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Simplified kinetic theories for electron-hole condensation

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It is shown that expressions for electron-hole droplet nucleation and decay currents, derived in earlier papers by the author and others, can be applied to problems of time-dependent exciton densities only in restricted conditions. The induction time, which characterizes the response of nucleation and decay currents to changes in the exciton density, must be shorter than the inverse logarithmic time derivative of the nucleation and decay currents when these are significant. Numerical studies show that the induction time is too long for steeply rising high-intensity pulses, and for most decay phenomena except for extremely slow changes in the laser intensity.

I. INTRODUCTION

In two previous papers,[1,2] the author developed a theory of the effect of finite particle lifetimes on the nucleation kinetics of electron-hole droplets in semiconductors. This problem has also been addressed by Westervelt[3] and studied by several experimental groups.[4-6] Since the infinite set of coupled kinetic equations are difficult to solve numerically, it is desirable to determine the conditions where they may be replaced by a simplified kinetic theory involving the expressions for nucleation and decay currents which have been derived in the limit of time-independent exciton densities.[2,3] Staehli[7] and, in a more approximate way, Bagaev *et al.*[6] have shown that such a replacement can lead to predictions which compare well with experiment. In this comment, I present an alternative derivation of the nucleation and decay rates which also provides the leading correction due to the nonzero induction time for the rates to adjust to exciton density variations. This derivation is an extension to finite lifetimes of the method of Wakeshima,[8] as described in the book by Abraham.[9] The results of numerical calculations are then described which show that a simplified kinetic theory cannot be justified for steeply rising high-intensity pulses, nor for decay phenomena except at low temperatures or extremely slow changes in laser intensity.

II. DERIVATION OF AN INDUCTION TIME INEQUALITY

The Fokker-Planck approximation to the kinetic equations for electron-hole condensation[1,10] may be written

$$\frac{\partial C(n)}{\partial t} = -\frac{\partial}{\partial n} I(n) , \tag{1}$$

where $C(n)$ is the concentration of clusters of n electron hole pairs and $I(n)$ is a current given by

$$I(n) = -g_n \bar{C}(n) \frac{\partial}{\partial n}\left(\frac{C(n)}{\bar{C}(n)}\right) . \tag{2}$$

The steady-state concentration $\bar{C}(n)$ is related to the growth g_n and decay l_n terms defined in previous papers[1,2] by

$$\bar{C}(n)/\bar{C}(1) = \exp - [G(n) + \mu_1]/kT . \tag{3}$$

Here μ_1 is the exciton, or "monomer," chemical potential, $C(1)$ the exciton density, and $G(n)$ is the "generalized" Gibbs potential defined by

$$G(n) = kT \int_1^n \ln\left(\frac{l_n}{g_n}\right) . \tag{4}$$

Expressions (3) and (4) are consistent with the requirement of detailed balance in the infinite lifetime limit. Above a minimum exciton density for condensation, $\bar{C}(n)$ has a minimum at the unstable, or critical, droplet size n_2 and maxima about $n = 1$ and about the stable droplet size n_3, as discussed previously.[1]

From (2) one may derive for $n'' > n_2$ and $n < n_2$

$$-\int_n^{n''} \frac{I(n')\,dn'}{g_{n'}\bar{C}(n')} = \frac{C(n'')}{\bar{C}(n'')} - \frac{C(n)}{\bar{C}(n)} . \tag{5}$$

The denominator of the integrand in (5) is peaked about $n' \simeq n_2$ and $n' \gg n_3$. Expand $I(n')$ in a power series about n_2, and keep only terms to order $(n' - n_2)^2$. Thus

$$I(n') \simeq I(n_2) + \frac{\partial I}{\partial n'}(n_2)(n' - n_2) + \frac{1}{2}\frac{\partial^2 I}{\partial n'^2}(n_2)(n' - n_2)^2 . \tag{6}$$

From (1),

$$\frac{\partial^2 I(n)}{\partial n^2} = \frac{-\partial}{\partial t}\frac{\partial}{\partial n} C(n) \tag{7}$$

and, since $\partial\bar{C}(n_2)/\partial n = 0$, from (2),

$$\frac{\partial}{\partial n} C(n_2) = -\frac{I(n_2)}{g_{n_2}} . \tag{8}$$

Thus we can substitute in (6)

$$\frac{\partial^2}{\partial n^2} I(n_2) = \frac{1}{g_{n_2}} \frac{\partial I(n_2)}{\partial t} . \tag{9}$$

Take $n'' \leq n_3$. Since $g_{n'} \overline{C}(n')^{-1}$ is almost Gaussian distributed about n_2, the second term in (6) does not contribute to the integral in (5), and one obtains

$$-I(n_2) \int_n^{n''} \frac{dn'}{g_{n'} \overline{C}(n')} - \frac{1}{2g_{n_2}} \frac{\partial I(n_2)}{\partial t} \times \int_n^{n''} \frac{(n'-n_2)^2 dn'}{g_{n'} \overline{C}(n')} = \frac{C(n'')}{\overline{C}(n'')} - \frac{C(n)}{\overline{C}(n)} . \tag{10}$$

For convenience, a parameter γ is defined by

$$\gamma \equiv \int_n^{n''} dn' \, [g_{n'} \overline{C}(n')]^{-1} \Big/ \int_n^{n''} dn' \, (n'-n_2)^2 [2 g_{n'} g_{n_2} \overline{C}(n')]^{-1} . \tag{11}$$

This is independent of n and n'' for n and n'' slightly different from n_2, and $n'' \leq n_3$, since $[g_{n'} \overline{C}(n'')]^{-1}$ is so sharply peaked about n_2. Then, from (9)–(11),

$$\frac{dI(n_2)}{dt} + \gamma I(n_2) = \gamma \left(\int_n^{n''} dn' \, [g_{n'} \overline{C}(n')]^{-1} \right)^{-1} \left(\frac{C(n)}{\overline{C}(n)} - \frac{C(n'')}{\overline{C}(n'')} \right) , \tag{12}$$

which is an equation for the nucleation current $I(n_2)$ in terms of the concentrations $C(n)$.

Equation (12) can only be self-consistent when the right-hand side is independent of n and n'' as is the left-hand side. The integrand in the denominator of the right-hand side is independent of n and n'' for the reasons stated previously. The rest of the right-hand side is independent when: (i) the steady-state distribution is achieved separately in the regions $n < n_2$ and $n > n_2$ so that $C(n) \propto \overline{C}(n)$ and $C(n'') \propto \overline{C}(n'')$ (this situation was discussed previously by the author[2]); and (ii) $C(n) \propto \overline{C}(n)$ and $C(n'') \ll \overline{C}(n'')$, i.e., the exciton density is so high that the steady state number of droplets is extremely large, or equivalently, relaxation to the steady state for $n > n_2$ has not occurred. In these two cases one can substitute without appreciable error

$$C(n'')/\overline{C}(n'') \rightarrow C_D / \overline{C}_D , \tag{13}$$

where the droplet concentration C_D is defined by

$$C_D \equiv \int_{n_2}^{\infty} C(n) \, dn . \tag{14}$$

Take $n = 1$ so that $C(1) = \overline{C}(1)$ by definition and approximate $\int_0^{n_2} C(n) \, dn$ by $C(1)$. Then, from (1), Eq. (12) becomes

$$\frac{\partial^2 C_D}{\partial t^2} + \frac{\gamma \partial C_D}{\partial t} = \gamma g C(1) - \gamma l C_D . \tag{15}$$

Here g is the nucleation rate defined previously[2] by the author

$$g^{-1} \cong C(1) \int_1^{n_3} dn' \, [g_{n'} \overline{C}(n')]^{-1} , \tag{16}$$

and the decay rate l is related to g by[2]

$$l \overline{C}_D = g \overline{C}(1) . \tag{17}$$

Consider, therefore, the physics contained in Eq. (15). First, if γ is extremely large so that the first term on the left-hand side may be neglected, there are two interesting limits: (i) when the exciton density is high, so that $\overline{C}_D \gg C_D$, nucleation dominates

$$I(n_2) \simeq g C(1) ; \tag{18}$$

and (ii) when the exciton density is near threshold, so that $\overline{C}_D \ll C_D$, decay dominates

$$I(n_2) \simeq -l C_D . \tag{19}$$

Second, when γ is finite but $\gamma \gg l$, the solution to (15) for fixed exciton density $C(1)$ is

$$C_D(t) = C_D(0) e^{-lt} + \overline{C}_D (1 - e^{-lt}) + (1/\gamma) I(n_2, 0)(e^{-lt} - e^{-\gamma t}) \tag{20}$$

and

$$I(n_2, t) = [g C(1) - l C_D(0)] (e^{-lt} - e^{-\gamma t}) + I(n_2, 0) e^{-\gamma t} \tag{21}$$

Clearly, γ is the parameter governing the rate at which the current can adjust to a change in exciton density. The inverse of γ is the finite lifetime analog of the "induction time."

A simple interpretation of γ can be obtained by observing that γ is approximately equal to

$$\gamma \cong -\frac{2 g_{n_2}}{kT} \frac{d^2 G(n_2)}{dn^2} = -2 \left(\frac{dl_{n_2}}{dn} - \frac{dg_{n_2}}{dn} \right) . \tag{22}$$

If one considers the nonstochastic equation

$$\frac{dn}{dt} = g_n - l_n \tag{23}$$

and linearizes about n_2, one finds

$$\frac{dn}{dt}\cong\tfrac{1}{2}\gamma(n-n_2)\,. \tag{24}$$

Thus γ is simply related to the rate of growth of a classical cluster away from an unstable point n_2. In terms of parameters defined in previous papers,[1,2] γ is given by

$$\gamma=-\frac{2}{3\tau}+\frac{4}{9}\,\frac{(4\pi R_n^2)^2}{kTn^2}SAT^2\exp\left(\frac{-\phi_\infty}{kT}+\frac{2}{3}\,\frac{4\pi R_n^2 S}{nkT}\right), \tag{25}$$

where $n=n_2$ (or for relaxation about the stable droplet, $n=n_3$). At the minimum exciton density for condensation, γ is zero, and with increasing supersaturation, $n_2\to 0$ and γ increases monotonically. Thus, γ is considerably larger during nucleation than it is during decay.

When the exciton density can vary with time, Eq. (15) provides a criterion for when the current can be taken to be

$$I(n_2)=J\equiv gC(1)-lC_D\,. \tag{26}$$

It is that

$$\gamma\gg\frac{1}{J}\,\frac{dJ}{dt}\,, \tag{27}$$

where the variation of J with time is due to variations of the exciton density $C(1)$. If this inequality is satisfied, the current may be assumed to follow the changes in exciton density. The numerical calculations described below show that in typical experimental conditions the inequality (27) is satisfied for nucleation but not for decay. We refer to (27) as the "induction time inequality." It provides a bound on the domain of applicability of a simplified kinetic theory. While a parameter akin to γ was discussed by Staehli,[7] there was no discussion of with what it should be compared.

III. NUMERICAL RESULTS AND DISCUSSION

In order to determine the experimental conditions where replacement of the full kinetic equations by a simplified kinetic theory violates Eq. (27), a numerical study was performed. The calculations were similar to those of Staehli except in the following respects: (i) the growth of droplets for $n>n_2$ was described in terms of four equations for moments of the cluster size distribution which form a closed set in the limit of negligible surface tension; (ii) calculations were carried out for a full range of temperatures and supersaturations; and (iii) situations where droplet decay is important were studied.

Figure 1 illustrates what happens in the particular case of step function excitation of Ge at 2 °K to an excitation level sufficient to product a supersaturation of ~8 before nucleation begins. $C(1)$ rises until significant droplet nucleation occurs. At this point γ exceeds $d\ln J/dt$ by one to two orders of magnitude. The growth of embryonic droplets then causes the exciton density to fall, shutting off further nucleation. At this high excitation level too many embryonic droplets have been nucleated to be sustained when they grow to the minimum

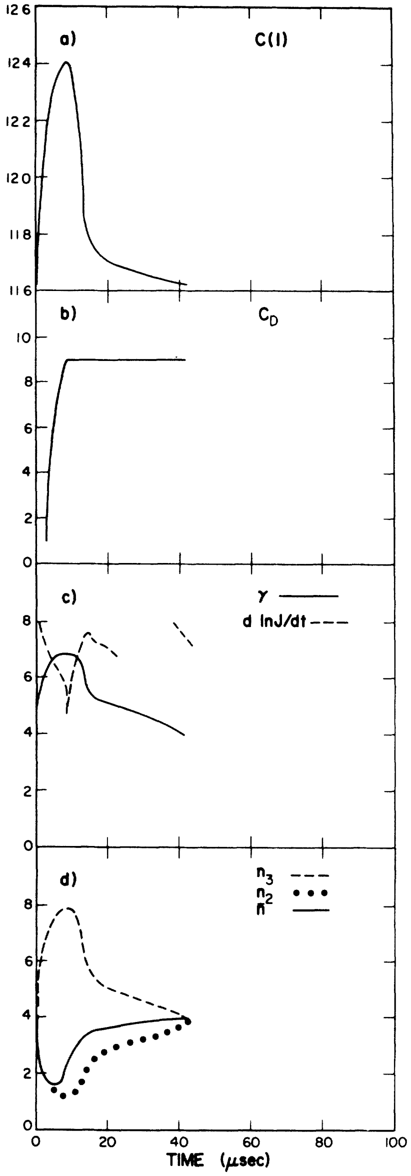

FIG. 1. Vertical axis is the $\log_{10}$ of the corresponding quantity. (a) is the exciton density $C(1)$; (b) is the droplet density C_D; (c) Solid line is the induction parameter γ, dashed line is $d\ln J/dt$; (d) Solid line is average droplet size $\bar{n}$, dashed line is the stable droplet size n_3, dotted line is critical droplet size n_2. The horizontal axis is the time in μsec. The curves drawn correspond to step function excitation to a supersaturation of 8.0 at 2 °K in Ge.

stable radius. The exciton density must fall to a level where decay can occur. However, as may be seen from the calculation, $d\ln J/dt$ exceeds γ by four orders of magnitude at the point where decay becomes significant and hence the condition (27) for application of the simplified kinetic theory is violated. The calculation has been terminated at this point.

The same kind of violation of (27) occurs in a variety of decay situations which have been studied. These include droplet decay at the end of a pulse and various kinds of slow decrease of the excitation intensity. The reason for this behavior is as follows. The decay rate l is proportional to exponential of $[G(n_2)-G(n_3)]/kT$, which is negligibly small except for exciton densities extremely close to the minimum density for the existence of stable droplets. The exciton density crosses the region where the l is significant in a very short time compared to γ^{-1}. At 2 °K the figure shows that the characteristic time for variations of the decay current must be greater than 100 μsec for a simplified kinetic theory to be applicable.

It is also found that at excitations sufficient to create a supersaturation much greater than 10, Eq. (27) is also violated in nucleation. At temperatures from about 1–1.6 °K it is found that (27) can be satisfied in both nucleation and decay. At lower temperatures the nucleation theory is no longer applicable since hysteresis phenomena disappear and the minimum density for the existence of stable droplets crosses into the region where the gas phase cannot be approximated as ideal.

IV. CONCLUSION

Restrictions have been determined on the application to situations of time dependent exciton density of expressions for electron-hole droplet nucleation and decay rates derived in earlier papers.[2,3] The density variation must be sufficiently slow that an induction time inequality (27) be satisfied. Numerical studies show this cannot be satisfied for steeply rising high intensity pulses, nor in most of the common decay situations. The description of these situations requires a return to the full set of coupled kinetic equations.

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