

DIFFRACTION STUDIES OF LIQUID AND AMORPHOUS MATERIALS

AT SPALLATION NEUTRON SOURCES

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ABSTRACT

The static properties of liquid and amorphous metals have been explored very extensively over the last thirty years. The studies have usually been performed by neutron scattering at steady state reactors and only recently at advanced spallation neutron sources. From such measurements one determines the static structure factor $S(Q)$ in a wide Q -region which then gives information on the structure of the metal, i.e. the spatial arrangement of atoms or magnetic moments. The structure factor $S(Q)$ is now more easily determined at spallation neutron sources, where the effective flux of neutrons, particularly at higher energies, is much greater than that previously available at steady state reactors. The two limiting values of $S(Q)$ for Q small and Q large are difficult to measure with good accuracy. In the case of liquid metals and small Q -values, the difficulty stems from the low cross-section. In the case of amorphous materials a lot of structure still remains at large Q -values between $20\text{-}30\text{ \AA}^{-1}$. For example in the metal-metaloid amorphous alloys it is necessary to measure the scattered intensity up to $25\text{-}30\text{ \AA}^{-1}$, which can easily be done at the neutron spallation sources such as the SNS, IPNS-1 etc.

1. INTRODUCTION

Before presenting some recent results on the structural investigations of liquid and amorphous materials, we shall outline some advantages of spallation sources (pulsed neutron techniques) over the steady state reactors (the continuous neutron source) [1-6]. First of all, the neutron flux that can be obtained at the pulsed source is biased towards higher

energies, say 8 to 0.08 eV, i.e. 0.1 and 1Å [7]. This makes spallation sources preferable for the investigation of large energy and large Q transfer experiments. In the case of liquid metals this energy change is associated with the existence of collective excitations [8] and in the case of amorphous materials, short range order [9]. The major problems in the study of collective excitations in liquid metals are associated with the limited resolution of the spectrometers and with the need for different corrections which have to be applied to the experimental data. One additional limitation of such measurements is that the velocity of the incoming neutrons has to be of the order of twice the velocity of sound in liquid metals, corresponding to neutron wavelengths less than or equal to 1.1Å for liquid lead and 0.35Å for liquid aluminium. Such neutrons are best provided at sufficient intensity at the pulsed spallation sources. The epithermal neutrons from the spallation sources can be moderated to wavelengths similar to those in conventional reactors, but with fluxes of higher intensity. Proper utilisation of the pulse structure of the flux requires the use of time-of-flight techniques.

One further advantage of the pulsed technique in the study of the static properties of liquid metals at high temperatures is the possibility of performing the experiments at fixed scattering angle. This method eliminates many difficulties associated with shielding and screens around the sample.

2. STRUCTURE STUDIES

In the pulsed neutron technique a white pulsed beam impinges on the sample and the scattered neutrons are collected into a fixed angle θ_{Sc} , figure 1a, where their distribution is resolved by the time-of-flight technique. In the case of continuous neutron sources the scattered neutrons are counted at different angles θ_{Sc} , at fixed wavelength, figure 1b. The neutron time of flight t serves to identify neutron wavelength or wavevector Q as [10]

$$Q[\text{\AA}^{-1}] = 31.75 * \frac{L[\text{m}]}{t[\mu\text{sec}]} * \sin \frac{\theta_{Sc}}{2} \quad (1)$$

L is the flight path between the moderator and the sample. To demonstrate the accuracy of the SNS diffractometer for liquid and amorphous materials [11] we show in figure 1c $\frac{dQ}{Q}$ vs θ_{sc} . At relatively small scattering angles θ_{sc} , the values of $\frac{dQ}{Q}$ takes high values of around a few percent. This means that the demand for measuring the structure factor $S(Q)$ at small Q values with the accuracy round 1% cannot be easily realised at the spallation sources. In order to increase the resolution $\frac{dQ}{Q}$ at small values of the scattering angles θ_{sc} , it is useful to insert a guide tube (rectangular shape, figure 2) between the neutron source and the furnace-sample as well as between the furnace and the detector. Divergency of such guide tubes is smaller than 90 minutes [12]. In general it is easier to use guide tubes and run experiments at fixed scattering angles on pulsed neutron sources than the corresponding experiment on continuous neutron sources.

As already mentioned, to determine the spatial arrangement of atoms in a sample it is necessary to measure precisely the structure factor in a wide Q -region. On the other hand, studies of short range order in amorphous materials require higher resolution than shown in figure 1c. This is achieved by placing, between the moderator and furnace, one or more guide tubes, and in that case the resolution $\frac{dQ}{Q}$ at figure 1c drops below 1% at 10-15°.

3. CORRELATIONS

It is found that for high density liquid metals, for example Al, Pb, Bi..., short wavelength density oscillations are overdamped especially near the position of the main peak in $S(Q)$. Thus if one measured $S(Q)$ up to $12-15 \text{ \AA}^{-1}$ one will be able to determine the shape of the repulsive part of the interatomic potential $X(r)$. In the case of amorphous materials density oscillations are less overdamped which means that one has to measure $S(Q)$ in a much higher Q domain, even up to $20-30 \text{ \AA}^{-1}$. In figure 3 we show the Fourier transform of $S(Q)$, i.e. the pair correlation function $g(r)$ for a liquid metal and the radial distribution function $RDF(r)$ for amorphous alloys [13] :

$$g(r) = 1 + (2\pi^2 nr)^{-1} \int_0^\infty Q [S(Q)-1] \sin(Qr) dQ \quad (2)$$

$$RDF(r) = 4\pi \cdot r^2 \cdot n \cdot g(r) = \frac{2}{\pi} \int_0^\infty rQ [S(Q)-1] \sin(Qr) dQ$$

where n is the number of atoms per unit volume. It is obvious from figure 3 that a difference is noticeable not only in the number of peaks but also in the height. Such differences in height are a consequence of the different structural order in the liquid and amorphous phase, there being obviously more structural ordering in the amorphous phase than in the liquid. From a previous study of amorphous alloys it is known that two kinds of short range ordering exist [13], topological and compositional (chemical). Structural ordering is caused by the existence of different structural defects, such as the vacancies corresponding to the free volume in liquids and amorphous metals [14-15]. The atomic structure of liquid and amorphous materials is shown schematically in figure 4. One should notice the redistribution of the first and second neighbours around the structural defect (V-vacancy) which is manifested by shifts in the RDF(r) [16] before and after annealing [13]. On annealing, the metastable phase of amorphous metals changes to a more stable phase. To follow this change one has to study the atomic mechanism of structure relaxation. From the RDF(r) analysis one only obtains averaged local one-dimensional information about the three-dimensional structures of the amorphous metals varied locally. By time-of-flight neutron diffraction the changes of RDF(r) caused by structural relaxation can be seen up to 20-30 Å, figure 3. Srolovitz et al [16] have shown that the so-called reduced radial distribution function $G(r)$ expressed by

$$G(r) = \frac{\text{RDF}(r)}{r} - 4\pi nr \tag{3}$$

$$= \frac{2}{\pi} \int_0^\infty Q[S(Q)-1] \sin(Qr) dQ - 4\pi nr$$

This is accompanied by the relation to the hydrostatic isothermal stress tensor p . For this case $G_p(r)$ can be related to the second moment of $\langle p^2 \rangle$ [16]

$$G_p(r) = G_0(r + \xi p) \\ \cong G_0(r) + \frac{\xi^2}{2} \frac{\partial^2 G_0(r)}{\partial r^2} \langle p^2 \rangle + \dots \tag{4}$$

where $G_0(r)$ is the RDF(r) from atoms with $p=0$ and ξ is constant beyond the first peak in $G(r)$.

In order to probe the structure relaxation before and after thermal annealing one needs relations between the changes in the $\Delta RDF(r)$ and the second moment of hydrostatic internal stress distribution $\langle p^2 \rangle$ which can be written as

$$\Delta RDF(r) \sim - \frac{\xi^2}{2} \frac{\partial^2 G_o(r)}{\partial r^2} [\langle p^2 \rangle_{\text{annealed}} - \langle p^2 \rangle_{\text{quenched}}] \quad (5)$$

Using a spallation source to provide thermal neutrons one can study precisely the change of $\Delta RDF(r)$, i.e. the parameter ξ , the proportionality coefficient $\frac{\partial^2 G_o(r)}{\partial r^2}$ and the distribution $\langle p^2 \rangle$. The last describes the fluctuation in the local density which is proportional to the gradient of interatomic potential $\psi(r)$. This study is now in progress.

In the case of liquid metals the relaxation phenomena can be studied by the full space and time correlation function $G(r,t)$ which also of course can be measured at the SNS.

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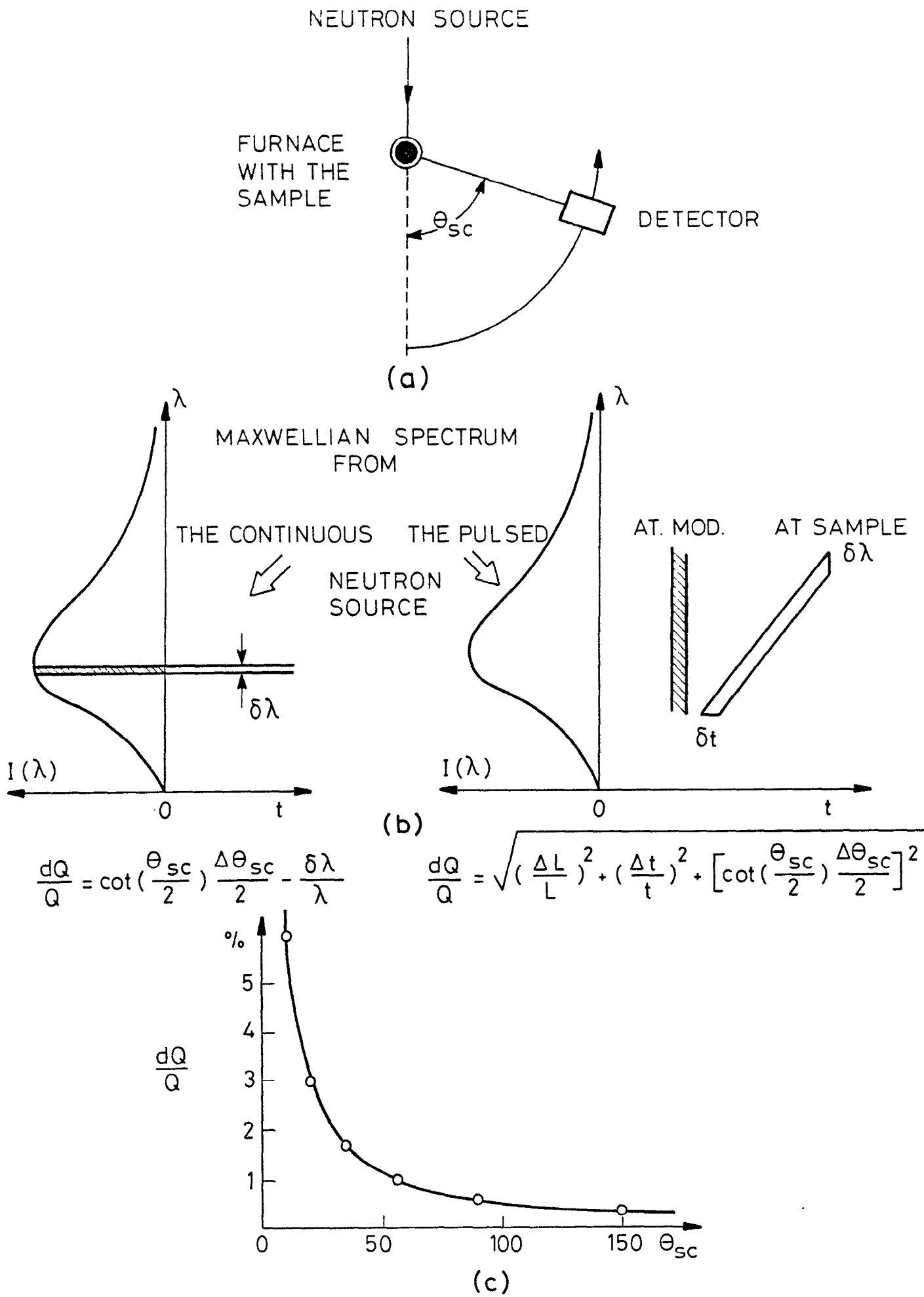


Figure 1

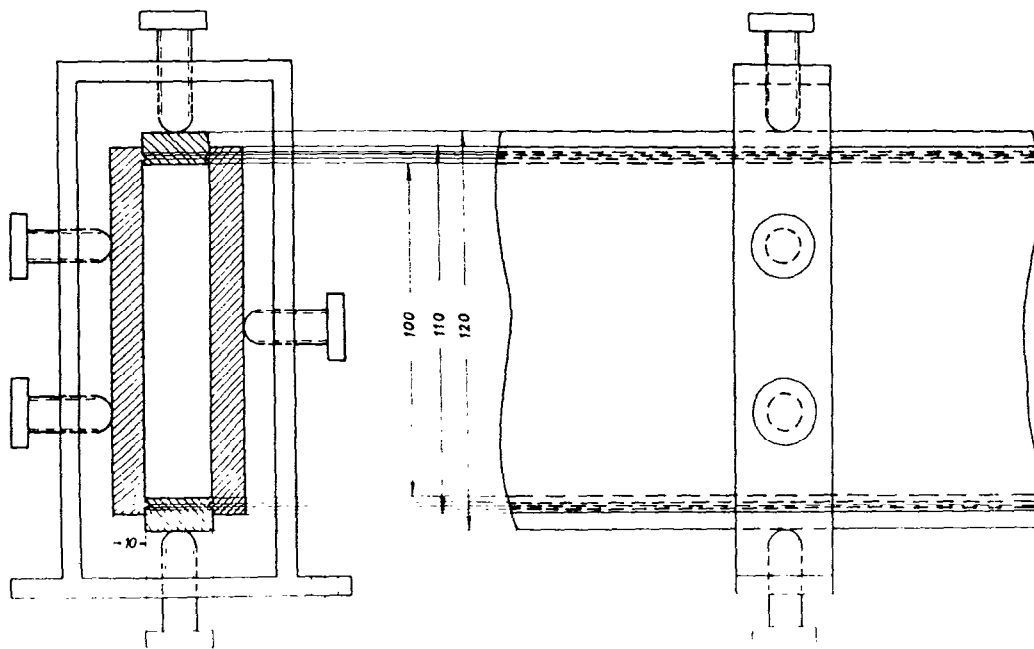


FIGURE 2

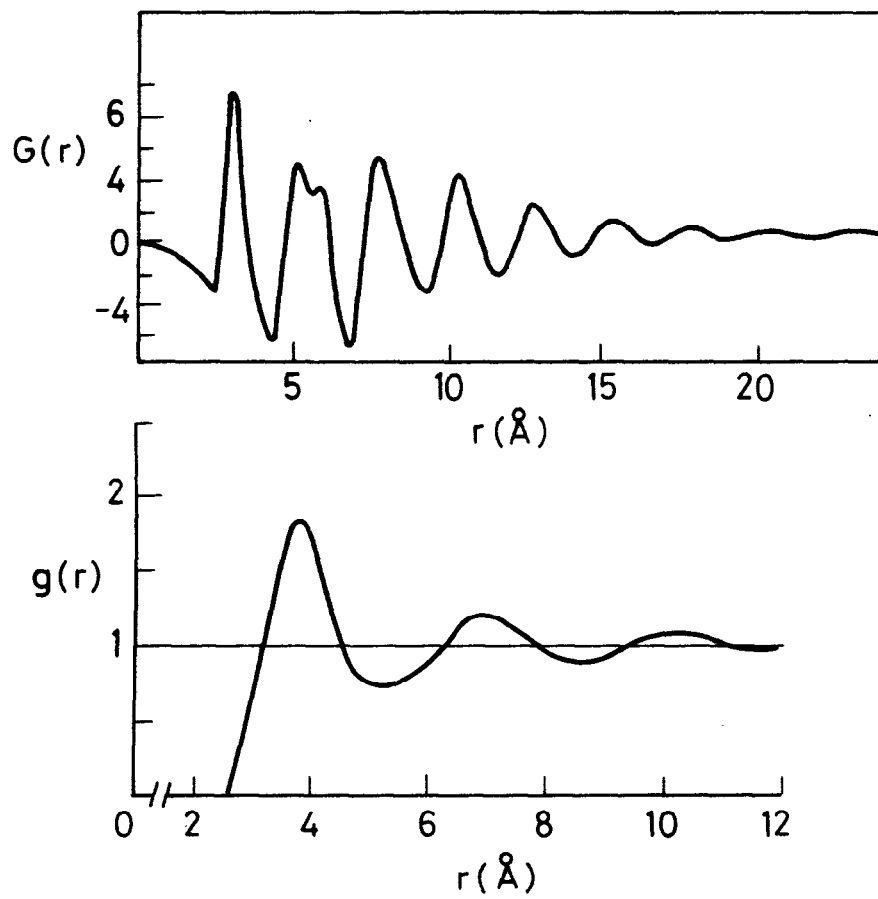


Figure 3

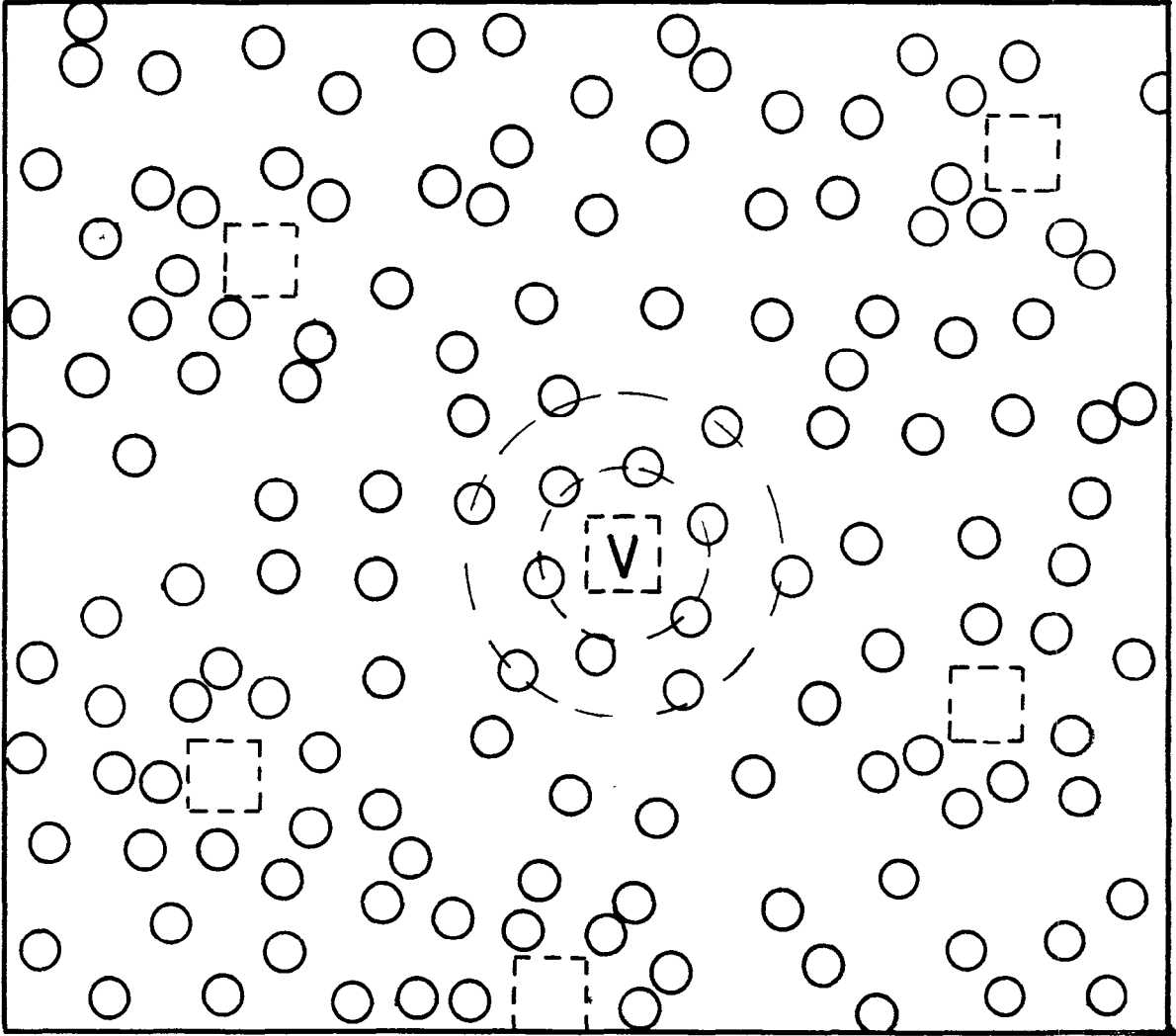


FIGURE 4