thus must correspond to the temperature at which the lithium was diffused into the silicon, that is, to very high values of Θ. This conclusion is supported by Fig. 12. The latter gives the result of comparing this sample with sample 20 by means of the similarity relations. Although the agreement is not very good at low temperatures T, the two curves are close enough to indicate an almost random distribution. The disagreement at low T may, in this case, well be due to the Tanaka-Fan traps, since sample $L56$ has very low compensation.

Note added in proof. After submitting the article for publication, a previous work by E. M. Pell on lithium-boron ion pairing in silicon [J. Appl. Phys. **31**, 1675 (1960)] was brought to our attention. The comparison between his result on the pair size, 2.5–2.7 Å, and ours of 2.87 Å is quite satisfactory.

Generalized Master Equation for Arbitrary Initial States

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(Received 4 May 1965)

Exact generalized master equations, for both quantum and classical systems, are derived for completely arbitrary initial states (arbitrary initial "correlations") in the form of a "density expansion." This result is a generalization of a previous equation which was restricted to initially "uncorrelated" states.

I. INTRODUCTION

IN a previous article[1] (hereafter referred to as I) an exact equation for the evolution of the density matrix of a quantum-mechanical system (generalized master equation) was derived as a "formal" expansion in powers of the density—for density matrices which are initially diagonal.

It is the purpose of the present article to extend that result to completely arbitrary initial states (arbitrary initial density matrices). We shall thus derive a master equation, for both quantum and classical systems, which is exact for *arbitrary initial states* (at all times) and which is expressed as a "formal" expansion in the density.

The comparable master equations of Prigogine and Resibois,[2] Van Hove,[3] Zwanzig,[4] Peterson,[5] and Janner,[6] on the other hand, are expressed as formal expansions in the interaction potential whereas Swenson's[7] equation is expressed as an expansion in the two-body scattering matrix.

The present article is a continuation of I, to which the reader is referred for definitions and nomenclature.

II. QUANTUM MASTER EQUATION FOR ARBITRARY INITIAL STATES

We begin with Eq. (43) of I which is valid for arbitrary initial states of the system [arbitrary $\rho(0)$]. The problem now, as in I, is to obtain an expression for $O_D g_N \rho(0)$ in terms of $\rho_D(t)$ which, when substituted into Eq. (43), yields a closed equation for $\rho_D(t)$ (master equation). This was done in Appendix D of I for initially diagonal density matrices (initially independent of particle configurations in momentum representation) by setting $O_D g_0(E)\rho(0)[=g_0(E)O_D\rho(0)]$ equal to zero. To obtain an expression for $O_D g_N \rho(0)$ which is valid for arbitrary initial states we need only add $g_0(E)O_D\rho(0)$ to the right-hand side of Eqs. (D1) and (D3) of I. If we then follow the remaining steps of Appendix D and keep all terms which appear postmultiplied by $g_0(E)O_D\rho(0)$ we eventually obtain, in place of (D10),

$$O_D g_N(E)\rho(0) = {}^{nmc}\left\{\sum_{k=1}^{\infty}(O_D T g_0^{-1})^k\right\}D g_N(E)\rho(0)$$

$$+ {}^{nmc}\left\{\sum_{k=0}^{\infty}(O_D T g_0^{-1})^k\right\}g_0(E)O_D\rho(0)$$

$$= {}^{nmc}\left\{O_D T g_0^{-1}(1-O_D T g_0^{-1})^{-1}\right\}D g_N(E)\rho(0)$$

$$+ {}^{nmc}\left\{(1-O_D T g_0^{-1})^{-1}\right\}g_0(E)O_D\rho(0). \quad (1)$$

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[2] I. Prigogine and P. Resibois, Physica **27**, 629 (1961); P. Resibois, *ibid.* **29**, 721 (1963).
[3] L. Van Hove, Physica **23**, 441 (1957).
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[5] R. L. Peterson, J. Math. Phys. **5**, 85 (1964).
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[7] R. J. Swenson, J. Math. Phys. **4**, 544 (1963).

Equation (1) is an exact expression for the off-diagonal part of the Laplace transform of the density matrix for *arbitrary initial states*—in the limit of an infinite system.

[If $\rho(0)$ is diagonal then the last term on the right-hand side of Eq. (1) would vanish and Eq. (1) would be the same as Eq. (D10) of I.]

Substituting (1) into the sum on the right-hand side of Eq. (43) of I and making use of Eqs. (29) and (36) of I we obtain, instead of Eq. (46) of I,

$$D \sum_{s} \sum_{i_1 < \cdots < i_{s+1}} T_s(i_1 \cdots i_{s+1}) g_0^{-1} \mathbf{O}_D g_N (\neq i_1 \cdots i_{s+1}) \rho(0)$$

$$= D(^{nmc} \{ T g_0^{-1} (1 - \mathbf{O}_D T g_0^{-1})^{-1} \mathbf{O}_D T \}) E D g_N \rho(0)$$

$$+ D(^{nmc} \{ T g_0^{-1} (1 - \mathbf{O}_D T g_0^{-1})^{-1} \}) g_0 \mathbf{O}_D \rho(0)$$

$$\equiv K(E) E D g_N \rho(0) + [DT + K(E)] \mathbf{O}_D \rho(0), \qquad (2)$$

where $K(E)$ is defined in Eq. (47) of I. If we now substitute Eq. (2) into Eq. (43) of I we obtain, after evaluating the formal inverse Laplace transforms, the following closed equation for the diagonal part of the density matrix $\rho_D(t)$:

$$\rho_D(t) = \rho_D(0) + [K(t) + \sum_{s=1}^{\infty} \beta_s(t)] \mathbf{O}_D \rho(0)$$

$$+ \int_0^t dy [K'(t-y) + \sum_{s=1}^{\infty} \beta_s'(t-y)] \rho_D(y), \qquad (3)$$

where, as in I, we have used $K(t)]_{t=0} = 0$.

Differentiating both sides of (3) with respect to t and using Eq. (37) of I we finally obtain

$$\partial \rho_D(t) / \partial t = [K'(t) + \sum_{s=1}^{\infty} \beta_s'(t)] \mathbf{O}_D \rho(0)$$

$$+ \int_0^t dy [K''(t-y) + \sum_{s=1}^{\infty} \beta_s''(t-y)] \rho_D(y). \qquad (4)$$

Equation (4) is an exact equation for $\rho_D(t)$ at all times for completely arbitrary initial states—in the limit of an infinite system.

The range of validity of this equation is somewhat more general than the master equation of Prigogine and Resibois[2] in that it is valid for inhomogeneous systems (as well as homogeneous systems) and for any pair-interaction potential. Otherwise, the distinction between the two equations is that the terms in Eq. (4) are arranged as a "formal" expansion in the particle density

whereas the corresponding terms in the Prigogine-Resibois equation are arranged as a "formal" expansion in the interaction potential.

Equation (4) differs from Eq. (49) of I in that it is valid for all initial states, whereas Eq. (49) is valid for only initially diagonal states (no initial "correlation"). The term $[K'(t) + \sum_s \beta_s'(t)] \mathbf{O}_D \rho(0)$, in Eq. (4), fully describes the effects of initial "correlations" on $\rho_D(t)$ but has not been fully investigated. Presently one can only say that this term will eventually vanish if the initial "correlations" are of finite range.

III. CLASSICAL MASTER EQUATION FOR ARBITRARY INITIAL STATES

The classical master equation [see Ref. 8] is an equation for the N-particle momentum distribution function $\varphi(t)$ defined by

$$\varphi(t) \equiv V^{-N} \int d\{\mathbf{R}\} F_N(\{\mathbf{R}\}, \{\mathbf{P}\}, t),$$

where $\{\mathbf{R}\}$ and $\{\mathbf{P}\}$, respectively, denote the configurations and momenta of all N particles of the system, and F_N is the distribution function of all N particles (solution of Liouville's equations).

The master equation for $\varphi(t)$ can be immediately obtained from Eq. (4) by simply replacing the quantum mechanical Liouville operators (see I) by the corresponding classical Liouville operators and replacing the diagonal part D of an operator by the configuration integral $V^{-N} \int d\{\mathbf{R}\}$. We thus obtain from (4)—after noting that $K(t)$ vanishes exactly for a classical system [see I and Ref. 8]—

$$\frac{\partial \phi(t)}{\partial t} = \sum_{s=1}^{\infty} \beta_s'(t) \mathbf{O}_D F_N(0)$$

$$+ \int_0^t dy [\sum \beta_s''(t-y)] \phi(y), \qquad (5)$$

where β_s is the classical collision operator defined in Ref. 8 and $\mathbf{O}_D$ is defined by $\mathbf{O}_D \equiv (1 - V^{-N} \int d\{\mathbf{R}\})$.

Equation (5) differs from the exact classical master equation in Eq. (29) of Ref. 8 in that it is valid for all initial values of F_N (all initial distribution functions), and hence contains the initial "correlation" term $\sum_s \beta_s'(t) \mathbf{O}_D F_N(0)$, whereas the latter equation is valid only when $\mathbf{O}_D F_N(0) = 0$.

[8] J. Weinstock, Phys. Rev. **132**, 454 (1963).