

RESOLVING THE FREE BOUNDARY  
PROBLEM FOR ELECTRON HOLE DROPS

By



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## ABSTRACT

The prediction of the stable configuration of a cloud of electron-hole drops involves the resolution of a "free boundary" problem. That is to say, the constraint of steady state relationships is not enough to uniquely determine a stable steady state. There are an infinite number of states which satisfy the boundary conditions. If these stationary states are metastable due to isolation or freedom from large scale fluctuations then different system histories will produce different observable states and hysteresis phenomena. However, if configurational changes can occur through fluctuations, either by creation or annihilation of drops, however slowly, it is necessary to specify an optimizing process to identify a unique stable solution.

In this thesis a simple model is used to describe the cloud, explicitly demonstrating the "free boundary" problem. The optimizing function is taken to be the rate of entropy production, the optimum being a maximum in the dissipation. The optimization process leads to linear global and local flux-force relationships and to explicit expressions for drop density and exciton gas density which are in good functional and quantitative accord with experiments.

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## TABLE OF CONTENTS

	<u>PAGE</u>
INTRODUCTION	1
EXCITONS AND ELECTRON HOLE DROPS	5
THE SPATIAL PROBLEM - CALCULATING THE ELECTRON HOLE DROP RADIUS AND DENSITY	7
THE THEORETICAL MODEL	19
BOUNDARY CONDITIONS	24
THE FREE BOUNDARY VALUE PROBLEM	25
SOLUTIONS TO THE EQUATIONS OF FLOW	27
RESOLVING THE FREE BOUNDARY PROBLEM	29
A FUNCTIONAL FORM FOR $V(R)$	34
COMPARISON WITH EXPERIMENT	39
DYNAMICAL AND CLOUD SHAPE EFFECTS	52
CONCLUSIONS	57
APPENDIX 1 - VALUES OF PARAMETERS	59
APPENDIX 2 - SOLUTIONS TO THE DIFFERENTIAL EQUATIONS	60
BIBLIOGRAPHY	62

## INTRODUCTION

In germanium and silicon at sufficiently low temperatures under laser excitation, an exciton gas exists. Excitons are a bound state of an electron and hole analogous to the bound state of an electron and positron forming positronium. At lower temperatures (the critical temperature is about  $6.5^{\circ}\text{K}$  in germanium) the exciton gas condenses into a Fermi liquid phase of electrons and holes which takes the form of a cloud (of) liquid drops in the gas. Despite the manifest nonequilibrium characteristics of the system (electrons and holes are continuously recombining) the phase transition shows a remarkable correspondence to classical equilibrium phase diagrams [Fig. 1].

The principle difference between this system and equilibrium systems is that the two phase region is characterized by a spatial organization in which the liquid phase is separated into a number of drops, all surrounded by the gaseous phase. This is to be compared to a normal equilibrium system in which the liquid phase takes one large amorphous form.

This spatial separation into liquid drops is entirely due to the nonequilibrium nature of the system. In the steady

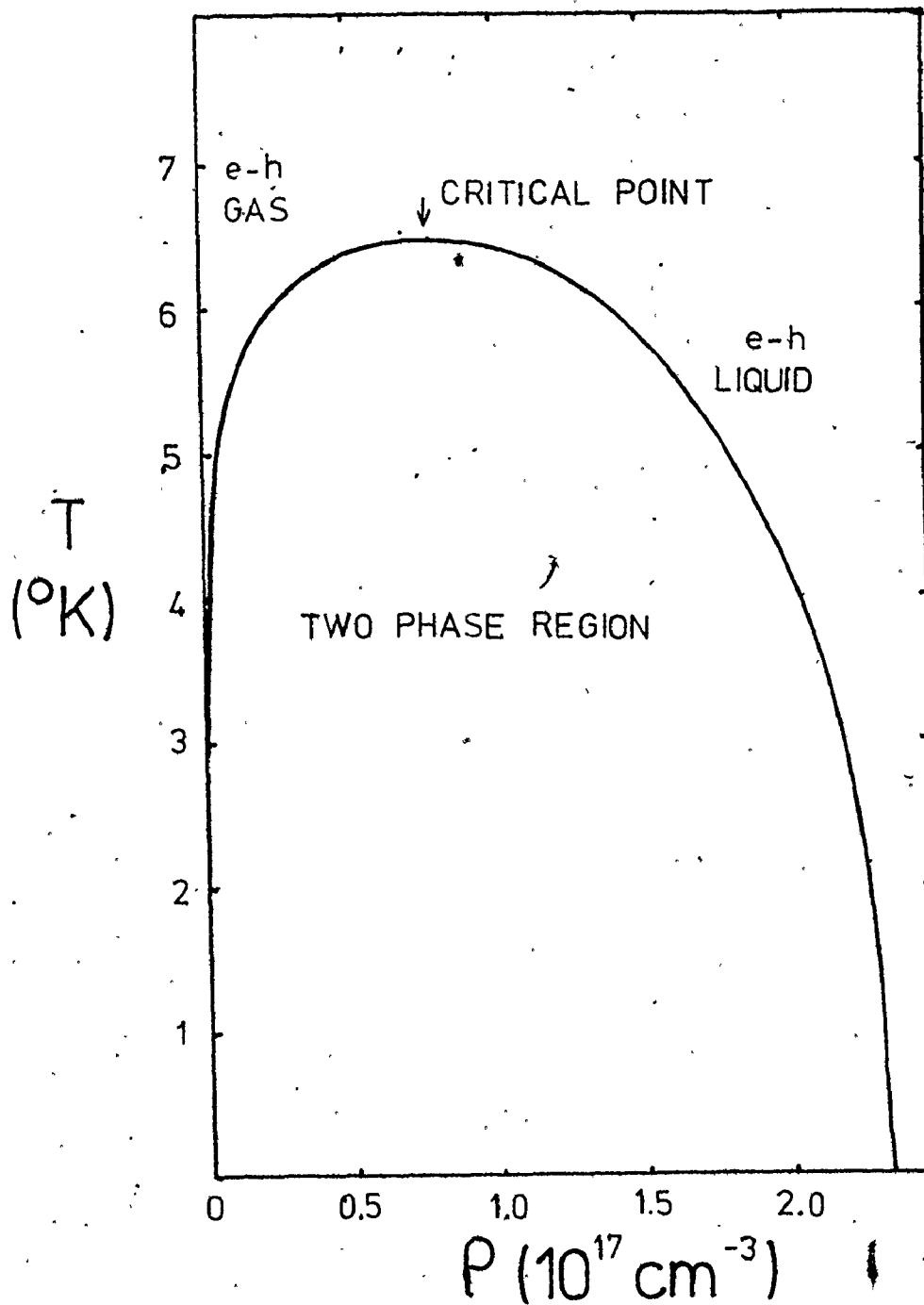


Fig. 1

Phase diagram for Germanium. Gas densities are determined from onset conditions, Hensel et al. [1b].



state volume recombination within the liquid region depletes the liquid as fast as the gas condenses. A low surface to volume ratio for large drops prevents them from growing indefinitely and instead forces finite sized drops.

The problem then is to identify the stable spatial steady state(s) of the system. Such a steady state will be characterized by a certain drop radius, drop density and flux of excitons into the drops. (These are not independent quantities.)

Several previous approaches to this problem in the literature have been based on rate equations describing the rate of loss and gain of excitons for drops of a given size. This approach represents a microscopic viewpoint concerned with the action of individual electrons. There have also been macroscopic approaches, notably by Bagaev et al. [10,14] using diffusion equations.

We here attack the problem from a purely macroscopic point of view, solving the differential equations governing the bulk flow of the exciton gas within a cloud of drops. The purpose of this is twofold, firstly to demonstrate clearly the nature of the phenomenological problem and secondly to draw a connection with irreversible thermodynamics which focusses on a macroscopic formulation.

It is shown that the system gives rise to a free boundary value problem; that is to say the system has an internal

degree of freedom and is therefore insufficiently constrained to yield a unique steady state solution. As a consequence the system is able to exhibit metastable configurations and history-dependent effects as is indeed observed experimentally.

To the extent that the cloud of drops forms a fluctuation space in which transitions from one metastable state to another occur and the initial conditions are accordingly "forgotten", a unique final stable steady state will evolve. To identify this state the extremal point of the rate of entropy production is calculated, thus removing the degree of freedom.

Besides these general results, a relationship for the volume fraction of drops is found and the hitherto "a priori" assumption of constant gas density is justified.

The theory developed is subject to the assumption of constant volume pumping, which unfortunately is rarely (if ever) the experimental case. Effects of non volume pumping on the ideal solution are discussed, and given these effects, the solution is shown to be consistent with experimental evidence.

## EXCITONS AND ELECTRON HOLE DROPS

At temperatures of a few degrees Kelvin there are essentially no electrons in the conduction band of typical pure semiconductors. If electrons are excited into the conduction band by a laser they will normally quickly drop back to the valence band. However, in indirect gap semiconductors such as germanium or silicon the recombination process is inhibited because of the need for the participation of a phonon. Recombination time thus increases to microseconds from nanoseconds. As a result it is possible to attain relatively high densities of excited electrons and holes. These electrons and holes are treated in the quasiparticle approximation and interact via the Coulomb field moderated by the dielectric constant of the medium. They can form a bound state, the exciton, similar to that of the hydrogen atom, or more accurately positronium.

There are other possible states, excitonic molecules and a high density metallic liquid comprising electrons and holes. The binding energies of these two states have been calculated by various investigators (for example [2,3,4]. See also [1a] for a further list) and depend strongly on the details of the band structure such as the degeneracy, anisotropy and relative effective masses. For germanium and silicon it turns out that the excitation molecules are only weakly bound [2] whereas

the liquid phase has a significantly lower energy [3,4]. It is then possible to observe a phase transition from gas to liquid at low enough temperatures and high enough exciton gas densities. Phase diagrams have been constructed from onset measurements [Fig. 1].

THE SPATIAL PROBLEM - CALCULATING THE  
ELECTRON HOLE DROP RADIUS AND DENSITY

The first approach to this problem was taken by Pokrovskii [5] by writing down the steady state rate equation for the gain and loss of electron-hole pairs by a drop, viz.,

$$\frac{4\pi R^3}{3} \frac{\rho}{\tau_0} = 4\pi R^2 (a\rho(R) - b\rho_0) = 4\pi R^2 V(R) \rho(R) \quad (1)$$

Here  $\rho$  and  $\rho_0$  are gas and liquid densities,  $\tau_0$  is the liquid recombination time and  $V(R)$  is the net rate of inflow. "a" and "b" are rate coefficients for condensation and evaporation. These coefficients are not known "a priori" so it is the standard approach in the literature to evaluate them by considering the principle of detailed balance. In equilibrium the right hand side of (1) should be zero and this yields

$$a\rho_{eq} - b\rho_0 = 0 \quad (2)$$

or

$$\frac{b\rho_0}{a} = \rho_{eq} \quad (3)$$

where  $\rho_{eq}$  is the exciton density that would exist if the gas were in thermodynamic equilibrium with the drops. The well known result for free particles [6,8] is

$$\rho_{eq} = \gamma \left( \frac{M_{ex} kT}{2\pi\hbar^2} \right)^{3/2} e^{-\phi/kT} e^{2\zeta/\rho_0 RkT} \quad (4)$$

where  $\gamma$  is the degeneracy of the excitons, ( $\gamma = 16$  for germanium),  $\phi$  is the work function between liquid and gas,  $R$  is the radius of the drops and  $e^{2\zeta/\rho_0 RkT}$  represents the correction to the work function due to the surface tension energy  $\zeta$ . Experimentally, values for  $R$  are large enough (1 - 10  $\mu\text{m}$ ) that this last term can be neglected ( $\zeta = 10^{-4}$  ergs  $\text{cm}^{-2}$  [1a,7]). However, due to nonparabolicity of the density of states for excitons (4) is not quite correct and the preexponential factor should be smaller [1a,1b].

With the use of (3) and (4) the coefficient "b" can be eliminated from (1) leaving the coefficient "a" for the rate of condensation to be determined. The assumption is then made that every exciton hitting the drop condenses and is absorbed by the drop. The justification for this is that the work potential between gas and liquid is large with respect to  $kT$  ( $\phi/k$  is about 21°K for germanium) and so the excitons should just "fall in" the potential well. The number of excitons hitting the drop is then calculated by assuming an equilibrium velocity distribution. This gives the incoming flux as

$$J_{in} = a\rho_{eq} = \frac{1}{2} \rho_{eq} V_T \langle \cos\theta \rangle = \rho_{eq} \frac{V_T}{4} \quad (5)$$

where  $V_T$  is the thermal velocity of the excitons. "a" is thereby identified as  $V_T/4$ .  $V(R)$  then becomes

$$V(R) = \frac{V_T}{4} \left( 1 - \frac{\rho_{eq}}{\rho} \right) \quad (6)$$

Use of (6) for  $\rho$  different from  $\rho_{eq}$  requires that "a" not be a function of density. In addition, for  $\rho > \rho_{eq}$  there is a cooperative flow of gas towards the drop and the assumption of an equilibrium velocity distribution is clearly erroneous.

However, even accepting the approximations for "a", the equations (6) and (1) do not completely specify R and  $\rho$ . There are too few equations to solve for too many variables. This feature of the rate equations can not be removed as the requirement of a steady state is not a sufficient constraint. One must have information describing the establishment and evolution with time of the system.

Attempts to provide information on time dependent behavior have been made by Silver [11,12] and Westervelt [7,13]. Their approaches are essentially similar, the basis for the approach being a generalization of (6) to non steady state situations where  $\frac{dR}{dt}$  is not zero and the number density of drops changes with time.

Before describing the approaches of Silver and Westervelt, consider

$$\rho_0 4\pi R^2 \frac{dR}{dt} = - \frac{4\pi R^3}{3} \frac{\rho_0}{\tau_0} + \pi R^2 V_T (\rho - \rho_{eq}) \quad (7)$$

or

$$\frac{dR}{dt} = - \frac{R}{3\tau_0} - \frac{V_T}{4\rho_0} \rho_{eq} + \frac{V_T}{4\rho_0} \quad (8)$$

which follow directly from (1) and (6) for  $\frac{dR}{dt} \neq 0$ . Here  $\rho_{eq}(R)$  is given by (4) with the R dependence included. Disregarding for the moment the last term  $\frac{V_T \rho}{4\rho_0}$  in (8)  $\frac{dR}{dt}$  can be plotted as a function of R for a given T. (See Fig. 2. This demonstration is that of Rice [1a].) For small R ( $R < 0.1 \mu\text{m}$ ) the  $\frac{1}{R}$  in the exponential for  $\rho_{eq}$  drives  $\frac{dR}{dt}$  strongly negative while for large R the first term  $-\frac{R}{3t_0}$  in (8) has the same result. Now the value of  $\rho$  in the last term determines the zero line for  $\frac{dR}{dt}$ . If  $\rho$  is too small (line A in Fig. 2), there will be no value of R for which  $\frac{dR}{dt}$  is not negative and drops are not stable. As  $\rho$  is increased it will meet the maximum in  $\frac{dR}{dt}$  at  $R^*$  (line B in fig. 2) and a steady state is possible. (It is not stable against fluctuations, however.) For still larger  $\rho$  (line C in Fig. 2) there are two solutions for which  $\frac{dR}{dt} = 0$ . The first zero at small R is also unstable against fluctuations and is the critical size for the nucleation of drops. The second zero, however, is stable against fluctuations (if R is perturbed the sign of  $\frac{dR}{dt}$  is such that it will relax back to the zero point) and represents a possible steady state. Consistent with the previous remark that R is not determined by (1) and (6) there are many possible choices for  $\rho$  which give a steady state, in fact for all  $\rho > \rho_B$  in Fig. 2.

The methods of both Silver and Westervelt were to modify (7) to pertain to a drop with  $\nu$  electron-hole pairs. It is assumed that electron-hole pairs are gained (or lost) one pair



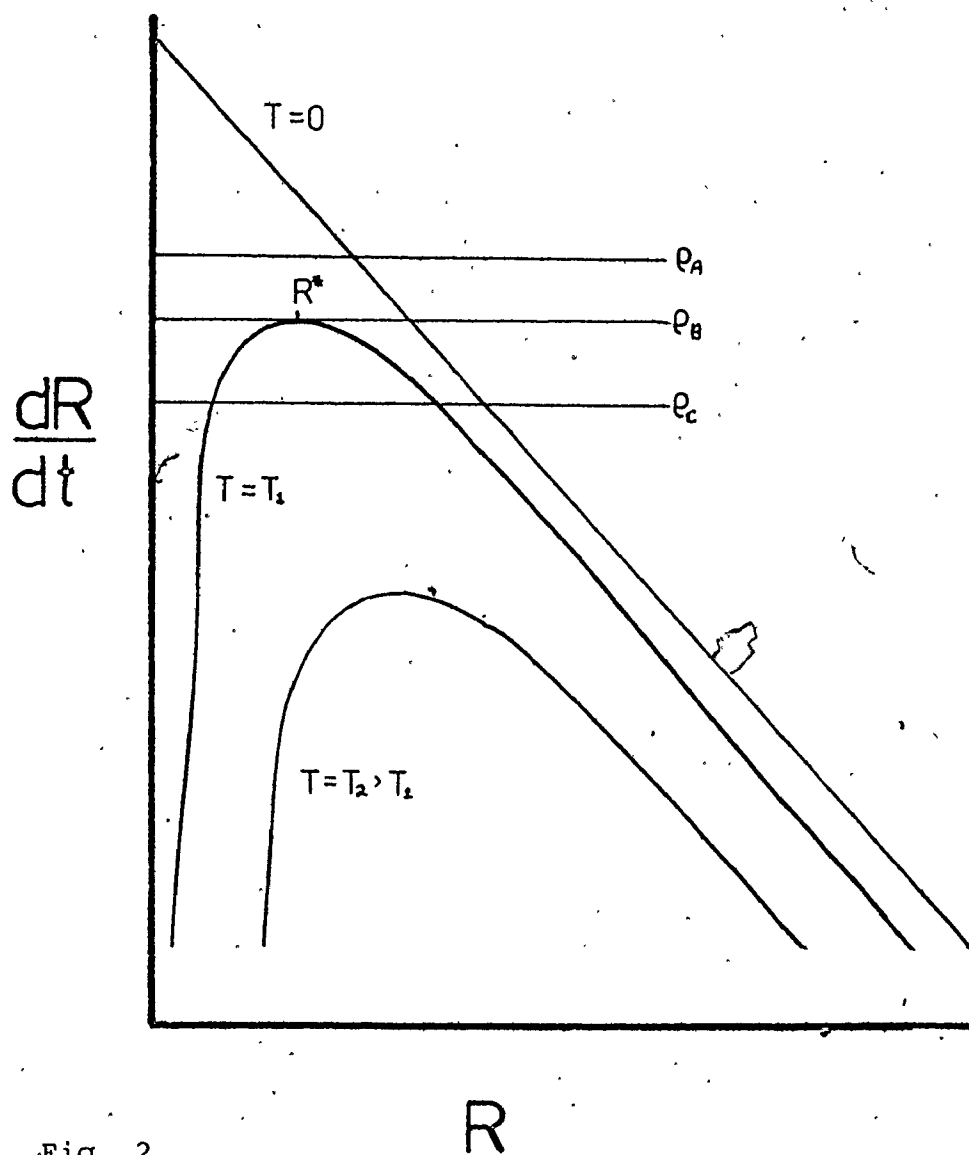


Fig. 2

$dR/dt$  versus  $R$  for various temperatures as given by equation (8). The zero line is set by the value of the exciton density, i.e., lines  $\rho_A$ ,  $\rho_B$ ,  $\rho_C$  with  $\rho_A < \rho_B < \rho_C$ . After Rice [1a].

at a time to form a drop of size  $v+1$  or  $v-1$ . In this manner a set of recursion relations relating drops to the gas ( $v=1$ ) can be written down. In this way Silver [11] obtained

$$\begin{aligned} \frac{dP}{dt}(v,t) = & \{V_T \rho 4\pi (R_{v+1}^2 P(v-1,t) - R_v^2 P(v,t))\} \\ & + \left\{ \frac{v+1}{\tau_0} P(v+1,t) - \frac{v}{\tau_0} P(v,t) \right\} \\ & + \{4\pi V_T \rho_{eq}(v) (P(v+1,t) R_{v+1}^2 - P(v,t) R_v^2)\} \end{aligned} \quad (9)$$

for the rate equations for a drop condensing on an impurity\*. The three sets of curly brackets earmark the contributions from condensation, recombination and evaporation, respectively.  $P(v,t)$  is the probability of there being a complex of size  $v$  bound to the impurity at time  $t$ . The steady state is described by  $\frac{dP(v,t)}{dt} = 0$  for all  $v$ .

Westervelt [13] preferred to write an equivalent pair of equations obtaining

$$J_v = g_{v-1} \rho \beta (v-1)^{2/3} - g_v \left( a_v v^{2/3} + \frac{v}{\tau_0} \right). \quad (10)$$

$$\frac{dg_v}{dt} = J_v - J_{v+1}. \quad (11)$$

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\* Note that Silver uses  $V_T$  for "a" not  $V_T/4$  as in equation (5). He also considers drops bound to an impurity. Westervelt, however, has considered both homogeneous and inhomogeneous cases and has shown that free nucleation (i.e. not bound to a defect) is not significantly different [7,13].

Here  $g_\nu$  is the number of drops of size  $\nu$  and  $J_\nu$  is the rate of creation of new drops from drops of smaller size. The terms involving  $\beta(\nu-1)^{2/3}$  and  $a_\nu \nu^{2/3}$  are condensation and evaporation rates, respectively (i.e.  $\beta(\nu-1)^{2/3} = 4\pi R_{\nu-1}^2 \frac{V_T}{4}$ ). The steady state is described by  $\frac{d}{dt} g_\nu(t) = 0$  and  $J_\nu = J_{\nu+1} = 0$ .

These sets of recursion relations (9) or (10) and (11) can be solved for the steady state. This gives the steady state size distribution  $P(\nu)$  or  $g_\nu$  as a function of  $\rho$ . For  $\rho$  greater than a certain value ( $\rho_B$ ) these distributions show a pronounced sharp peak for large  $\nu$ . This peak is the electron hole drop.

It is important to realize that the equations (9), (10), (11) and their steady state solutions do not contain any more information on the determination of the steady state than does (8). Indeed they could not, for (9), (10), (11) were derived from (8) with no additional input. Having  $\rho_\nu(\rho)$  or  $g_\nu(\rho)$  still results in a indeterminacy in  $\rho$ . Silver thus makes the conjecture that the system will relax nearly to the minimum value  $R^*$  (see Fig. 2) [11]. (It cannot relax all the way back to  $R^*$  because as previously noted, a drop of radius  $R^*$  is unstable with respect to fluctuations to smaller  $R$ .) The conjecture is made without a basis for support and is not discussed further.

The use of the recursion relation approach is in the application to time rates of change of size distributions,  $\rho(\nu)$  or  $g_\nu$ , which are not solutions to the steady state relations. This is most

easily seen in Westervelt's formalism. In equation (10) for steady state solutions of  $g_v$  the right hand side is by definition zero. However if a non steady state distribution  $g_v$  is specified then  $J_v \neq 0$  and the rate of production of drops can be calculated. In particular, Westervelt chose distributions equivalent to i) only exciton gas present and no drops present, ii) drops present but not enough gas present. The resulting rates of production of drops he calls, respectively,  $J_+$  and  $J_-$ . The findings of Silver and Westervelt are that even if a non steady state size distribution exists,  $J_+$  and  $J_-$  can be very slow, indeed that relaxation times can be as long as 10 days. As conditions are made more and more extreme there comes a point where  $J_+$  and  $J_-$  increase suddenly by many orders of magnitude. For example if no drops are present and  $\rho$  is gradually made greater than  $\rho_{eq}$ ,  $J_+$  is at first extremely small, but then at a well defined turning point,  $J_+$  "turns on" and drops are produced. This is the well known phenomena of superaturation, observable in classical gas-liquid systems. A similar event occurs with  $J_-$ . Having initially drops and gas in equilibrium, the gas density can be reduced without noticeable loss of drops until a threshold is reached and  $J_-$  "turns on" and all the drops evaporate. Westervelt's calculated results for these thresholds are shown in [Fig. 3] [7]. Silver has a similar result [12].

Although the threshold for  $J_+$  in [Fig. 3] defines a maximum  $\rho_+$  that can exist without drops, it does not represent

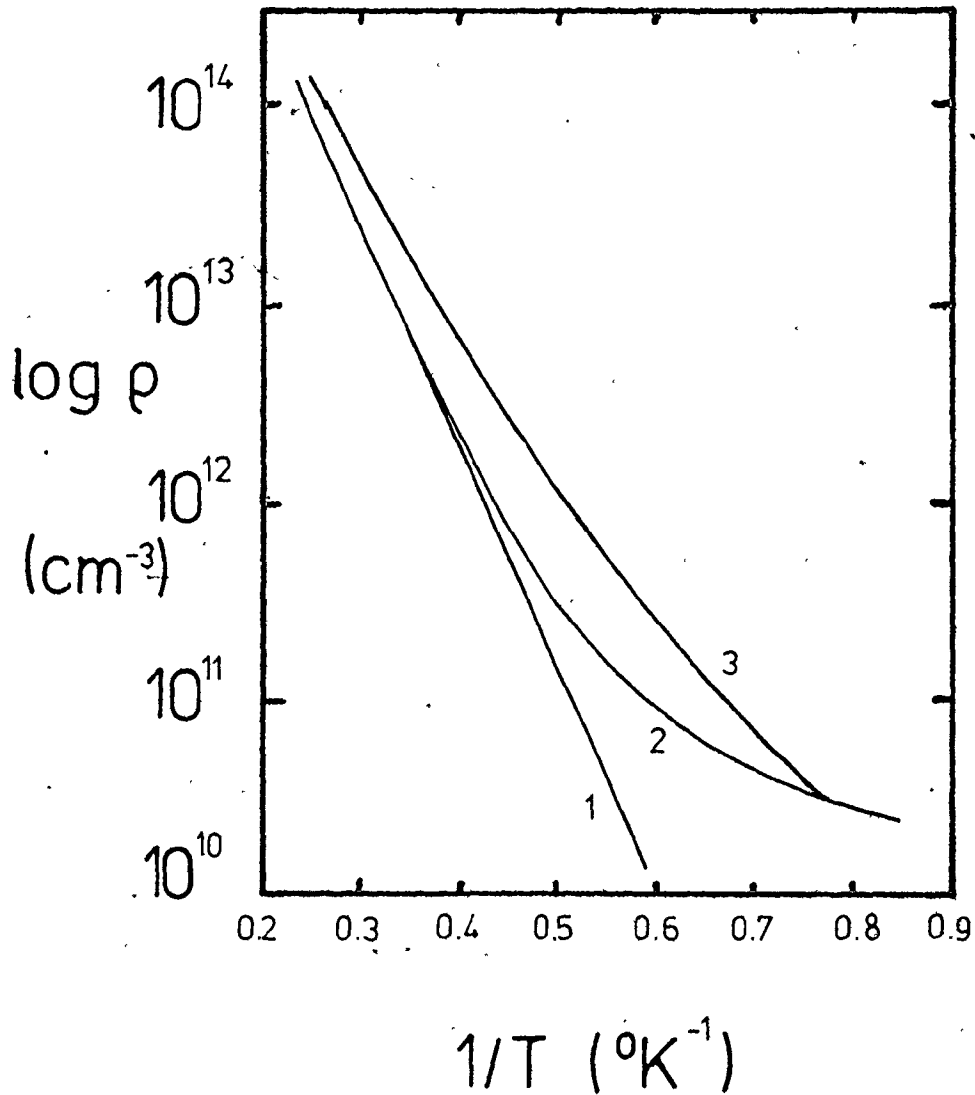


Fig. 3

$\ln \rho$  versus  $1/T$ , threshold curves (Westervelt [7]). Curve 1 shows the classical  $\rho_{eq}$  line given by  $Ae^{-\beta\phi}$ . Curve 2 shows the  $J_-$  line. Curve 3 shows the  $J_+$  line.

a maximum for  $\rho$  in conjunction with the existence of drops. The maximum calculated for  $J_+$  represents a very special non steady state size distribution, all gas and no drops. If there are drops the situation changes to a different initial size distribution and  $\rho$  can be greater than  $\rho_+$ . If the reader has any doubt about this consider the experimental measurements of density made by Gershenson et.al. [9] in [Fig. 4] with [Fig. 3]. The densities do not approach a unique density independent of the pumping level  $G$ . In fact the solid line drawn marks the onset of phase separation of gas to liquid and as such is probably the  $\rho_+$  line in [Fig. 3]. As can be seen,  $\rho$  can be greater than the onset criterion density.

Both Silver and Westervelt seem to have misinterpreted the significance of these rates for they both give the unique steady state as being that state where  $J_+ = J_-$ . This is not an allowable procedure as  $J_+$  and  $J_-$  are calculated for highly specific, different deviations from a steady state size distribution as determined by the spectrum of solutions to (9), (10) and (11). One system cannot be simultaneously in a distribution that applies to  $J_+$  and in a distribution that applies to  $J_-$ .

There are two problems then in defining a unique steady state, i) the steady state condition is not sufficiently constraining, ii) away from a steady state, relaxation times can be very long. The aim of this thesis is to show that

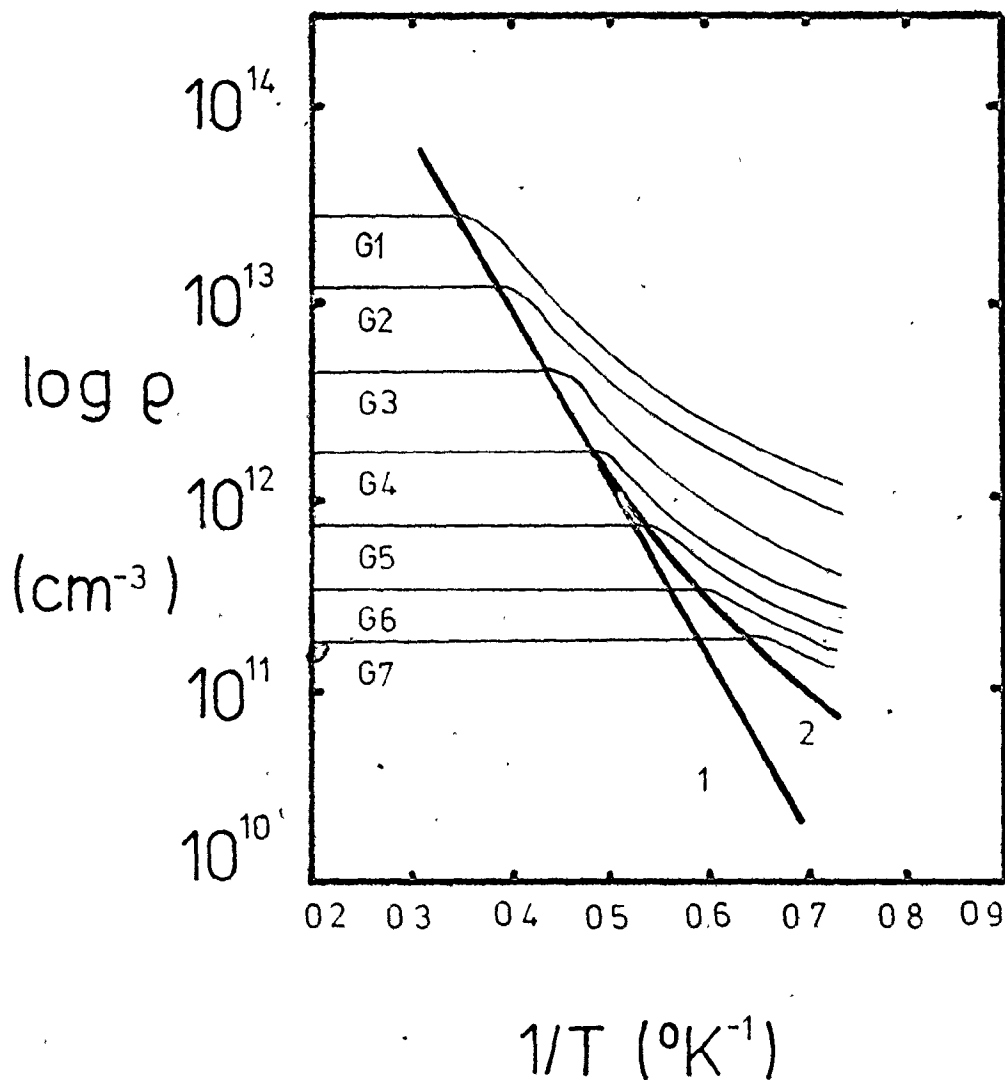


Fig. 4

Experimental values of  $\ln \rho$  versus  $1/T$  for different pump powers  $G$ . (Gershenson et.al. [9]). Line 1 is the straight line fit to the onset points for  $G_1, G_2, G_3$  giving  $Ae^{-\phi/KT}$  with  $\phi = 1.65 \pm 0.1$  meV. Curve 2 fits all of the onsets. The slope of line 1 being less than that determined by luminescence is consistent with the supersaturation concept. Compare to line 3 in Fig. 3.

i) is an inherent characteristic of the problem (indeed of all non equilibrium steady state problems) and that a unique solution can be chosen only by appealing to an optimization principle. Unfortunately, once such a unique solution is found, its experimental verification is limited by ii).



### THE THEORETICAL MODEL

The drops are taken to be uniformly distributed in a region of constant volume excitation. Each drop of radius  $R$  is surrounded by a spherical region of gas of radius  $R^*$  where  $\frac{4\pi}{3} R^{*3}$  is the volume of the Wigner Seitz cell of the drop lattice, [Fig. 5]. The exciton gas flows inward from the perimeter  $R^*$  to the drop which acts as a sink. The rate of creation of excitons per unit volume is denoted by  $G$  and the rate of recombination by  $\rho/\tau_x$  where  $\rho$  is the exciton density and  $\tau_x$  is the exciton recombination time.

The flow of the exciton gas is described by the continuity equation and the Navier-Stokes equation with the inclusion of appropriate terms to describe the creation and recombination of excitons. As an approximation, viscous terms have been omitted from the Navier-Stokes equation. The ideal gas law provides the necessary constitutive relation. The justification for the use of the ideal gas law lies in

- 1)  $\tau_x \gg \tau_{\text{collision}}$  ( $\sim 10^{-11}$  sec) so that local thermodynamic equilibrium is maintained, and
- 2) the density of the excitons is such that the volume per exciton is much larger than the size of the excitons so that the excitons are effectively non-interacting point particles [15].

In addition we invoke a steady state condition.

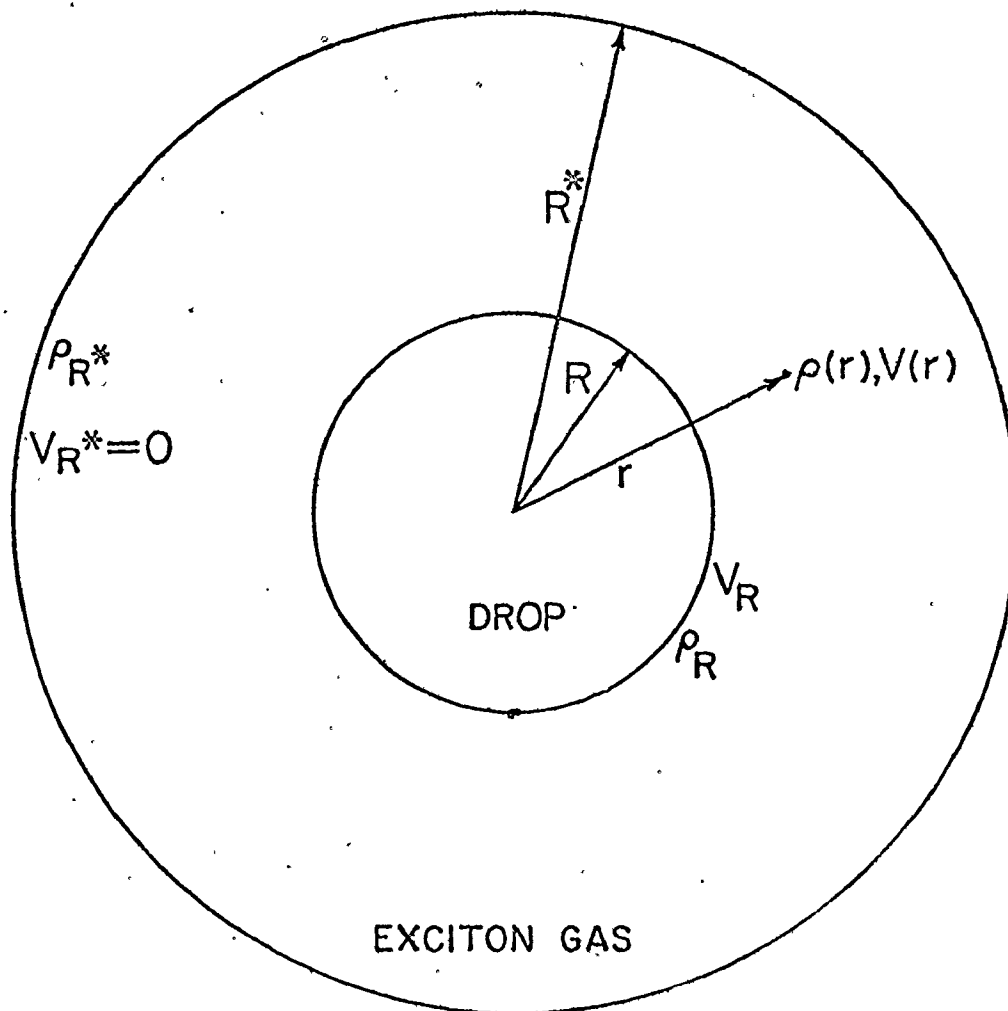


Fig. 5

The Model. An electron hole drop surrounded by a sphere of exciton gas.

The differential equations are the continuity equation

$$(G - \frac{\rho}{\tau_x}) = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho v) \quad (12)$$

and the Navier-Stokes equation

$$-\frac{\partial \rho}{\partial r} \frac{kT}{M} = -\frac{\partial \rho}{\partial r} \frac{V_T^2}{2} = \rho v \frac{\partial v}{\partial r} - (G - \frac{\rho}{\tau_x}) v \quad (13)$$

where  $V_T$  is approximately the thermal velocity

$$\langle v \rangle = \left( \frac{8kT}{\pi M} \right)^{1/2} \sim \left( \frac{2kT}{M} \right)^{1/2} = V_T \quad (14)$$

Validity of this model is conditional upon 1) the mean free path of the excitons must be of the same size or smaller than the dimensions of the drop 2) and a steady state or quasi-steady state situation exists.

The first condition is met at the upper ranges of temperature for which electron-hole drops are observed. To estimate the temperature range for which this condition is met we use the steady state relation relating the number of electron-hole pairs recombining in the drop to the surface influx of excitons\*

$$\frac{4\pi}{3} \frac{R^3 \rho_0}{\tau_0} = 4\pi R^2 \rho(R) V(R) \quad (15)$$

\* Strictly speaking one should allow for electrons and holes excited in the region of space occupied by the liquid. In this case the electrons and holes would drop directly to the liquid energy level instead of an exciton level and equation (15) should be  $\frac{4\pi R^3}{3} \left( \frac{\rho_0}{\tau_0} - G \right) = 4\pi R^2 \rho(R) V(R)$  where  $G$  is the rate of generation of excitons. However  $\frac{\rho_0}{G\tau_0}$  is at least 100 so that  $G$  is negligible with respect to  $\frac{\rho_0}{\tau_0}$ .

where  $\rho_0$  is the liquid density and  $\tau_0$  its recombination time, and the classical expression for the mean free path

$$\lambda = \frac{1}{\sqrt{2}\pi\rho a} \quad (16)$$

where  $a$  is the exciton cross sectional area. We require that

$$1 \lesssim \frac{\bar{R}}{\lambda} = \frac{3\tau_0\rho^2(R)V(R)\sqrt{2}\pi a}{\rho_0} \quad (17)$$

The worst case is if  $\rho(R) = \rho_{eq}$  as given by (4) without the  $R$  dependent term. Substituting numerical values (see Appendix 1) we obtain

$$T > \frac{42}{21 + \ln\left(\frac{V(R)}{V_T}\right) + 3\ln\left(\frac{T}{3}\right)} \quad (18)$$

The weak dependence on  $V(R)/V_T$  means that even if  $V(R)/V_T \sim 10^{-3}$  the range is  $T > 3.0^\circ\text{K}$ . As typical experimental saturation temperatures are  $> 4^\circ\text{K}$  there does exist a significant range of temperatures for which the model is valid.

The second condition (that the system be in a quasi-steady state) implies that external boundary conditions such as the amount of laser pumping be constant in time as well as that the physical system represented by the drops be stable with time. This requires that phenomena which would change the drop concentration, such as drop collisions or drop nucleation be negligible or that there is a steady state balance between such processes.

As diffusion equations have been frequently used in the literature [5,7,9,10] to describe the transport process instead of the Navier-Stokes equation, a comment on its use is required. Diffusion equations apply to transport processes of a dilute system moving through a host medium via a random walk of the dilute system particles [16]. If the interactions between the particles of the dilute system are dominant the process cannot be described by a diffusion equation but is a cooperative process which must be described by nonlinear transport equations such as the Navier-Stokes equations.

Specific instances in which inapplicable use of diffusion equations has been made are firstly in [7] where a self diffusion equation is used for the exciton gas flow to a liquid drop. Self diffusion equations apply to situations such as heat conduction but not to bulk flow as is the case here. The other use of diffusion equations [5,9,10] has interpreted the host medium as being the phonons. However the phonon-exciton collision time can be estimated by considering recombination times as these are events involving the interaction of electrons and holes with phonons. The recombination time in germanium is  $\sim 7 \mu\text{s}$  whereas collision times between excitons in the gas is  $\sim 10^{-11}$  sec (with  $\rho \sim 10^{14} \text{ cm}^{-3}$ ). Clearly, the bulk cooperative interactions of excitons is the more important transport process.

BOUNDARY CONDITIONS

Solutions to equations (12) and (13) must be consistent with several boundary conditions. These are i) the rate of flow of excitons into the drop must equal the rate of recombination of electron-hole pairs within the drop (equation (15)) and ii)  $V(R^*) = 0$ .

Condition ii) can be shown by placing an infinitesimally thin pillbox on the boundary between two drops and integrating the continuity equation (12) over surface and volume integrals, viz.,

$$\int_S \rho \vec{V} \cdot d\vec{A} = \int_V \left( G - \frac{\rho}{\tau_x} \right) dV . \quad (19)$$

The right hand side goes to zero, and owing to the symmetry between drops, the left hand side is  $2A\rho(R^*)V(R^*)$ . As  $\rho(R^*) \neq 0$  condition ii) follows.

THE FREE BOUNDARY VALUE PROBLEM

Before developing solutions to equations (12) and (13) we shall clarify the structure of the boundary value problem. It is a problem dealing with a cooperative phenomena (the flow of the gas into an array of drops) and as such need not be expected to give a unique steady state solution. Rather, it may have many possible steady state solutions consistent with the boundary conditions. Examples of this are known in other fields (hydrodynamics and materials science) such as the eutectic problem dealing with the steady state growth of a bicrystal into a melt [17,44].

As the present problem is set up there are six variables to be solved for;  $\rho(R)$ ,  $\rho(R^*)$ ,  $V(R)$ ,  $V(R^*)$ ,  $R$ ,  $R^*$ . Applied to these variables we need six constraints to yield a unique solution. Indeed, we have

$$4\pi R^2 V(R) \rho(R) = \frac{4\pi R^3}{3} \frac{\rho_0}{\tau_0} \quad \text{i)}$$

$$V(R^*) = 0 \quad \text{ii)}$$

$$\text{equation (12)} \quad \text{iii)}$$

$$\text{equation (13)} \quad \text{iv)}$$

and we further require specific values of  $V(R)$  and  $\rho(R)$ .

Derivatives of  $\rho$  and  $V$  are fixed by equations (12) and (13) so that they cannot serve as independent boundary conditions.

Generally speaking, there exists a single further relation between  $\rho(R)$  and  $V(R)$  and the other variables. This further relationship can readily be visualized by noting that in principle the rate coefficients for condensation and evaporation ("a" and "b" in equation (1)) can be calculated from matrix elements and a Monte Carlo calculation.

The boundary value problem thus has six variables and yet only five constraints viz; i), ii), iii), iv) and the further functional relationship described above. The system is insufficiently constrained to give a unique solution. This has been noted in the literature [1a,1b] and indeed the procedure adopted by Silver and Westervelt leads to an indeterminacy in  $\rho$ .

We interpret this internal degree of freedom as pertaining to a spectrum of solutions representing possible metastable states which can be exhibited by the system. For a given experiment the specific state that is observed depends in detail on the history of the system, on how many drops were nucleated and destroyed during the history up to the final pumping level and subsequent evolution of the system. For example, once a given number of drops have been nucleated and stabilized via the pumping history (pulse risetime and pump power) this number determines the volume per drop ( $R^*$ ) which in turn serves as the sixth constraint. Only then is the solution uniquely defined. Such hysteresis effects are observed experimentally [14,18].



SOLUTIONS TO THE EQUATIONS OF FLOW

Equations (12) and (13) are trivially solvable if the source terms  $(G - \frac{\rho}{\tau_x})$  are ignored. The procedure is then to treat the source terms as a perturbation. This is permissible as  $r/\tau_x V_T$  is a small quantity for all reasonable  $r$ . To second order in  $(\frac{V}{V_T})$  and  $(\frac{r}{\tau_x V_T})$  the solutions are (see Appendix.2)

$$V = - \frac{V(R)R^2}{(1 - \frac{R^3}{R^{*3}})r^2} + \frac{1}{3} \frac{(G\tau_x^{-\rho(R^*)})}{\rho(R^*)} \frac{r}{\tau_x} \quad (20)$$

$$\approx - \frac{V(R)R^2}{r^2} + \frac{1}{3} \frac{(G\tau_x^{-\rho(R^*)})}{\rho(R^*)} \frac{r}{\tau_x}$$

$$\rho \approx \rho(R^*) \exp \left[ - \frac{V(R)^2}{V_T^2} \frac{R^2}{r^4} + \frac{2}{9} \frac{(G\tau_x^{-\rho(R^*)})^2 r^2}{\rho(R^*)^2 V_T^2 \tau_x^2} + \frac{8}{3} \frac{V(R)(G\tau_x^{-\rho(R^*)})R^2}{V_T^2 \rho(R^*) r \tau_x} \right] \quad (21)$$

In the above  $G\tau_x$  is the exciton density in the absence of drops,  $V(R)$  is a positive quantity and  $(1 - \frac{R^3}{R^{*3}}) \approx 1$ .

If the undercooling is not too great, e.g.  $(G\tau_x^{-\rho(R^*)})/\rho(R^*) \leq 100$ , then the last two terms in the exponential of (22) are negligible for all reasonable values of  $r$ . This gives

$$\rho(R) = \rho(R^*) \exp(-V(R)^2/V_T^2) \quad (22)$$

If  $V(R) \leq V_T/3$ ,  $\rho(R) \approx \rho(R^*)$  and  $\rho(r)$  is essentially constant. Using equation (15) and the numerical values  $\rho(R) \sim 10^{14}$  (at

$T \sim 3.5^\circ\text{K}$ ),  $\rho_0 \sim 2 \times 10^{17}$ ,  $\tau_0 = 40 \text{ } \mu\text{s}$ ,  $R_{\text{max}} = 10^{-2} \text{ cm}$  ( $R^*$  is a maximum of 1 mm because the dimensions of the sample are only a few millimeters and  $R$  is perhaps  $\frac{1}{10} R^*$ ). Of course  $R^*$  and  $R$  are by experiment much less than these magnitudes. We thus find  $V(R) < V_T/6$  in this temperature region. Thus for high temperatures we confirm that  $\rho(r)$  is constant.

A useful result from the foregoing is a form for the volume fraction  $f$ , which is the fraction of volume of liquid occupied by liquid and equal to  $\frac{R^3}{R^{*3}}$ . From i), ii) and (20) this is

$$f = \frac{R^3}{R^{*4}} = \frac{(G\tau_x - \rho) \tau_0}{\rho_0 \tau_x} . \quad (23)$$

For  $R^3 \ll R^{*3}$  this result also extends to low temperatures despite the fact that  $\rho(r)$  is no longer constant and the continuum model is no longer applicable. The excess of excitons created in the gas that flows into the drop is  $\int dV \left( \frac{G-\rho}{\tau_x} \right)$ . However, at low  $T$ ,  $\rho$  is everywhere much less than  $G\tau_x$  so the integral is  $\cong 4\pi GR^{*3}/3$  (as  $R^3 \ll R^{*3}$ ). Equating this to the recombination rate within the drop,  $4\pi R^3 \rho_0/\tau_0$ , we recover (23) with  $\rho \ll G\tau_x$ . (23) may thus be regarded as being valid over the entire temperature range.

## RESOLVING THE FREE BOUNDARY PROBLEM

As has been noted, the model presented here shows clearly that the electron-hole drop problem is a boundary value problem with an internal degree of freedom, the degree of freedom implying the possibility of a spectrum of metastable states. However, nothing has been said about how these states are set up or about processes which would change one state to another. Obvious candidates for such processes are nucleation (or evaporation) of drops and collisions between drops. Another possibility occurs if the laser excitation is localized in space in which case the expansion of the cloud can change the state of the drops. We suppose that such processes exist and that a metastable state can drift to other states over a period of time (hence our use of the term quasi-steady state instead of steady state). Presumably, after a suitably long period of time has passed (determined by the rates of the above mentioned processes), a unique steady state is reached, although what characterizes such a state has yet to be specified.

The free boundary problem encountered here is typical of many problems in irreversible thermodynamics such as the eutectic problem [17], hydrodynamics [19], and boiling liquid films [20]. In some of these problems the different metastable

states implied by the internal degree of freedom can be observed, (in particular, we have in mind the well known results of Jackson and Hunt [21] in the eutectic problem) but they remain stable in time only under tightly controlled conditions where perturbations that cause fluctuations between states have been removed or made unimportant. Under normal conditions where fluctuations between the metastable states can occur, the experimentally observed evolution of the system is to move from one metastable state to another until it has reached a final steady state. This final state is a steady state both in the sense that it is a solution of the free boundary problem and is one of the spectrum of metastable solutions and also in the sense that it is stable in time against fluctuations to other metastable states. It is also an experimentally reproducible state. The implication is that there is a further criterion that is necessary to describe free boundary problems.

The existence of a degree of freedom in these systems ultimately stems from the fact that they are not in a state of thermodynamic equilibrium and are thus not constrained to be in a state of minimum free energy or equivalently, with energy levels populated in the Boltzmann ratio. For the electron-hole drop case, this is reflected by the exciton gas density not being given by the equilibrium value  $\rho_{eq} = 16 \left( \frac{MkT}{2\pi\hbar^2} \right)^{3/2} e^{-\beta\phi}$ . However the observed tendency for non equilibrium systems reaching a unique steady state within the spectrum of solutions

to the free boundary problem leads naturally to the idea of the existence of a nonequilibrium optimizing function. Just as isolated equilibrium systems are characterized by an optimum in the entropy (entropy is a maximum), nonequilibrium systems would be characterized by an optimum in some other function.

This idea has been pursued by various authors [20, 22, 23, 24, 25, 26, 27] and in some cases the relevant functional has been shown to be the rate of entropy production. Near equilibrium with constraints on the boundary forces, it is well known that the steady state of continuous systems is described by a minimum in the rate of entropy production [25]. Far away from equilibrium and with different constraints the situation is less clear. Empirically, for systems with an internal degree of freedom over topology changes (for example the eutectic problem and liquid film boiling problem) the optimal state is described as a maximum in the rate of entropy production [17, 20].

Recognizing that the electron-hole drop problem is such a free boundary value problem with an internal degree of freedom (drop size) we will conjecture maximal rate of entropy production to be the correct variational principle. Our point of view here is a purely empirical one in much the same manner as maximizing entropy in equilibrium cases can be thought of as an empirical observation (via the Kelvin-Planck statement of the second law). There do exist however, axiomatic arguments in the spirit of Carathéodory based on analyticity [28].

We now evaluate the entropy production rate per unit volume as the flux of excitons times the free energy change per exciton per unit volume.

$$T\sigma = [\rho V_R 4\pi R^2] [\Delta F] / \left[ \frac{4\pi R^*{}^3}{3} \right] \quad (24)$$

where  $\Delta F$  is taken as the classical expression

$$\Delta F = kT \ln \left( \frac{\rho}{\rho_{eq}} \right) \quad (25)$$

Using (1) and (23) we obtain

$$T\sigma = \frac{G_{1x}^{-\rho}}{t_x} kT \ln \left( \frac{\rho}{\rho_{eq}} \right) \quad (26)$$

Interesting is the lack of dependence of  $T\sigma$  on explicit configurational parameters ( $R, R^*$ ).

In (26),  $\rho$  represents the internal degree of freedom so  $T\sigma$  can be optimized with respect to  $\rho$ . This yields a unique maximal state. The optimal value of  $\rho$  is given by the following transcendental equation.

$$\rho_{opt}^{-\rho_{opt}} \exp \left[ \frac{G_{1x}}{\rho_{opt}} - 1 \right] = 0 \quad (27)$$

Owing to the intractability of dealing with equation (26) in an analytic way and also for the purposes of comparing with the linear limit of irreversible thermodynamics it is convenient to expand (26) to a linear form viz.;

$$TJ = \frac{kT}{\tau_x \rho_{eq}} (G\tau_x - \rho) (\rho - \rho_{eq}) \quad (28)$$

The corresponding linear limit of (27) for the optimal value of  $\rho$  is

$$\rho_{opt} = \frac{G\tau_x + \rho_{eq}}{2} \quad (29)$$

This is an interesting result in itself, stating that in the linear range (near saturation) the final steady state density is the mean of the input flux and the equilibrium density.

As must be emphasized nothing has been said about how long it will take the system to arrive at the optimum state described by (27) and (29). The time constant describing such evolution and indeed the validity of using an optimization argument depends critically on the existence of macroscopic fluctuations (i.e., the creation or destruction of drops) to provide a mechanism for evolution. As may be seen from the results of Silver and Westervelt [12,7,13] such processes may take an extremely long time.

### A FUNCTIONAL FORM FOR V(R)

The free boundary problem has been resolved with equations (27) and (29) and gives a unique solution. However, to proceed further requires a functional relationship  $V(R)$  other than the mere statement that it exists. The form (6), which is the form often used in the literature could be used. However, as will be discussed later, it leads to a stronger dependence of  $R$  on  $G$  than observed and anomalously large values of  $R$ . We will instead derive a form for  $V(R)$  based on comparing (28) and (29) with constraints imposed by the linear limit of irreversible thermodynamics. In passing, this will illustrate the power of the method of linear irreversible thermodynamics.

It is possible to write in general the rate of entropy production as [29,30]

$$\frac{dS}{dt} = \int_V \sum_i J_i X_i dV \quad (30)$$

where the  $J_i$  are generalized fluxes and  $X_i$  are generalized forces. In the electron-hole  $d\rho_{op}$  case there is only one set of forces and fluxes so the sum over  $i$  may be dropped.  $J$  and  $X$  are conceived of as being independent and  $\frac{dS}{dt}$  is defined for all



possible values of  $J$  and  $X$  [Fig. 6]. Empirically  $J$  and  $X$  are functionally related (that is to say the degree of freedom associated with steady state problems can be removed) which in the limit of small  $J$  and  $X$  is linear, viz;

$$J \propto X. \quad (31)$$

The process of optimizing the rate of entropy production consists of considering  $J$  and  $X$  as independent variables and taking virtual fluctuations in them. The optimum then "finds" the steady state and defines the functional relationship between  $J$  and  $X$ . In optimizing (26) and (28) we have defined the global flux  $J = (\rho V_R \frac{4\pi R^2}{4\pi R^* 3})$  and the force  $X = (kT \ln \frac{\rho}{\rho_{eq}})$  and hence the relationship between them. The difficulty is that although  $V(R)$  is in principle calculable, as of yet we don't know what it is.

The solution (29) does indeed result in a linear flux-force relation as required by (31). From (26) the global flux (flux per unit volume) is

$$J = \frac{G \tau_x^{-\rho}}{\tau_x} \quad (32)$$

while the linear expansion of the force (25) is

$$F = \frac{kT}{\rho_{eq}} (\rho - \rho_{eq}) \quad (33)$$

Using the optimum value (29) we find

$$J = \frac{\rho_{eq}}{kT \tau_x} F \quad (34)$$

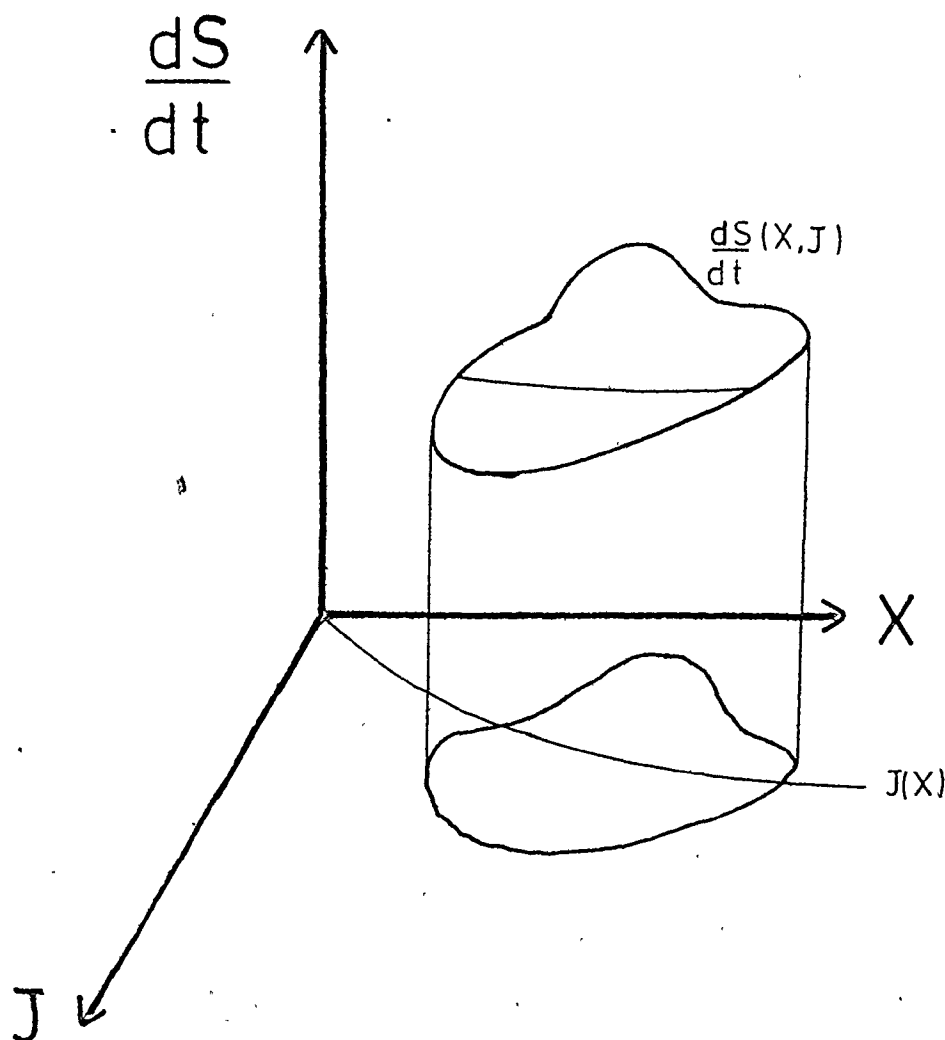


Fig. 6

The  $\frac{dS}{dt}$ ,  $J$ ,  $X$  coordinate system.  $\frac{dS}{dt}$  as a function is defined for all  $J$ ,  $X$  and is 0 at the coordinate axes ( $J=0$  or  $X=0$ ). Shown is a section of the  $\frac{dS}{dt}$  functional projected onto the  $J$ - $X$  plane.  $J$  and  $X$  are regarded as independent variables. The optimization procedure defines a functional relationship  $J(X)$  which near the origin reduces to the linear limit of irreversible thermodynamics.

i.e., the global flux  $J$  is proportional to the force.

We have distinguished here between the global flux which is flux per unit volume and the local flux which is the rate of flow in a local region viz.  $J_{\text{local}} = \rho V_R$ . This local flux must also be proportional to  $F$  and therefore also to the global flux. From (26) and (32)

$$J_{\text{global}} = \frac{G \tau_x^{-\rho}}{\tau_x} = \rho V_R \left( \frac{4\pi R^2}{\frac{4\pi R^* 3}{3}} \right) = J_{\text{local}} \left( \frac{3R^2}{R^* 3} \right) \quad (35)$$

To maintain the proportionality the geometric factor on the right hand side cannot be a function of  $\rho$  but only a function  $B = B(G, T)$ . Thus we have

$$V_R = \frac{G \tau_x^{-\rho}}{\rho} \frac{1}{\tau_x^{B(G, T)}} \quad (36)$$

We will now perform a virtual variation on  $V_R$  by taking  $\rho$  to the phase boundary  $\rho = \rho_{\text{eq}}$ , keeping  $B$  constant. It is clear from the functional dependence of (36) on  $\rho$  that this variation will give a maximal  $V_R$ . We can also take  $\rho_{\text{eq}} \ll G \tau_x$  also giving a maximal  $V_R$ . However,  $V_R$  has a maximum value of  $\frac{V_T}{4}$  where  $V_T$  is the thermal velocity. Thus the value of  $B(G, T)$  is asymptotically established to be  $\frac{4G}{V_T \rho_{\text{eq}} \tau_x}$ . The value of  $V_R$  at the optimum is then

$$V_R = \frac{V_T}{4} \frac{\rho_{\text{eq}}}{G} \frac{(G \tau_x^{-\rho_{\text{opt}}})}{\rho_{\text{opt}}} \quad (37)$$

With this form for  $V_R$  the problem is now completely described. The weakness of this argument is that in taking  $\rho_{eq}$  small with respect to  $G$  the linearity condition is strained (compare equations (27) and (29)) and thus  $V_R$  may depart from (37).

In passing,  $V_R$  as given by (37) and (27) or (29) is small enough that the assumption of constant  $\rho$  is confirmed. (Refer to equation (22) and following discussion.)

### COMPARISON WITH EXPERIMENT

The relations (1), (20), (22), (27) or (29) and (37) now form a complete if approximate solution to the problem and can be tested against experiment. Directly testable relations are the density (27), the steady state radius,

$$R = \frac{3\tau_0}{\rho_0} \rho_{opt} V_R = \frac{3\tau_0}{\rho_0} \frac{V_T}{4} \frac{\rho_{eq}}{G\tau_x} (G\tau_x - \rho_{opt}) \quad (38)$$

and the density of drops

$$N_d = \frac{1}{\frac{4\pi R^3}{3}} = \frac{f}{\frac{4\pi R^3}{3}} = \frac{16G^3 \tau_x^2}{9\pi V_T^3} \left(\frac{\rho_0}{\tau_0}\right)^2 (G\tau_x - \rho_{opt})^{-2} \rho_{eq}^{-3} \quad (39)$$

or

$$\ln N_d = \ln \left( \frac{16G^3 \tau_x^2}{9\pi V_T^3} \left(\frac{\rho_0}{\tau_0}\right)^2 (G\tau_x - \rho_{opt})^{-2} \right) - 3 \ln \rho_{eq} \quad (40)$$

In addition the volume fraction  $f$  given by (23) can be used to provide some insight on the expansion of the electron-hole drop cloud. The temperature restriction of (18) can be relaxed somewhat as it was only brought in because of the use of the Navier-Stokes equation. In the region where  $\rho$  can be considered constant the Navier-Stokes equation is not used explicitly and the temperature restriction in (18) does not apply. More to the point is that although we can use the nonlinear form (27) for  $\rho_{opt}$  in (38) and (39) we do not have a result for  $V_R$  that necessarily applies to the nonlinear region. However, for

lack of a nonlinear form, the linear result must be used.

The solutions for  $\rho_{opt}$  in equation (27) are shown in [Fig. 7] along with (29) for comparison for different saturation densities  $G\tau_x$ . The solutions for different  $G$  lie parallel to each other and are to be compared to the results of Gershenson et al. in [Fig. 4]. The qualitative behavior of [Fig. 7] is evidently correct. Direct quantitative comparison is uncertain because of possible supersaturation effects. [Fig. 8] shows [Fig. 4] and [Fig. 7] superimposed with the onset line of [Fig. 4] equal to  $\rho_{eq}$ . However, as previously noted the onset line of [Fig. 4] is probably the supersaturation line and is not the same as  $\rho_{eq}$ . Correcting for this [Fig. 9] is obtained. Because of supersaturation the measured density is higher than the optimal value at higher temperatures while at lower temperatures, expansion of the cloud lowers the effective  $G$  and hence lowers  $\rho$ .

$\ln N_d$  is shown in [Fig. 10] with the results from Bargiev et al [10] for different pulse risetimes 100  $\mu s$  and 3  $\mu s$ . As the time of formation of a drop is  $t \sim \tau_0 = 40 \mu s^*$  the two kinetic methods of preparation presumably bracket the optimum final

\* Using  $\frac{dN}{dt} = 4\pi R^2 \rho_0 \frac{dR}{dt} = 4\pi R^2 \rho_R V_R - \frac{4\pi R^3}{3} \frac{\rho_0}{\tau_0}$ , taking  $\rho_R$  and  $V_R$  roughly constant during growth, and integrating, the time of growth is easily estimated to be  $t \sim 40 \mu s$ .

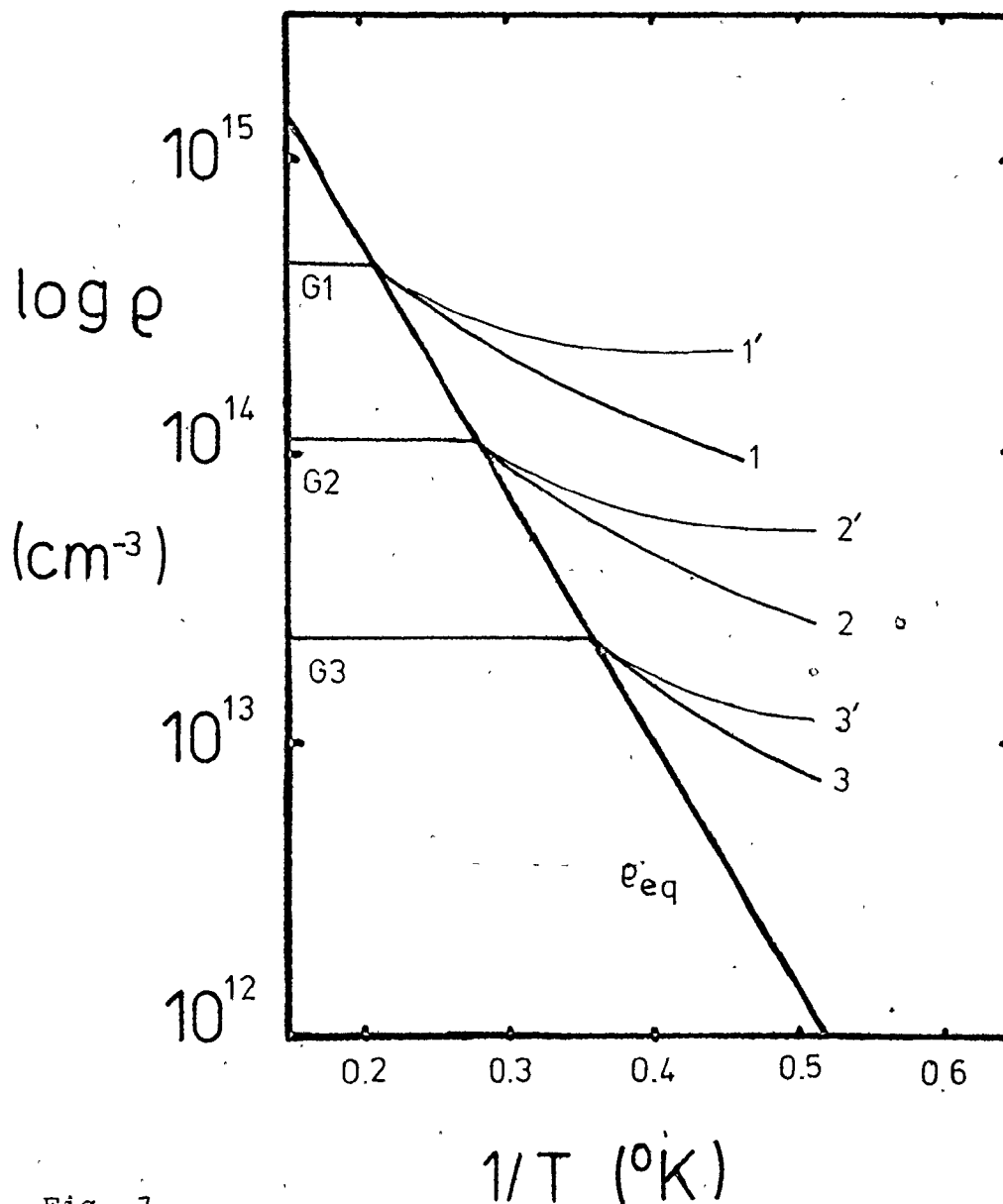


Fig. 7

$\log \rho_{opt}$  versus  $1/T$  for various pump powers  $G$ . Lines 1, 2, 3 are  $\rho_{opt}$  as given by equation (27). The primed lines are the approximation (29), valid near saturation.

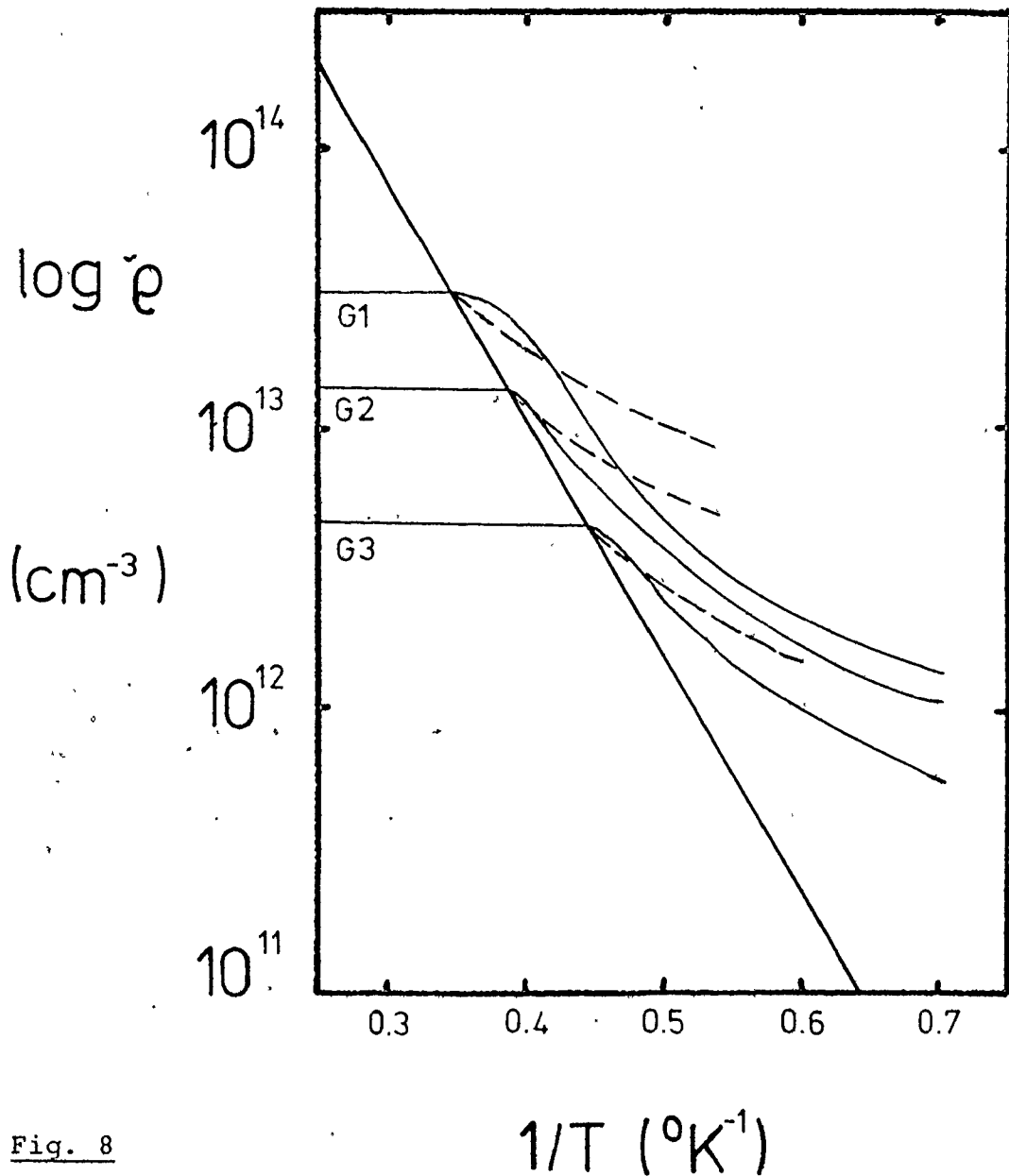


Fig. 8

$\log \rho_{opt}$  (as given by equation (27)) compared to Gershenson's results [9]. The solid lines are the experimental data, dashed lines are  $\rho_{opt}$ . Here  $\rho_{eq}$  is taken to be given by the onset line; i.e.  $\phi = 1.65$  meV,  $\rho_{eq}(3^{\circ}K) = 4 \times 10^{13} \text{ cm}^{-3}$ . G1, G2, G3 correspond to the pump powers G1, G2, G3 in Fig. 4. Capillarity effects are ignored.



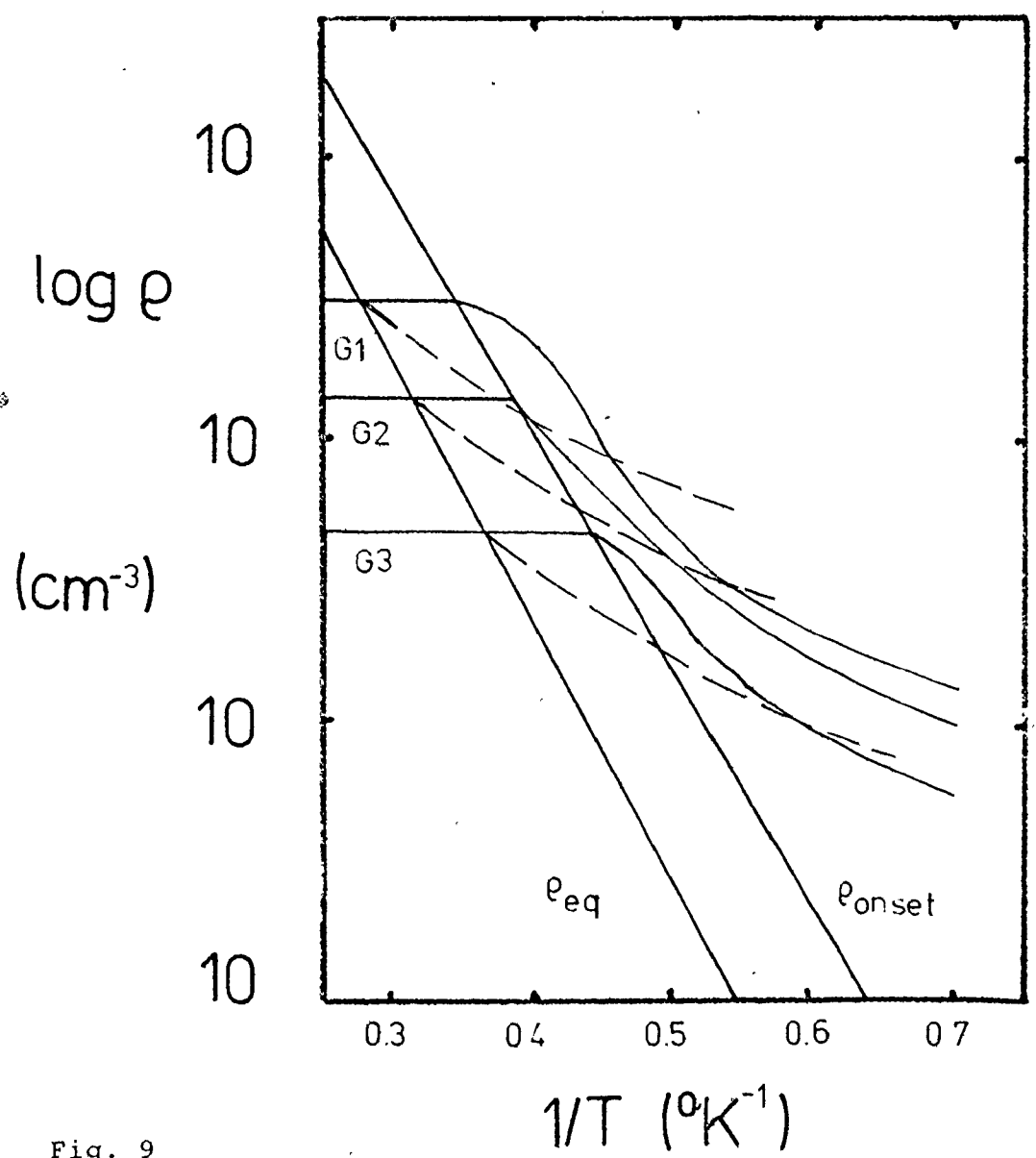


Fig. 9  
 $\log \rho_{opt}$  compared to experimental data. Saturation effects have been corrected for.  $\rho_{eq}(3^{\circ}K) = 10^{13} \text{ cm}^{-3}$ ,  $\phi = 1.8 \text{ meV}$  [1b,13]. The saturation line is the same as in Fig. 8.

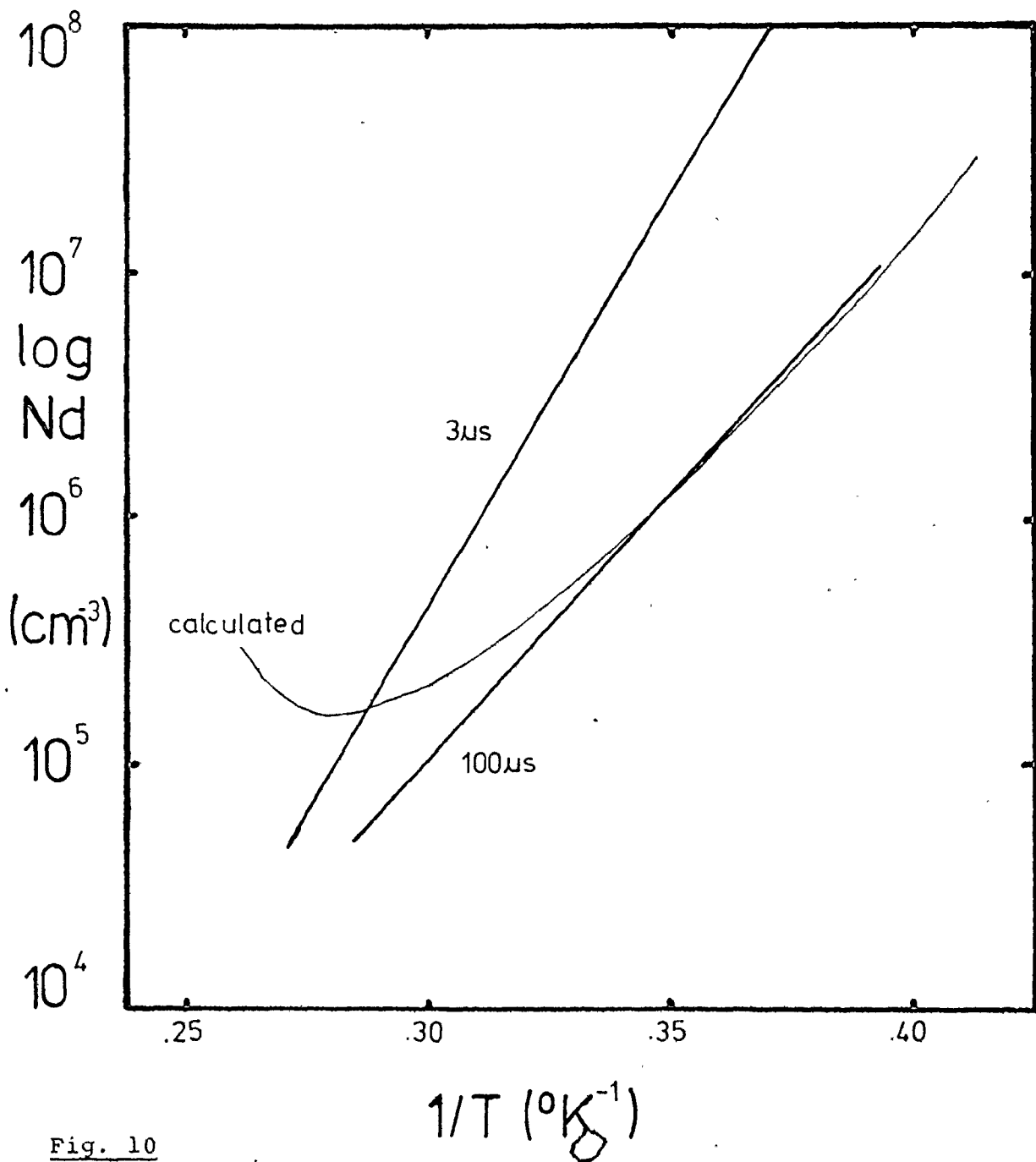


Fig. 10

$\log Nd$  calculated and experimental. The experimental data is that of Bagaev et.al. [10] for short and long rise times respectively. Bagaev observed a saturation temperature of  $3.55^\circ\text{K}$ . Correcting for supersaturation effects gives a saturation temperature of  $\sim 4^\circ\text{K}$ .  $\rho_{\text{eq}}(3^\circ\text{K}) = 10^{13} \text{ cm}^{-3}$ ,  $\phi = 1.8 \text{ meV}$ . [1b,13].

steady state, the 3  $\mu$ s rise time nucleating more drops than required and 100  $\mu$ s rise time too few. As shown in [Fig. 10] this is indeed the case. Agreement with experiment is satisfactory.

Finally in Fig. [11] the predicted value of  $R$  (neglecting capillarity effects, i.e., dependence of  $\rho_{eq}$  on  $R$ ) is shown against the results of Bagaev et al. [10]. Agreement here is not good. At high temperatures the experimental values saturate at  $\sim 10 \mu$ m independent of  $G$  and risetime. The predicted values do saturate but at a larger value dependent on  $G$ . However, this saturation effect may be due to limitations on cloud size. The experiment of Bagaev et al. is nominally volume pumped but above 2.5°K the exciting radiation was focussed to a spot of  $\sim 100 \mu$ m radius. With  $R = 10 \mu$ m and  $R^* = 50 \mu$ m [Fig. 12], the cloud is at most two or three drops wide. Given the spatial restriction it is not surprising that the higher values of  $R$  are not observed. Similar effects have been noted in other non volume pumped experiments [32,31,16].

Additional evidence that cloud size is of importance comes from consideration of the volume fraction  $f$  plotted in [Fig. 13] for Bagaev's data. At temperatures far below the saturation temperature  $\rho$  is much less than  $G \rho_x$  (this is true even if  $\rho$  is not  $\rho_{opt}$ ) and (23) reaches a limiting constant value proportional to  $G$ . As shown,  $f$  for Bagaev's data does reach a maximum value dependent on  $G$  but for lower temperatures it drops. This is interpreted as showing that the volume of the cloud is in-

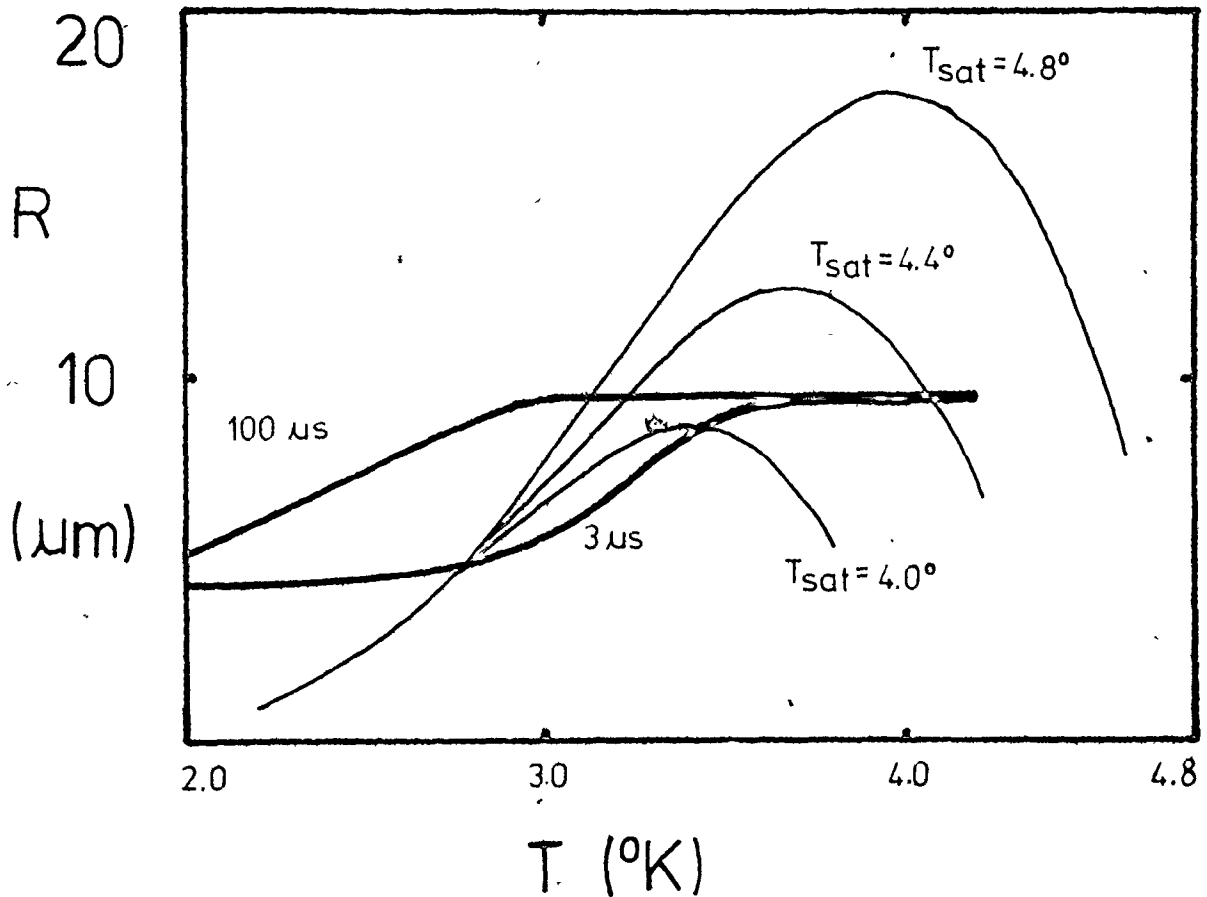


Fig. 11

$R$ , calculated and experimental. The experimental data is from Bagaev et.al. [10] for different pulse rise times as noted. There is also a weak  $G$  dependence (not shown) below  $R = 10 \mu\text{m}$ . The saturation temperature for the data shown is  $\sim 4.2^{\circ}\text{K}$  or possibly higher if supersaturation is important. Temperature dependence of  $\tau_0$  is included.

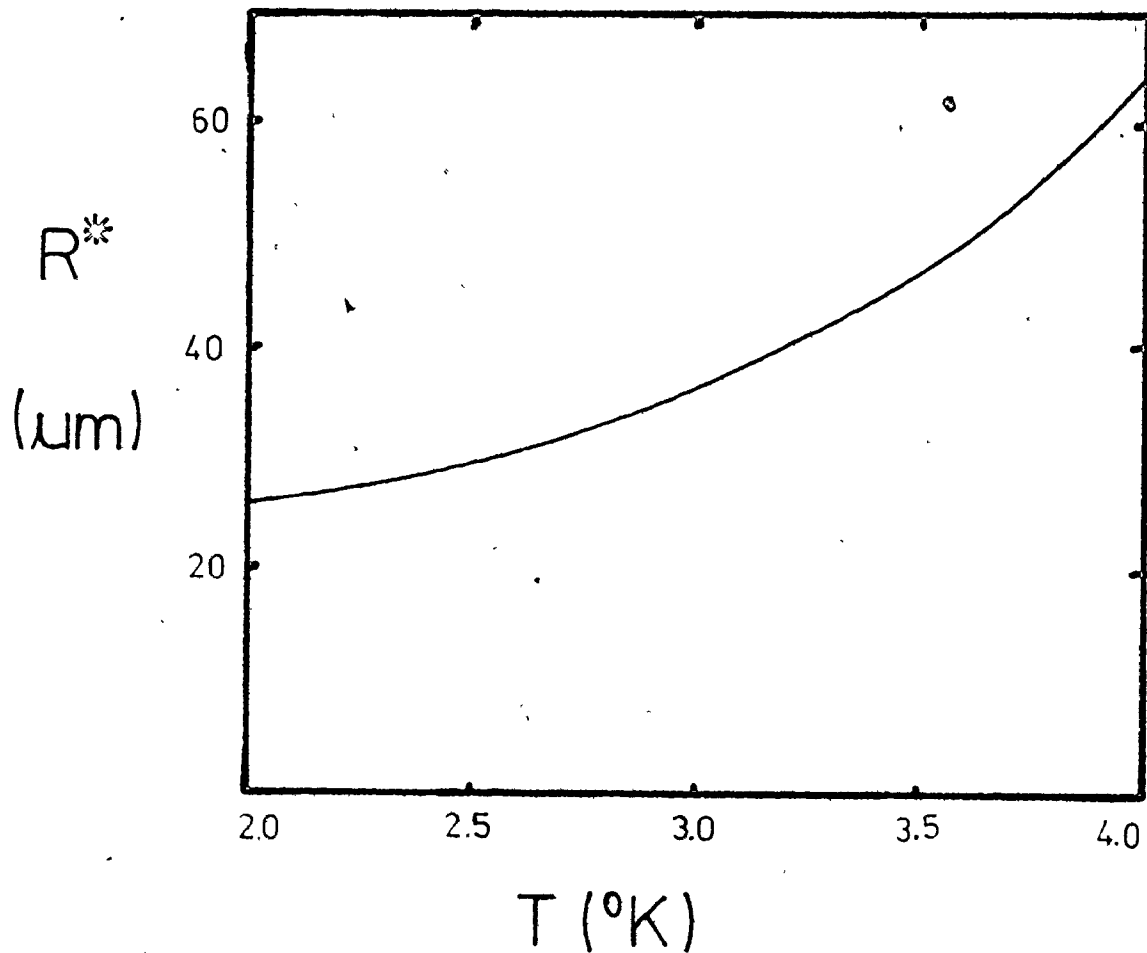


Fig. 12

$R^*$  versus  $T$  for Bagaev's et.al. data [10]. The line shown is for a saturation temperature of  $\sim 4.2^\circ\text{K}$  and a laser pulse risetime of 100  $\mu\text{s}$ .

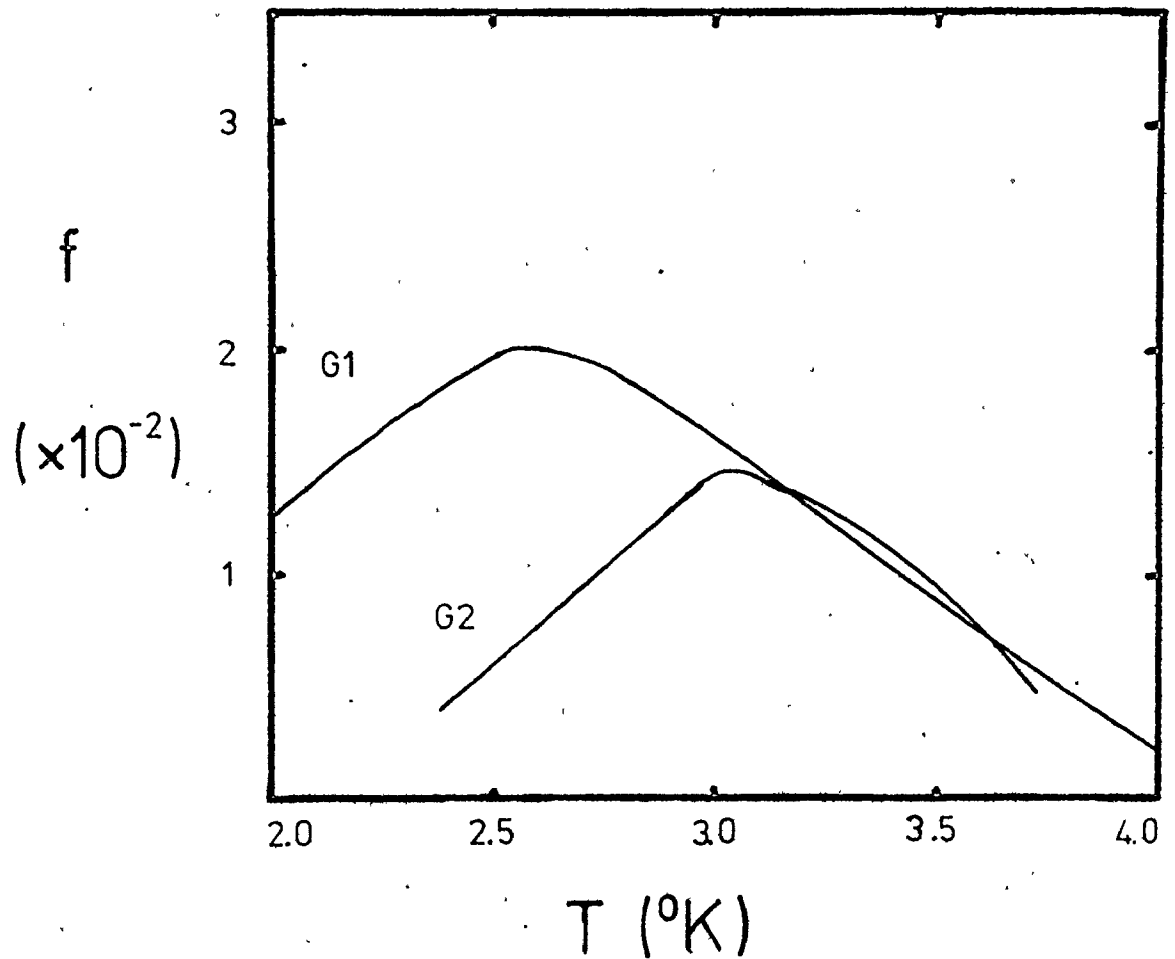


Fig. 13

The volume fraction  $f$  plotted for Bagaev's et.al. data [10]. Two different pump powers are plotted, one with saturation at  $\sim 4.2^{\circ}\text{K}$  and the other at  $\sim 3.0^{\circ}\text{K}$ .

creasing with decreasing temperature.

A point of agreement with the theory is the minimal G dependence at low temperatures. If the commonly accepted form for  $V_R(6)$  is used, the dependence of R on G is linear and is also much higher [Fig. 14]. These values are much too high and depend too strongly on G. This problem was also encountered by Gershenson et.al. [9]. The predicted values with  $V_R$  given by (37) do not depend on G in this region but as Bagaev's data is evidently not at the optimum some weak dependence can be allowed for.

Observations of a linear G dependence for R have been made by Zarate and Timusk [33] [Fig. 15] for small R. They attribute this dependence to sample heating.

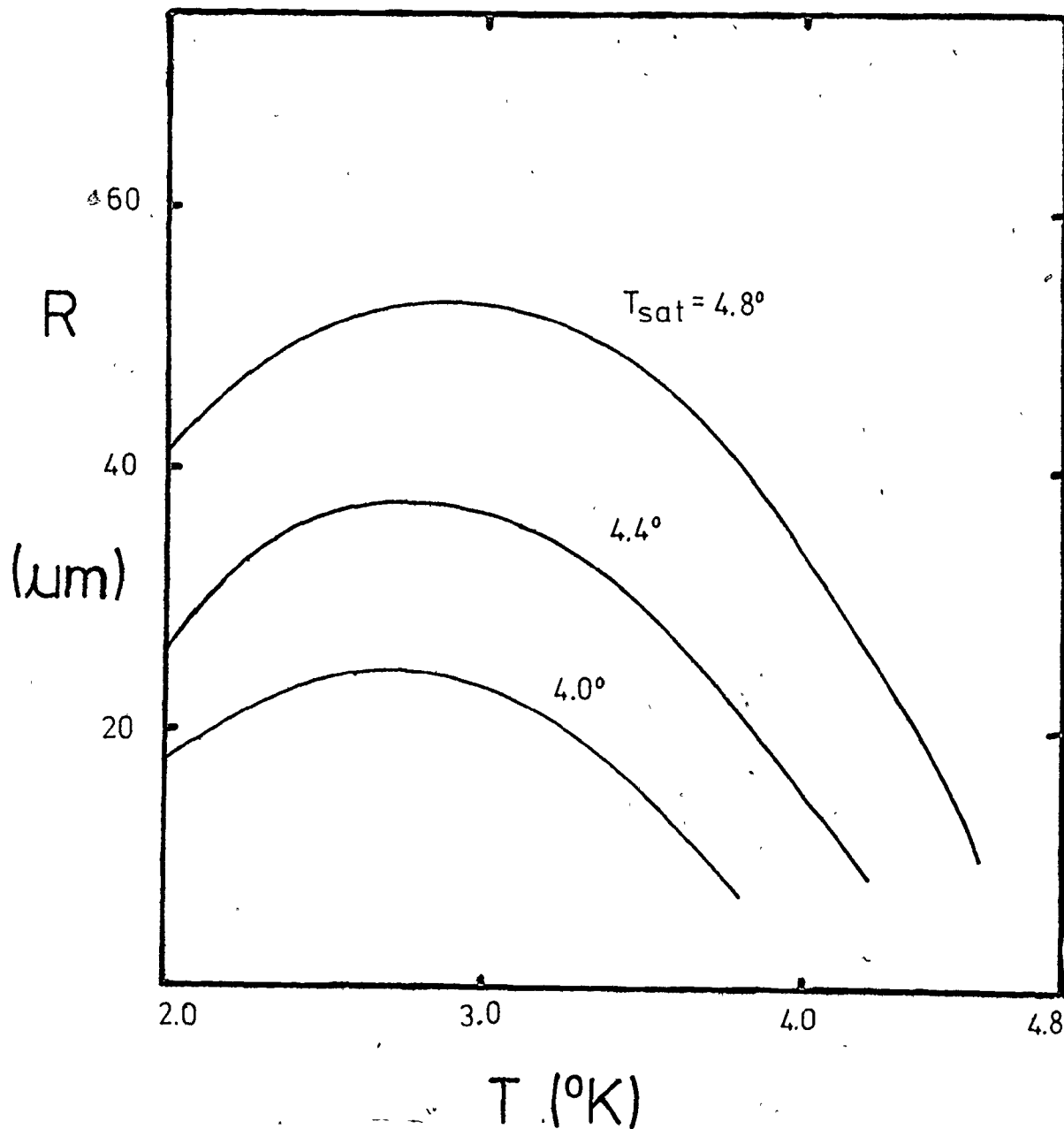


Fig. 14

$R$  as calculated using equation (6) for the velocity. This is to be compared to Fig. 11.



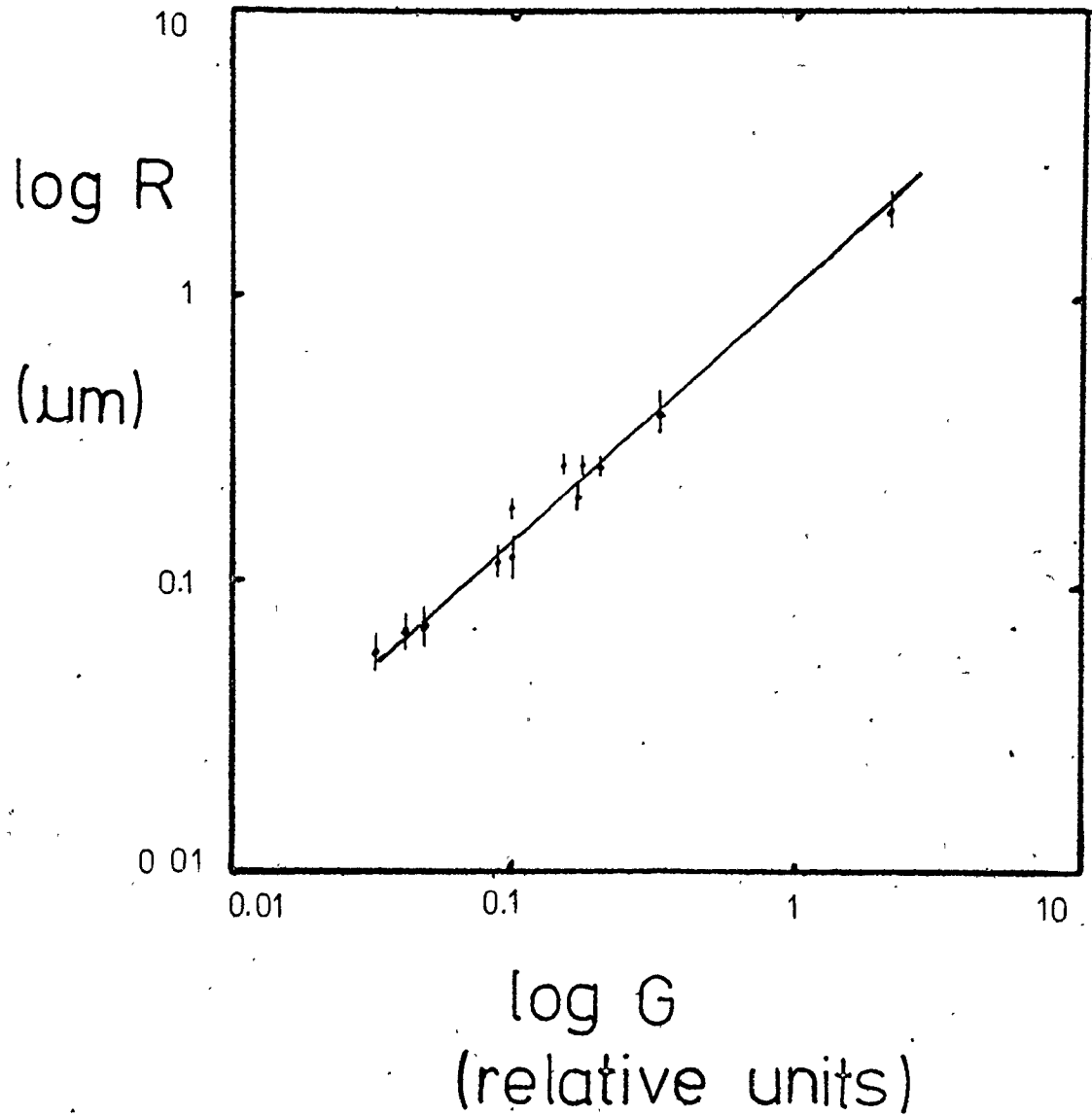


Fig. 15

Experimental data of  $R$  versus  $G$ . Timusk [33].

### DYNAMICAL AND CLOUD SHAPE EFFECTS

The theory developed is based on an ideal case, that of a uniformly pumped, close packed lattice of drops. Uniform volume excitation however is difficult to achieve experimentally and many experimentalists do not even try to achieve volume pumping, working instead with point or stripe excitation geometries [31,32,35,36,37,38,39,40]. Even those studies which purport to achieve volume excitation such as Baqaev [10] fall short of their goal as shown by [Fig. 13]. It is necessary then to consider the effects of dynamics and the pumping of a limited volume of space on the model.

Measurements of the spatial extent of the electron-hole drop cloud for non-volume pumped configurations show that the cloud is localized and has a well defined edge [38,40,41]. Conditions inside the cloud are uniform or at least drop radii are uniform. The effect of changing the pump power  $G$  is to expand or contract the cloud appropriately, maintaining the conditions within the cloud constant [Fig. 16].

Several dynamical cloud models have been proposed to explain these observations. Balslev and Hvam [42] proposed that density gradients in the stationary exciton gas move the drops towards low density regions. Excess condensation of excitons on

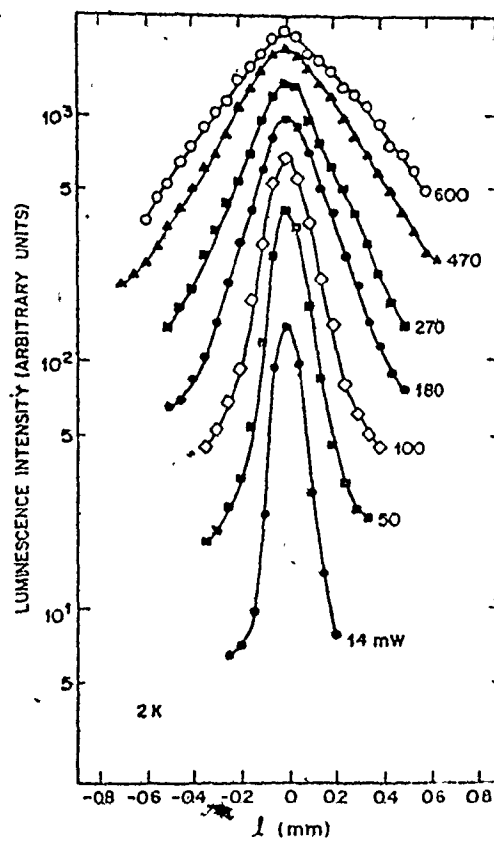


Fig. 16

Expansion of the droplet cloud with pump power  $G$ . (Here measured by luminescence intensity.) Pokrovskii [36].

the high density side of the drop leads to a net momentum transfer to the drop in the direction of the exciton gas density gradient. Countering this force is the viscosity of the gas which exerts a Stoke's law drag on the drop. The model is artificial in that in the presence of an exciton gas density gradient the exciton gas would itself move. The model also does not lead to a uniform drop radius within the cloud.

Combescot [43] considers the drops to be "blown out" from the laser spot. On the way out the exciton gas slows the drops down until they stop near the edge. Drop radius in the cloud is constant and fixed by the process which creates and blows away the drops at the center. Again, however, it requires a stationary exciton gas.

The consistent application of the viewpoint of drops surrounded by a freely moving gas requires that the region of pumping is a high pressure region. The space surrounding the pumped volume is essentially a vacuum into which the exciton gas will expand at some velocity which is proportional to  $V_T$ . The gas will then exert an accelerating viscous drag on the existing drops. By way of estimation the acceleration of an isolated drop due to the Stoke's law force is

$$a = \frac{9 \mu V}{2m^* \rho_0 R^2} \quad (41)$$

where  $V$  is the mean gas velocity and  $\mu$  is the kinetic theory viscosity.

$$\mu = \frac{2}{(3\pi)^{3/2}} \frac{\sqrt{m^*kT}}{d^2} \quad (42)$$

$d$  is the collision diameter of the excitons. Thus with  $d \sim 3.6 \times 10^{-6}$  cm,  $m^* \sim 0.6 \times 10^{-27}$  g and  $T = 3^\circ\text{K}$ ,  $\mu \sim 4.6 \times 10^{-12}$  g/cm/sec. If  $V$  is taken to be  $\sim 10^5$  cm/sec =  $0.1 V_T$  and  $R \sim 1 \mu\text{m}$  the acceleration is about  $1.7 \times 10^{12}$  cm/sec<sup>2</sup>. Thus small drops just nucleated can be accelerated to the gas velocity in less than  $0.1 \mu\text{s}$  and reach the edge of the cloud in as little as  $1 \mu\text{s}$ . At the edge they will meet the evaporation line and disappear. Given that the time of formation of drops is about  $\tau_0$  it is clear that drops cannot invariably reach their maximal value but reach some particular value dependent on the nature of nucleation and the geometry of the pumped region. This qualitatively agrees with the results of Bagaev et.al. [Fig. 11] at high temperatures and with the results of the various focused pumping experiments.

If the non ideal configuration were to be set up as a boundary value problem it would of course still be a free boundary value problem by the nature of irreversible processes. In the excited region, the system still has freedom to adjust internal local configurational parameters ( $R, R^*$ ) to optimize the rate of entropy production. As has been demonstrated this particular variation leads to a maximum. However, now the system has another type of fluctuation which it can explore, that of expansion of the cloud. This has the effect of lowering the effective

G over the cloud and will reduce the rate of entropy production per unit volume. (Refer to equation (28)). This parallel global trend is thus towards a minimax in the rate of entropy production. The overall configuration of the steady state is thereby characterized as a minimum, i.e., as a simultaneous minimum and maximum with respect to different variations. The above defines a procedure (although perhaps impractical) to find the optimal steady state for the general case as an extension of the ideal problem.

As in the ideal problem, for the optimization procedure to be valid and to observe the optimal state, there must be suitable fluctuation processes which explore the available phase space. In the ideal static problem, such processes are limited to rare nucleation events or perhaps the occasional collision. Hence, evolution to the optimum may be slow and hysteresis effects are observable. In the non volume pumped case, the violent dynamical nature of the cloud provides rapid fluctuations which quickly lead to an optimal state. Thus for these configurations hysteresis should not be observed. This is indeed the case.

## CONCLUSIONS

The electron-hole drop system forms a free boundary value problem. That is, it has an internal degree of freedom which cannot be removed by steady state relationships. Thus there is a spectrum of possible solutions to the boundary value problem.

It is expected on the basis of general experience that the system will in the course of time find a unique stable steady state. The removal of the degree of freedom to identify this state requires an optimization principle. This principle is the nonequilibrium parallel of the equilibrium principle of optimizing entropy. The relevant functional is identified as the rate of entropy production with the optimum being either a maximum or minimum. In the ideal volume pumped case the optimum is a pure maximum while in the non ideal case it is a minimax.

The optimization process requires that the system be able to fluctuate and wander through the various possible metastable states in the spectrum of solutions to the boundary problem. In the non ideal case such fluctuation processes exist due to the dynamical nature of the system. Evolution to the optimum is rapidly attained. Hysteresis is thus not observed or possible in this case. The ideal case on the other hand is static and lacks dynamical methods of searching its phase space. Evo-

lution toward the optimum is thereby correspondingly slower and hysteresis effects are observed. We distinguish here two types of hysteresis, i) that type described by Silver and Westervelt in which although the state is not a solution of the boundary problem, relaxation to a solution may take considerable time and ii) the hysteresis associated with the system being in different solutions to the boundary problem before evolving to the optimum.

It is verified theoretically that the common assumption of constant gas density is valid. New results are found; notably the volume fraction  $f$  and a functional form for  $V_R$ . This last was achieved by comparing the forms of the fluxes and forces to the linear limit of irreversible thermodynamics.

Agreement with experiment is fair to good. The existence of hysteresis effects and non ideal conditions provide a convenient scapegoat for deviations. Unfortunately, this also prevents a rigorous test of the theory.



APPENDIX 1  
VALUES OF PARAMETERS

Parameter	Value	Reference
$\rho_0$	$2.2 \times 10^{17} \text{ cm}^{-3}$	[7]
$\tau_0$	40 $\mu\text{s}$ (temperature dependent)	[34]
$\tau_x$	7.7 $\mu\text{s}$	[7]
$M^* = (m_e^* + m_h^*)$ (effective mass)	0.34 ( $2m_0$ )	[1a]
d (exciton diameter)	$3.54 \times 10^{-6} \text{ cm}$	[1a]
$V_T$	$\sim 10^6 \text{ cm/sec}$	
$\phi$	1.8 meV	[1b]

## Appendix 2: Solutions to the Differential Equations

Solutions to the differential equations without the source terms

$(G - \rho/\tau_x)$  are found to be

$$\rho = A \exp\left(-\frac{V^2}{V_T^2}\right) \quad (A1)$$

$$\rho V = -\frac{D'}{r^2} \text{ or } V = -V(R) \frac{R^2}{r^2} \quad (A2)$$

$V(R)$  here is defined to be a positive constant. We use these solutions as the initial point in a perturbation calculation. First, we rewrite the continuity equation and Navier-Stokes equation as integral equations

$$\rho V = -\frac{D'}{r^2} + \frac{1}{r^2} \int (G - \frac{\rho}{\tau_x}) r^2 dr \quad (A3)$$

and

$$\rho = \rho' \exp\left\{-\frac{V^2}{V_T^2} + \frac{2}{V_T^2} \int (G - \frac{\rho}{\tau_x}) \frac{V}{\rho} dr\right\} \quad (A4)$$

where  $D'$  and  $\rho'$  are constants of integration. We now substitute  $\rho = AG \tau_x \exp\left\{-\frac{V^2}{V_T^2}\right\}$  into the right hand side of (A3), and working to second order in  $R/(V_T \tau_x)$  and  $V(r)/V_T$  we find

$$\rho V = -\frac{D'}{r^2} + (1-A) G \frac{r}{3} \quad (A5)$$

or

$$V = -\frac{D}{r^2} + \frac{(1-A)}{\lambda} \frac{r}{3 \tau_x} \quad (A6)$$

We iterate this into equation (A4) and find

$$\rho = AG \tau_x \exp\left\{-\frac{V^2}{V_T^2} + \frac{2(1-A)D}{A \tau_x r V_T^2} + \frac{(1-A)^2 r^2}{3V_T^2 A^2 \tau_x^2}\right\} \quad (A7)$$

$$= AG_{T_x} \exp \left\{ \frac{-D^2}{r^4 V_T^2} + \frac{8}{3} \frac{(1-A)D}{A_1 x r} + \frac{2}{9} \frac{(1-A)^2 r^2}{A_1^2 x^2 V_T^2} \right\} \quad (A8)$$

Further iterations do not change the result, and equations (A6) and (A8) are the solutions to second order in  $V(R)/V_T$  and  $R/(V_T x)$  as may be verified by direct substitution.

Using  $V(R^*) = 0$  we find

$$-V(R) = -\frac{D}{R^2} + \frac{DR}{R^{*3}} \quad (A9)$$

where  $V(R)$  is a positive quantity. This fixes  $D$  as

$$D = \frac{V(R) R^2}{1 - \frac{R}{R^{*3}}} - V(R) R^2 \quad (A10)$$

as  $\frac{R}{R^{*3}} \ll 1$  for any reasonable  $R \cdot R^*$ .

To fix  $A$  we use equation (A7) to find  $\rho(R^*)$

$$\rho(R^*) = AG_{T_x} \exp \left\{ \frac{2}{A} \frac{(1-A)V(R)R^2}{r^4 R^* V_T^2} + \frac{(1-A)^2 R^{*2}}{3V_T^2 A_1^2 x^2} \right\} \quad (A11)$$

Unless the undercooling is large ( $A \cdot 10^{-2}$  or smaller) the terms in the exponential are insignificant and  $\rho(R^*) = AG_{T_x}$ , thus fixing the other constant of integration.

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