring the diffuse intensity after 0, 2, 4, 200 and 500 hours after quench, the exponential decay of diffuse intensity with time was established and T_c was found to be in the range of 320 to 340 K.

NSAS is particularly useful for studying various static and dynamic properties of materials involving defects and in nonequilibrium situations.

The SAS is based on the fact that if a sample has a nonhomogeneous structure or if its lattice

is perturbed, diffraction effects are not merely confined to sharp Bragg reflections but give rise to extended regions of diffuse scattering whose intensity and distribution are related to the 'defects' in the material. Neutrons are especially useful to probe materials containing H and magnetic systems and do not suffer too much multiple Bragg scattering but the choice of radiation to be X-rays or neutrons is a matter of convenience.

NSAS has been used to study the shape, average size, volume fraction of the dispersed phase etc in alloys by use of the well-known Guinier's relation and Porod's law. We shall not discuss these aspects as they are not relevant to our discussion. Most of the experiments to date of NSAS on alloys, though, are related to these. Confining our attention to study of spinodal decomposition, we note that this phenomenon is governed by the diffusion equation.

$$\frac{\partial c}{\partial t} = \frac{M}{N_i} \left\{ (f'' + 2\eta^2 Y) \nabla^2 c - 2K \nabla^4 c \right\}, \quad (17)$$

where f'' is the second derivative of the Helmholtz free energy term with respect to composition and $\eta^2 Y$ is the coherent strain energy term. M is the atomic mobility and N_i is the number of atoms/unit volume. K is the gradient energy coefficient. Under appropriate conditions the solution of this equation is

$$C(x,t) - C_0 = \frac{1}{(2\pi)^3} \int I(\beta,t) \exp(i\beta \cdot x) d\beta \quad (18)$$

and the SAS intensity is given by

$$I(\beta,t) = I(\beta,0) \exp[2R(\beta)t], \quad (19)$$

$R(\beta)$, referred to as the amplification factor, is defined by

$$R(\beta) = -\frac{\bar{D}}{f''} (f'' + 2\eta^2 Y + 2K\beta^2) \beta^2. \quad (20)$$

For growth of composition fluctuations the expression in the parentheses on the RHS of

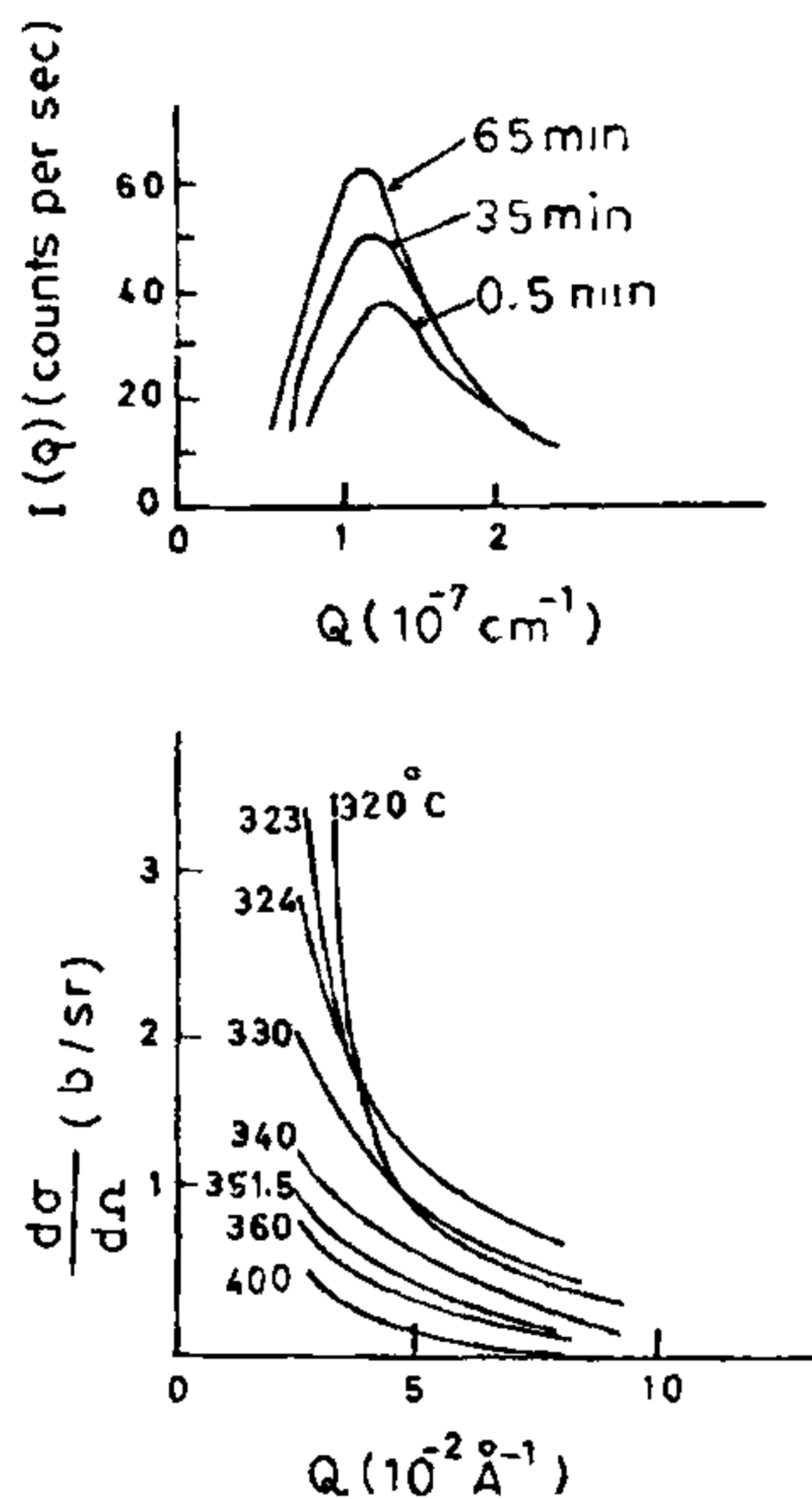


Figure 3. Results of study of Al-Zn using SANS technique: (a) Variation of scattered intensity as a function of wavevector transfer for three annealing times after a spinodal quench. (b) Variation of scattered intensity as a function of wavevector transfer for different annealing temperatures.

(20) must be negative, a condition that is satisfied only inside the coherent spinodal region. However this is possible only for $\beta < \beta_c$. Therefore, those wavelengths less than λ_c grow spontaneously and within a narrow range are highly favoured. Wavelengths greater than λ_c decay spontaneously. There have been very few experiments of NSAS related to spinodal decomposition. Figure 3 shows the results obtained in the study of Al-Zn corroborating what is stated here.

Near the critical point one finds large scale fluctuations as part of the dynamic equilibrium structure and this gives rise to critical opalescence which is generally suppressed in the solid state. Figure 4 shows the results from the recent neutron experiments which clearly exhibit this phenomenon. It should be noted

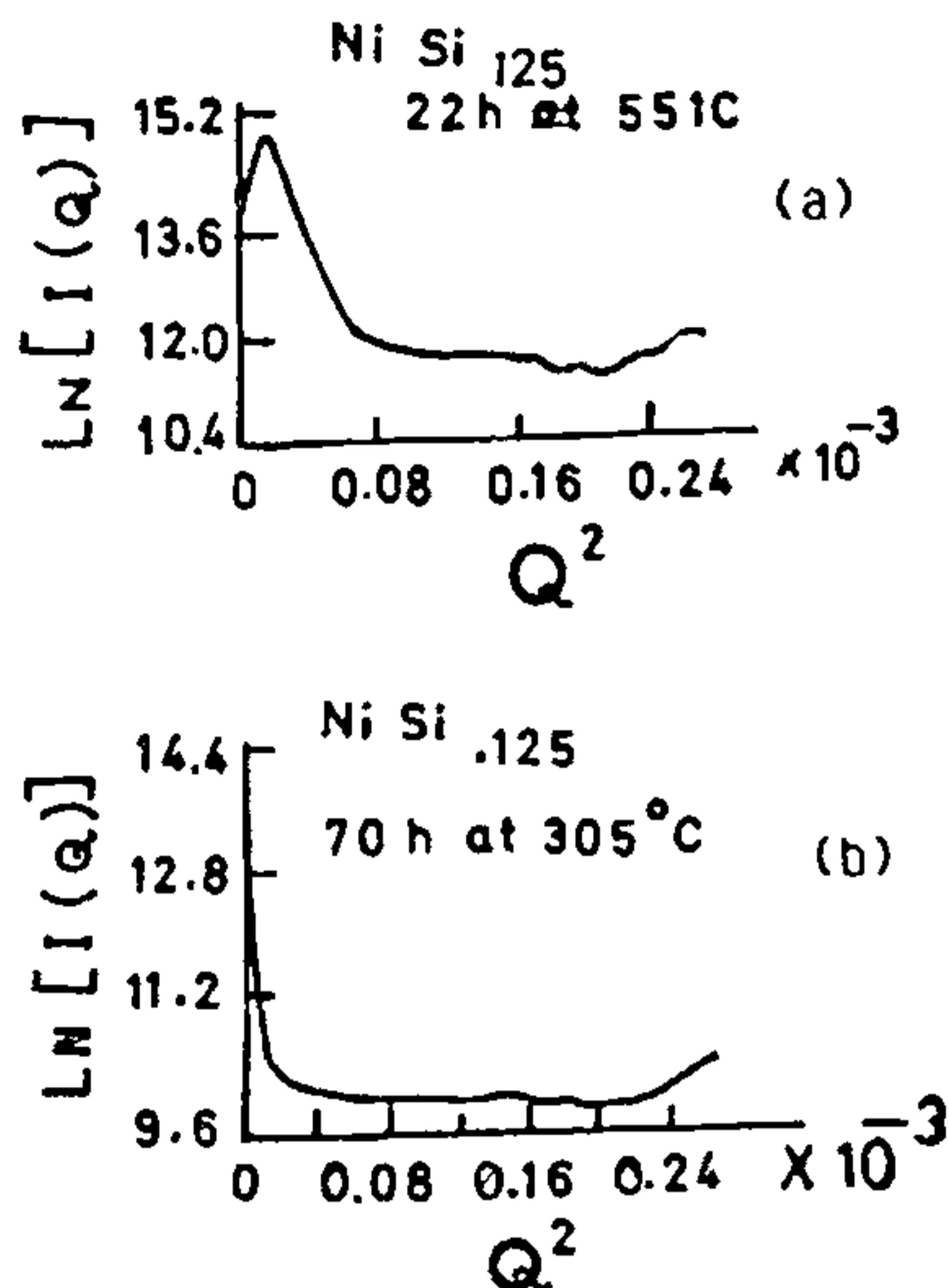


Figure 4. Results of study of NiSi₁₂₅ by SANS technique: (a) Variation of intensity as a function of square of wavevector transfer after 22 hr of annealing at 551°C, typical result corresponding to spinodal decomposition giving rise to a peak at finite Q^2 . (b) Same as above after 70 hr of annealing at 305°C. The shift of peak to zero wavevector corresponds to critical behaviour.

that this places one within the metastable region, hence a high intensity source is imperative in order that measurements are completed before significant decomposition occurs.

SUMMARY

Study of fluctuation of macroscopic properties like resistivity, strain etc as well as the intensity of scattered radiation (X-rays, neutrons, light) from a material undergoing mechanical deformation or going through an unstable state can be correlated to the intrinsic fluctuations of entities of interest to a materials scientist. In the latter category several X-ray and neutron small angle scattering experiments have corroborated so far our present theoretical understanding of spinodal decomposition. Further experiments are necessary to understand the nature of dynamics involved in the complicated mechanical deformation of materials.

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