Forward-backward transport theories of ion-solid interactions: Variational approach

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The relationship between the popular so-called backward or Lindhard-type transport equations for linear energetic cascades and the direct or forward Boltzmann equation description is rigorously examined for an arbitrary atomic species mix. A variational principle is systematically derived that characterizes the forward model with generalized boundary conditions (internal reflection at a free surface) and is extremized to yield self-consistently the adjoint equations and boundary conditions as components of the corresponding Euler-Lagrange system. The adjoint function is treated purely as a mathematical artifact, which follows naturally from the variational principle. Dubious physical arguments to assign adjoint boundary conditions are thereby avoided. A truly backward description is derived from the adjoint formalism, which under the assumption of space and time homogeneity, reduces to the familiar Lindhard form. The Lindhard-type equations are seen to be neither backward nor forward equations but assume a hybrid form. In contrast, the forward and truly backward (or adjoint) models are exact and of general validity. They are complementary approaches and thus describe a duality that is mediated by the variational principle.

I. INTRODUCTION

Successful theories of the evolution of energetic linear cascades in random media have centered on the ubiquitous Boltzmann equation in one form or another and have found extensive application in the study of ion implantation, radiation damage, sputtering, and in developing materials characterization and modification techniques. Starting from the pioneering work of Lindhard *et al.*[1-3] on integral equations for general physical effects, subsequently generalized by Winterbon, Sanders, and Sigmund to ion implantation, sputtering and radiation damage,[4-6] and culminating in the recent independent and unified approach of Williams,[7] the common thread of linear transport theory is evident.

Yet it appears from the literature that two distinct but evidently related approaches exist for modeling ion-solid interaction phenomena: the traditional and popular backward formulation due to Lindhard, Winterbon, and Sigmund (hereafter referred to as Lindhard type), and the more recent (but historically more established) forward Boltzmann equation approach, due largely to Williams[8] (although earlier instances of applications of this formalism do exist[9-11]).

The forward equation is an integrodifferential equation for the phase-space distribution function (or flux) of a moving species of particles that represent the cascade. From its solution for a given source, all desired physical quantities can be generated, such as reflection and sputtering yields,[12] implantation profiles,[7] energy deposition profiles,[13] etc., and in this sense constitutes a unified approach to modeling atomic collisions in solids. Important to this paper, complex boundary conditions (at free surfaces and interfaces) can be readily incorporated into such a description of the cascade. This so-called forward approach (the solution at a later time is sought, given some initial data) has an extensive history of applications, most notably in neutron transport theory[14,15] and kinetic theory of gases,[15,16] so that the powerful solution techniques and approximation models developed in these related fields carry over naturally to the applications envisioned here (see, for example, Refs. 7 and 17).

The typical Lindhard-type backward equation, although also integrodifferential in form, is an unusual equation in the sense of its operational variables—an unusual mix of source and field variables. It is neither a forward nor a backward equation, but, as will be shown below, a hybrid equation. Furthermore, there is not a single defining equation, as in the forward approach, but a different equation for each application is necessary, e.g., sputtering,[5] energy deposition,[18] etc. A major shortcoming of this formalism is that the equations are valid only in infinite, homogeneous media and consequently cannot incorporate realistic boundary conditions. It is worth noting that the forward approach is not subject to such limitations. Despite these restrictions, the Lindhard-type formalism has enjoyed extensive (indeed almost exclusive) favor in fundamental and analytical work on ion-solid interactions, and considerable work of practical value has resulted.

Truly backward equations are adjoint equations, i.e., describing evolution in reverse time. Williams[7,8] has noted qualitatively that the Lindhard-type equations do not satisfy this criterion, in that they are only partially adjoint. However, Williams[7] restricted his analysis to infinite media and did not discuss the role of the all-important boundary conditions, which are rather complex for charged-particle transport. Since the adjoint equation plays a pivotal role in establishing a link between the various approaches, it is worth examining this relationship rigorously, with proper accounting of boundary and initial conditions.

The object of this study is to develop a general framework for establishing the interrelationships within the family of forward-adjoint–backward-Lindhard formalisms. Following a presentation of the forward system, a variational characterization (central to our work) is given from which the adjoint system is seen to arise naturally and systematically. In this way we avoid the physically motivated arguments for generating adjoint boundary conditions that are popular in neutron transport.[19] As the adjoint function is purely a consequence of mathematics, it is desirable to generate the adjoint system in a mathematically consistent manner, and the variational method provides a satisfactory approach for doing so. A reciprocity relation[7] is then used to derive a truly backward description (for a desired physical quantity) as well as appropriate boundary conditions. We then make contact with the Lindhard-type equations by introducing suitable approximations. Finally, we conclude with a discussion of further advantages of the variational approach.

II. FORWARD BOLTZMANN EQUATION FORMULATION

We consider general geometry and an arbitrary mixture of randomly distributed atoms. The desired quantity is the space, time, energy, and angle-dependent flux of i-type particles in a cascade initiated by one k-type particle (here type refers to species type) and is given by $\phi_{ki}(\mathbf{r},E,\mathbf{\Omega},t)$. The latter satisfies the linearized Boltzmann equation[7] which may be written as:

$$\left[\frac{1}{v}\frac{\partial}{\partial t}+\mathbf{\Omega}\cdot\nabla\right]\phi_{ki}(\mathbf{r},E,\mathbf{\Omega},t)=\frac{\partial}{\partial E}(S_i\phi_{ki})+\sum_{j=1}^{N}\int_{E}^{\min(E/\alpha_{ij},E_0)}dE'\int d\mathbf{\Omega}'\Sigma_{ji}(E'\to E;\mathbf{\Omega}'\cdot\mathbf{\Omega})\phi_{ki}(\mathbf{r},E',\mathbf{\Omega}',t)$$
$$+\sum_{j=1}^{N}\int_{E/(1-\alpha_{ij})}^{E_0}dE''\int d\mathbf{\Omega}''\Sigma^{*}_{ji}(E'\to E;\mathbf{\Omega}''\cdot\mathbf{\Omega})\phi_{kj}(\mathbf{r},E'',\mathbf{\Omega},t)$$
$$-\sum_{j=1}^{N}n_j\sigma_{ji}(E)\phi_{ki}(\mathbf{r},E,\mathbf{\Omega},t)+\delta_{ik}\delta(\mathbf{r}-\mathbf{r}_0)\delta(E-E_0)\delta(\mathbf{\Omega}-\mathbf{\Omega}_0)\delta(t-t_0)\ . \tag{1}$$

Here,

$$\alpha_{ij}=(m_i-m_j)^2/(m_i+m_j)^2\ ,$$

where m_i is the mass of the ith particle, n_j represents the target atomic density of j-type particles, and the transition probabilities per unit length or differential cross sections describe the following interactions:

$$\Sigma_{ji}(E'\to E;\mathbf{\Omega}'\cdot\mathbf{\Omega})\equiv n_j\sigma_{ji}(E'\to E;\mathbf{\Omega}'\cdot\mathbf{\Omega})$$

is the differential cross section for an i-type particle with energy E' in direction $\mathbf{\Omega}'$ scattering off a stationary j-type particle and emerging with the energy E in direction Ω,

$$\Sigma^{*}_{ji}(E''\to E;\mathbf{\Omega}''\cdot\mathbf{\Omega})\equiv n_j\sigma^{*}_{ji}(E''\to E;\Omega''\cdot\Omega)$$

is the differential cross section for a j-type particle with energy E'' in direction $\mathbf{\Omega}''$ scattering off a stationary i-type particle, resulting in the i-type particle recoiling with energy E in direction $\mathbf{\Omega}$, and

$$\Sigma_{ji}(E)\equiv n_j\sigma_{ji}(E)$$

is the total cross section for scattering of i-type particles with energy E off stationary j-type particles.

The σ_{ji}'s are microscopic differential cross sections for elastic scattering collisions in the lab system and may be expressed in terms of corresponding center-of-mass cross sections (hence potentials) and the usual conservation laws. Their explicit forms are well known, given by Williams,[7] and are not relevant to the work described here. The Fokker-Planck term containing the stopping power S_i represents interactions with the electrons in the continuous-slowing-down approximation (CSDA), and the stopping power is assumed summed over all target species. Finally, the source term represents one k-type particle launched at $\mathbf{r}_0$ at time t_0 with energy E_0 in direction $\mathbf{\Omega}_0$, so that if p represents the set of phase space variables $(\mathbf{r},E,\mathbf{\Omega},t)$ and likewise p_0 for the source variables, then the solution of Eq. (1), $\phi_{ki}(p;p_o)$, represents the Green's function from which the solution for an arbitrary source distribution may be derived. To complete the forward description, initial and boundary conditions must be specified. At time $t=0$ we prescribe

$$\phi_{ki}(\mathbf{r},E,\mathbf{\Omega},0)=g_i(\mathbf{r},E,\mathbf{\Omega})\ . \tag{2}$$

In view of the differential (Fokker-Planck) operator, a boundary condition on energy is also required. As we are dealing with stationary target atoms here (not a restriction of this work, though), particles can only lose energy, and hence ϕ_{ki} must be zero for energies greater than the source energy E_0. The latter, however, is arbitrary and may assume a range of values (e.g., a Maxwellian distribution). Consequently, a suitably general boundary condition may be stated as

$$\lim_{E\to\infty}\phi_{ki}(\mathbf{r},E,\mathbf{\Omega},t)=0\ . \tag{3}$$

The spatial boundary condition requires some discussion. As we are assuming a finite medium, a free surface condition must clearly be imposed. For charged particles or atoms the Thompson surface barrier model[20] is commonly employed. This states that the energy corresponding to the perpendicular component of the outgoing particle's velocity must exceed the surface binding energy U_i for that particle to escape. If $\mathbf{n}$ is the outward unit normal at the surface, then this translates into the condition,

$$\left[\frac{U_i}{E}\right]^{1/2}-\mathbf{n}\cdot\mathbf{\Omega}<0\ , \tag{4}$$

with $\mathbf{n}\cdot\mathbf{\Omega}>0$ for outward directions. However, if this

constraint is not satisfied, the particle is assumed to undergo complete internal reflection, but in almost all calculations[5,12] this effect is ignored because of the tremendous complexity that it introduces. For completeness and to demonstrate the generalitly of the technique to be discussed, we retain this effect in our analysis. Thus, at some surface point $\mathbf{r}=\mathbf{r}_s$, a general reflecting boundary condition is assigned, as follows:

$$\phi_{ki}(\mathbf{r},E,\mathbf{\Omega},t)=\int_0^\infty dE'\int_{\mathbf{n}\cdot\mathbf{\Omega}'>0}d\mathbf{\Omega}'\Theta(E'-U_i)\Theta\left[\left[\frac{U_i}{E}\right]^{1/2}-\mathbf{n}\cdot\mathbf{\Omega}'\right]K_i(\mathbf{r}_s;E'\to E;\mathbf{\Omega}'\to\mathbf{\Omega})\phi_{ki}(\mathbf{r}_s,E',\mathbf{\Omega}',t) \tag{5}$$

for $\mathbf{n}\cdot\mathbf{\Omega}<0$ (representing incoming directions), i.e., outgoing particles not satisfying the surface barrier condition (also known as the planar potential[20,7]), given by the step functions $\Theta(\cdots)$ are reflected back into the medium ($\mathbf{n}\cdot\mathbf{\Omega}<0$) according to some law given by the kernel $K_i(\ldots)$. The latter is, in general, unknown, but even with simple models, such as specular reflection, the solution of the transport equation, Eq. (1), becomes prohibitively difficult.

In summary, and in a convenient compact notation, the forward system may be expressed as

$$\hat{B}_i\phi_{ki}-Q_{ki}(p)=0\ , \tag{6}$$

where $\hat{B}_i$ is just the Boltzmann operator and Q_{ki} the source, given by Eq. (1). The boundary conditions may be stated as

$$\phi_{ki}-\hat{K}_i\phi_{ki}=0,\quad \mathbf{r}=\mathbf{r}_s,\quad \mathbf{n}\cdot\mathbf{\Omega}<0\ , \tag{7}$$

$$\lim_{E\to\infty}\phi_{ki}=0 \tag{8}$$

and the initial condition as

$$\phi_{ki}=g_i,\quad t=0\ . \tag{9}$$

Our objective is to develop in a systematic manner the backward formalisms starting with the above system and to achieve that we must first consider the adjoint description.

III. VARIATIONAL CHARACTERIZATION AND THE ADJOINT SYSTEM

A systematic and rigorous derivation of the adjoint transport equation and associated boundary conditions can proceed from a variational characterization of the forward system. The idea is to develop a suitable variational principle that, when extremized, will yield the Boltzmann equation and its adjoint as Euler-Lagrange equations. Boundary conditions for both systems should emerge self-consistently, if the variational principle incorporates them appropriately. Such an approach would clearly be systematic and thus is to be preferred to the more *ad hoc* procedure popular in, for instance, neutron transport theory.[19] There, the adjoint function is first imbued with an "importance"[19] quality which is then used to assign boundary conditions. It presumably works well for the simple boundary conditions typically encountered in the neutron context, but is of doubtful value when constructing the adjoint boundary condition corresponding to, for example, Eq. (5). In the variational approach discussed below the adjoint function is treated simply as the mathematical artifact that it is. Relationship to physical quantities is subsequently shown through a reciprocity theorem which is another rigorous result.

A central role is played by the variational principle (VP) in our method. In order to construct a suitable VP, we consider first an arbitrary linear functional of the m-type particle flux

$$F[\phi_{km}]=\int_0^T dt\int_0^\infty dE\int_{4\pi}d\mathbf{\Omega}\int d\mathbf{r}\,f_m(\mathbf{r},E,\mathbf{\Omega},t)\times\phi_{km}(\mathbf{r},E,\mathbf{\Omega},t)$$
$$=(f_m,\phi_{km})\ , \tag{10}$$

where the inner product notation (a,b) signifying integration over phase space has been introduced. Note that we have allowed the upper bound on the energy variable to be infinity. This does not present any difficulty in the subsequent analysis as the flux is zero for energies greater than the source energy, or it approaches zero as the energy becomes infinitely large. Typically, f_m is chosen such that the functional corresponds to some desired physical quantity; for instance, if the sputtering yield at time t_1 of i-type particles is of interest then we would set

$$f_m=\delta_{im}\delta(t-t_1)\delta(\mathbf{r}-\mathbf{r}_s)|\mathbf{n}\cdot\mathbf{\Omega}|\Theta(E-U_m)\times\Theta\left[\mathbf{n}\cdot\mathbf{\Omega}-\left[\frac{U_m}{E}\right]^{1/2}\right], \tag{11}$$

where the step functions ensure that only those particles that can surmount the surface barrier escape from the medium. By appropriate choice of f_m, the functional can also describe internal distributions, such as the slowing down density of particles and energy,[7] which would describe implantation and damage distributions, respectively. We now construct a variational estimate for this functional and show that the result is a valid VP. It is difficult to guess or attempt to adapt established VP's[21] given the generality of the problem being considered. However, we may construct a VP systematically by appealing to the "conjugate variables" technique discussed in Morse and Feshbach[22] and employed by Pomraning[23] for inhomogeneous equations. The essence of the method is to consider the defining equations for the ϕ_{ki} (all species) as well as the boundary and initial data as constraints on the functional to be estimated, and the conjugate variables are introduced as generalized Lagrange variables (Lagrange functions[23]) to implement these constraints. Standard methods from the calculus of variations are then used to generate the corresponding Euler-Lagrange equations which provide the defining equations

for the Lagrange functions. The adjoint system is included in this, from which the backward form can then be derived.

Thus, we introduce a trial function, $\tilde{\phi}_{ki}$, which is a first-order accurate estimate of ϕ_{ki}, and the Lagrange functions $\tilde{\phi}_i^\dagger, \tilde{\lambda}_i, \tilde{\gamma}_i$, and $\tilde{\beta}_i$. Next we consider the following functional, obtained by constraining the original functional by the forward equations for all species and the boundary and initial conditions, but all evaluated using the trail functions

$$G[\tilde{\phi}_{ki},\tilde{\phi}_i^\dagger,\tilde{\lambda}_i,\tilde{\gamma}_i,\tilde{\beta}_i]=F[\tilde{\phi}_{km}]-\sum_{i=1}^{N}[(\tilde{\phi}_i^\dagger,B_i\tilde{\phi}_{ki}-Q_{ki})+(\tilde{\lambda}_i,\tilde{\phi}_{ki}-\hat{K}_i\tilde{\phi}_{ki})'_{\mathbf{r}-}+(\tilde{\gamma}_i,\tilde{\phi}_{ki}-g_i)'_0+(\tilde{\beta}_i,\tilde{\phi}_{ki})'_\infty] . \tag{12}$$

The prime denotes a restricted inner product, which excludes integration over $\mathbf{r}$ and is limited to $\mathbf{n}\cdot\Omega<0$ in the third term on the rhs, over t in the fourth term and over energy in the fifth term on the rhs, reflecting the boundary and initial conditions. Thus, $\tilde{\lambda}_i$ is a function only of $(E,\mathbf{\Omega},t)$ defined over $\mathbf{n}\cdot\mathbf{\Omega}<0$, $\tilde{\gamma}_i$ is a function of $(\mathbf{r},E,\mathbf{\Omega})$ and $\tilde{\beta}_i$ a function of $(\mathbf{r},\mathbf{\Omega},t)$, while $\tilde{\phi}_i^\dagger$ is defined over all phase space. We further regard these functions as first-order accurate estimates of corresponding exact functions $\phi_i^\dagger$, λ_i, γ_i, and β_i (i.e., without the tildes). Then, if $G[\,]$ is to be a valid VP for $F[\,]$, it must satisfy the following two conditions. (i) When evaluated using the exact function ϕ_{ki}, G, must yield the desired functional $F[\phi_{km}]$. (ii) First-order errors in ϕ_{ki}, $\phi_i^\dagger$, λ_i, γ_i, and β_i must result in second-order errors in the functional G.

The first condition is clearly satisfied by virtue of the forward system, Eqs. (6)–(9), i.e.,

$$G[\phi_{ki},\tilde{\phi}_i^\dagger,\tilde{\lambda}_i,\tilde{\gamma}_i,\tilde{\beta}_i]=F[\phi_{km}] . \tag{13}$$

The second condition is satisfied by requiring the first variation of G to vanish when evaluated with the exact functions. This should yield equations for the as yet undefined conjugate variables. Thus, taking the first variation of G, we get

$$\begin{aligned}\delta G=(f_m,\delta\tilde{\phi}_{km})-\sum_{i=1}^{N}[&(\delta\tilde{\phi}_i^\dagger,\hat{B}_i\tilde{\phi}_{ki}-Q_{ki})+(\tilde{\phi}_i^\dagger,\hat{B}_i\delta\tilde{\phi}_{ki})+(\delta\tilde{\lambda}_i,\tilde{\phi}_{ki}-\hat{K}_i\tilde{\phi}_{ki})'_{\mathbf{r}-}+(\tilde{\lambda}_i,\delta\tilde{\phi}_{ki}-\hat{K}_i\delta\tilde{\phi}_{ki})'_{\mathbf{r}-}\\&+(\delta\tilde{\gamma}_i,\tilde{\phi}_{ki}-g_i)'_0+(\tilde{\gamma}_i,\delta\tilde{\phi}_{ki})'_0+(\delta\tilde{\beta}_i,\tilde{\phi}_{ki})'_\infty+(\tilde{\beta}_i,\delta\tilde{\phi}_{ki})'_\infty] .\end{aligned} \tag{14}$$

We now rearrange and regroup terms such that all variational terms (involving $\delta\tilde{\phi}$, etc.) are free standing and not operated on. This will then enable us to consider arbitrary and independent variations. The terms requiring special consideration are the third and fifth terms on the rhs of Eq. (14), and we manipulate these below. Let

$$B=\sum_{i=1}^{N}(\tilde{\phi}_i^\dagger,\hat{B}_i\delta\tilde{\phi}_{ki}) . \tag{15}$$

We further decompose the Boltzmann operator:

$$\hat{B}_i=\hat{L}-\hat{T}_i , \tag{16}$$

where

$$\hat{L}\equiv\frac{1}{v}\frac{\partial}{\partial t}+\mathbf{\Omega}\cdot\nabla \tag{17}$$

which is the streaming component, and

$$\hat{T}_i\equiv\frac{\partial}{\partial E}S_i+\hat{S}_i+\hat{R}_i \tag{18}$$

which represents the interactions (continuous, scattering, and recoil). Considering the components individually, let

$$\begin{aligned}B_1&=\sum_{i=1}^{N}(\tilde{\phi}_i^\dagger,\hat{L}\delta\tilde{\phi}_{ki})\\&=\sum_{i=1}^{N}\int_0^T dt\int_0^\infty dE\int_{4\pi}d\mathbf{\Omega}\int d\mathbf{r}\tilde{\phi}_i^\dagger\left[\frac{1}{v}\frac{\partial}{\partial v}+\mathbf{\Omega}\cdot\nabla\right]\\&\quad\times\delta\tilde{\phi}_{ki} .\end{aligned} \tag{19}$$

Integrating by parts over t and using Gauss's theorem to transform the volume integral to a surface integral for the gradient term, B_1 reduces, after some algebra to

$$\begin{aligned}B_1=\sum_{i=1}^{N}\Bigg[&\left[\delta\tilde{\phi}_{ki},\frac{1}{v}\tilde{\phi}_i^\dagger\right]'_T-\left[\delta\tilde{\phi}_{ki},\frac{1}{v}\tilde{\phi}_i^\dagger\right]'_0\\&+(\delta\tilde{\phi}_{ki},\mathbf{n}\cdot\mathbf{\Omega}\tilde{\phi}_i^\dagger)'_{\mathbf{r}}+(\delta\tilde{\phi}_{ki},\hat{L}^\dagger\tilde{\phi}_i^\dagger)\Bigg] ,\end{aligned} \tag{20}$$

where the inner product is computed at $t=T$ in the first term on the rhs, at $t=0$ in the second term, and at $\mathbf{r}=\mathbf{r}_s$ in the third term. These are boundary terms that arise from the integration by parts and the surface integral. Also, we have introduced the operator

$$\hat{L}^\dagger\equiv-\frac{1}{v}\frac{\partial}{\partial t}-\mathbf{\Omega}\cdot\nabla . \tag{21}$$

(The adjoint operator is clearly seen to be emerging here.)

Consider next the interaction component

$$B_2=\sum_{i=1}^{N}(\tilde{\phi}_i^\dagger,\hat{T}_i\delta\tilde{\phi}_{ki}) . \tag{22}$$

We transform this term by term. The continuous interaction or stopping power term becomes

$$B_{21}=\sum_{i=1}^{N}\int_0^T dt\int_0^\infty dE\int_{4\pi}d\mathbf{\Omega}\int d\mathbf{r}\tilde{\phi}_i^\dagger\frac{\partial}{\partial E}(S_i\tilde{\phi}_{ki}) . \tag{23}$$

Integrating by parts over energy, this simplifies to

$$B_{21}=\sum_{i=1}^{N}\left[(\delta\tilde{\phi}_{ki},S_i\tilde{\phi}_i^{\dagger})'_{\infty}-(\delta\tilde{\phi}_{ki},S_i\tilde{\phi}_i^{\dagger})'_0+\left[\delta\tilde{\phi}_{ki},-S_i\frac{\partial\tilde{\phi}_i^{\dagger}}{\partial E}\right]\right]. \tag{24}$$

Here, the inner product in the first and second terms on the rhs is computed at $E=\infty$ and $E=0$, respectively.

The scattering term is modified as follows:

$$B_{22}=\sum_{i=1}^{N}\int_0^T dt\int d\mathbf{r}\int_{4\pi}d\Omega\int_0^{\infty}dE\,\tilde{\phi}_i^{\dagger}\sum_{j=1}^{N}\int dE'\times\int d\Omega'\Sigma_{ji}(E'\to E;\Omega'\cdot\Omega)\delta\tilde{\phi}_{ki}(\mathbf{r},E',\Omega',t)\,. \tag{25}$$

To isolate $\delta\tilde{\phi}_{ki}$ in Eq. (25), we first interchange the orders of integration over (E',Ω') and (E,Ω), and then switch the variables $E\leftrightarrow E'$ and $\Omega\leftrightarrow\Omega'$. The final result may be written down as

$$B_{22}=\sum_{i=1}^{N}(\delta\tilde{\phi}_{ki},\hat{S}_i^{\dagger}\tilde{\phi}_i^{\dagger})\,, \tag{26}$$

where

$$\hat{S}_i^{\dagger}\tilde{\phi}_i^{\dagger}=\sum_{j=1}^{N}\int_{\alpha_{ij}E}^{E}dE'\int d\Omega'\,\Sigma_{ji}(E\to E';\Omega'\cdot\Omega)\times\tilde{\phi}_i^{\dagger}(\mathbf{r},E',\Omega',t)\,. \tag{27}$$

The recoil operator is transformed in a similar manner, except that the summation over species i and j must also be interchanged, followed by the exchange $i\leftrightarrow j$. The final result, after some algebra, is given by

$$B_{23}=\sum_{i=1}^{N}(\tilde{\phi}_i^{\dagger},\hat{R}_i\delta\phi_{ki})=\sum_{i=1}^{N}(\delta\tilde{\phi}_{ki},\hat{R}_i^{\dagger}\tilde{\phi}_i^{\dagger})\,, \tag{28}$$

where

$$\hat{R}_i^{\dagger}\tilde{\phi}_i^{\dagger}=\sum_{j=1}^{N}\int_0^{(1-\alpha_{ij})E}dE''\int d\Omega''\,\Sigma_{ij}^{*}(E\to E'';\Omega\cdot\Omega'')\times\tilde{\phi}_j^{\dagger}(\mathbf{r},E'',\Omega'',t)\,. \tag{29}$$

Collecting terms, Eq. (15) may finally be written as

$$B=\sum_{i=1}^{N}\left[(\delta\tilde{\phi}_{ki},\hat{B}_i^{\dagger}\tilde{\phi}_i^{\dagger})+\left[\delta\tilde{\phi}_{ki},\frac{1}{v}\tilde{\phi}_i^{\dagger}\right]'_T-\left[\delta\tilde{\phi}_{ki},\frac{1}{v}\tilde{\phi}_i^{\dagger}\right]'_0+(\delta\tilde{\phi}_{ki},S_i\tilde{\phi}_i^{\dagger})'_{\infty}-(\delta\tilde{\phi}_{ki},S_i\phi_i^{\dagger})'_0+(\delta\tilde{\phi}_{ki},\mathbf{n}\cdot\Omega\tilde{\phi}_i^{\dagger})'_{\mathbf{r}}\right], \tag{30}$$

where

$$\hat{B}_i^{\dagger}\equiv\hat{L}^{\dagger}-T_i^{\dagger}\equiv\hat{L}^{\dagger}-\left[-S_i\frac{\partial}{\partial E}+\hat{S}_i^{\dagger}+\hat{R}_i^{\dagger}\right]. \tag{31}$$

Finally, we consider the fifth term in Eq. (14)

$$D=\sum_{i=1}^{N}(\tilde{\lambda}_i,\delta\tilde{\phi}_{ki}-\hat{K}_i\delta\tilde{\phi}_{ki})'_{\mathbf{r}^-} \tag{32}$$

which is a boundary term ($\mathbf{r}=\mathbf{r}_s$) restricted to $\mathbf{n}\cdot\Omega<0$, i.e., incoming directions. We note from Eq. (5) that $\hat{K}_i$ is an integral operator, so that we may transform Eq. (32) as we did the scattering and recoil operators above, i.e., by interchanging orders of integration and switching variables. After considerable algebra, the final result is

$$D=\sum_{i=1}^{N}[(\delta\tilde{\phi}_{ki},\tilde{\lambda}_i)_{\mathbf{r}^-}-(\delta\tilde{\phi}_{ki},\hat{H}_i^{\dagger}\tilde{\lambda}_i)_{\mathbf{r}^+}]\,, \tag{33}$$

where $\mathbf{r}^+$ refers to outgoing directions, i.e., $\mathbf{n}\cdot\Omega>0$, and we have introduced the operator

$$\hat{H}_i^{\dagger}\tilde{\lambda}_i=\Theta(E-U_i)\Theta\left[\left[\frac{U_i}{E}\right]^{1/2}-\mathbf{n}\cdot\Omega\right]\times\int_0^{\infty}dE'\int_{\mathbf{n}\cdot\Omega'<0}d\Omega'\,K_i(\mathbf{r}_s;E\to E';\Omega\to\Omega')\times\tilde{\lambda}_i(E',\Omega',t)\,. \tag{34}$$

Rearranging the other terms in the expression for the first variation, Eq. (14), is trivial, and the final result is given by

$$\delta G=\sum_{i=1}^{N}\left[(\delta\tilde{\phi}_{ki},f_i\delta_{im}-\hat{B}_i^{\dagger}\tilde{\phi}_i^{\dagger})-(\delta\tilde{\phi}_{ki}^{\dagger},\hat{B}_i\tilde{\phi}_{ki}-Q_{ki})-\left[\delta\tilde{\phi}_{ki},\frac{1}{v}\tilde{\phi}_i^{\dagger}\right]'_T-\left[\delta\tilde{\phi}_{ki},\tilde{\gamma}_i-\frac{1}{v}\tilde{\phi}_i^{\dagger}\right]'_0-(\delta\tilde{\lambda}_i,\tilde{\phi}_{ki}-\hat{H}_i\tilde{\phi}_{ki})'_{\mathbf{r}^-}-(\delta\tilde{\phi}_{ki},\mathbf{n}\cdot\Omega\tilde{\phi}_i^{\dagger}-\hat{H}_i^{\dagger}\tilde{\lambda}_i)'_{\mathbf{r}^+}-(\delta\tilde{\phi}_{ki},\mathbf{n}\cdot\Omega\tilde{\phi}_i^{\dagger}+\tilde{\lambda}_i)'_{\mathbf{r}^-}-(\delta\tilde{\gamma}_i,\tilde{\phi}_{ki}-g_i)'_0-(\delta\tilde{\beta}_i,\tilde{\phi}_{ki})'_{\infty}-(\delta\tilde{\phi}_{ki},\beta_i+S_i\tilde{\phi}_i^{\dagger})'_{\infty}+(\delta\tilde{\phi}_{ki},S_i\tilde{\phi}_i^{\dagger})'_0\right]. \tag{35}$$

In obtaining Eq. (35), two further changes were introduced. First, the functional $F[\ ]$ was written in a slightly different form

$$F=(f_m,\tilde{\phi}_{km})=\sum_{i=1}^{N}(f_i\delta_{im},\tilde{\phi}_{ki})$$

so that

$$\delta F=\sum_{i=1}^{N}(f_i\delta_{im},\delta\tilde{\phi}_{ki})$$

and, secondly, the following decomposition was used:

$$(\delta\tilde{\phi}_{ki},\mathbf{n}\cdot\Omega\tilde{\phi}_i^{\dagger})_{\mathbf{r}}=(\delta\tilde{\phi}_{ki},\mathbf{n}\cdot\Omega\tilde{\phi}_i^{\dagger})_{\mathbf{r}^+}+(\delta\tilde{\phi}_{ki},\mathbf{n}\cdot\Omega\tilde{\phi}_i^{\dagger})_{\mathbf{r}^-}$$

which allows a more convenient grouping of terms in Eq.

(35). Recall $\mathbf{r}^+$ and $\mathbf{r}^-$ refer, respectively, to outgoing ($\mathbf{n}\cdot\boldsymbol{\Omega}>0$) and incoming ($\mathbf{n}\cdot\boldsymbol{\Omega}<0$) directions at the free surface ($\mathbf{r}=\mathbf{r}_s$).

Equation (35) is now in the form suitable for extremizing. Taking independent and arbitrary variations about the exact functions and demanding that the first variation δG be zero, Eq. (35) yields the Euler-Lagrange equations that are equivalent to the variational formulation. These may be stated compactly as follows. For ϕ_{ki},

$$\hat{B}_i\phi_{ki}=Q_{ki} , \tag{36}$$

$$\phi_{ki}-\hat{H}_i\phi_{ki}=0, \quad \mathbf{r}=\mathbf{r}_s, \quad \mathbf{n}\cdot\boldsymbol{\Omega}<0 , \tag{37}$$

$$\phi_{ki}=0, \quad E\to\infty , \tag{38}$$

$$\phi_{ki}=g_i, \quad t=0 . \tag{39}$$

For $\phi_i^\dagger$,

$$\hat{B}_i^\dagger\phi_i^\dagger=\delta_{im}f_i , \tag{40}$$

$$\mathbf{n}\cdot\boldsymbol{\Omega}\phi_i^\dagger-\hat{H}_i^\dagger\lambda_i=0, \quad \mathbf{r}=\mathbf{r}_s, \quad \mathbf{n}\cdot\boldsymbol{\Omega}>0 , \tag{41}$$

$$\phi_i^\dagger=0, \quad E=0 , \tag{42}$$

$$\phi_i^\dagger=0, \quad t=T . \tag{43}$$

For λ_i,

$$\lambda_i+\mathbf{n}\cdot\boldsymbol{\Omega}\phi_i^\dagger=0, \quad \mathbf{r}=\mathbf{r}_s, \quad \mathbf{n}\cdot\boldsymbol{\Omega}<0 . \tag{44}$$

For γ_i,

$$\gamma_i-\frac{1}{v}\phi_i^\dagger=0, \quad t=0 . \tag{45}$$

For β_i,

$$\beta_i+S_i\phi_i^\dagger=0, \quad E\to\infty . \tag{46}$$

The boundary condition on $\phi_i^\dagger$, Eq. (41), depends on λ_i, which is defined for $\mathbf{n}\cdot\boldsymbol{\Omega}<0$ by Eq. (44) in terms of $\phi_i^\dagger$. Recalling that the operator $\hat{H}_i^\dagger$ is restricted to $\mathbf{n}\cdot\boldsymbol{\Omega}<0$, Eqs. (41) and (44) may be combined to give a closed form boundary condition for $\phi_i^\dagger$

$$\begin{aligned}&\mathbf{n}\cdot\boldsymbol{\Omega}\phi_i^\dagger+\hat{H}_i^\dagger(\mathbf{n}\cdot\boldsymbol{\Omega}\phi_i^\dagger)=0 ,\\ &\mathbf{r}=\mathbf{r}_s, \quad \mathbf{n}\cdot\boldsymbol{\Omega}>0 .\end{aligned} \tag{47}$$

The remaining Lagrange or conjugate functions γ_i and β_i are determined from Eqs. (45) and (46), respectively, once the complete solution for $\phi_i^\dagger$ is obtained.

Equation (40) is the adjoint Boltzmann equation, $\phi_i^\dagger$ being the adjoint particle flux for the ith species, and Eqs. (42), (43), and (47) are the corresponding adjoint initial and boundary conditions. Note the "backward" nature of this system, i.e., the adjoint equation is solved from a "final" condition at $t=T$ [given by Eq. (43)] to an initial time, speeding up from $E=0$ [see Eq. (42)] to a higher energy, and the boundary condition at the free surface is imposed on outgoing directions. This constitutes a true or complete backward system. Note, also, that the function f_i, defined in the functional representing the physically desired property given in Eq. (10), has emerged as the adjoint source in Eq. (40). This specializes the solution of the adjoint equation to the particular effect being considered and immediately indicates a kinship with the Lindhard-type backward equations, which are also application specific. However, the similarity ends here for now. In the next section the conditions under which Eq. (40) reduces precisely to the equation familiar in radiation damage work will be established.

To conclude this section, we emphasize that our approach in developing the adjoint description has systematically relied on the rigorous concepts of calculus of variations and that physical intuition about the adjoint function was not employed at any stage. Even the variational principle was derived using established and rigorous concepts[22,23] and is sufficiently general to be used in related problems described by the transport equation. We note in closing that setting $\tilde{\phi}_i=\phi_i+\delta\phi_i$, etc., in Eq. (35) for the first variation and using the defining equations and boundary conditions to eliminate various terms from Eq. (35), it is readily shown that δG is second-order accurate with respect to variations in all the trial functions, i.e., $\delta G\sim(\delta\tilde{\phi}_i^\dagger,\delta\tilde{\phi}_{ki})$ etc. Hence, our VP is a valid VP for the problem under consideration.

IV. BACKWARD AND LINDHARD EQUATION FORMULATIONS

Although the adjoint equation was seen to describe evolution in reverse time, the adjoint flux itself is not the desired quantity since it has no physical meaning as such. However, it can be related to physical quantities, and it is desirable to develop equations directly for the effects of interest. These should then constitute the complete backward equations from which the Lindhard-type equations will follow.

To this end, we first describe a reciprocity relation between the forward and adjoint fluxes.[24,7] Setting

$$f_i=\delta(p-p_1) \tag{48}$$

and

$$Q_{ki}=\delta_{ki}\delta(p-p_0) \tag{49}$$

(recall the p's represent the set of phase-space variables), the forward and adjoint equations become

$$\hat{B}_i\phi_{ki}=\delta_{ki}\delta(p-p_0) \tag{50}$$

and

$$\hat{B}_i^\dagger\phi_{mi}^\dagger=\delta_{mi}\delta(p-p_1) , \tag{51}$$

where we have allowed the adjoint flux to depend explicitly on the source species index. We now carry out the following operation:

$$\sum_{i=1}^{N}(\phi_{mi}^\dagger,\ \hat{B}_i\phi_{ki})-\sum_{i=1}^{N}(\phi_{ki},\ \hat{B}_i^\dagger\phi_{mi})$$

and manipulate using the defining equations and boundary and initial data to obtain eventually

$$\phi_{mk}^\dagger(p;p_1)=\phi_{km}(p_1;p) , \tag{52}$$

where we have replaced p_0 by p for notational conveni-

ence. The above result states that the forward and adjoint fluxes (to be more precise, the Green's functions) are identical but with interchanged source and field variables, as well as the species indices. This reciprocity is quite general, independent of the specific boundary conditions and the interaction physics. The advantage of this is that the adjoint flux may be replaced by the forward flux in the adjoint equation, which then becomes

$$\hat{B}_i^{\dagger}(p)\phi_{im}(p_1;p)=\delta_{mi}\delta(p-p_i)\ . \tag{53}$$

An interesting observation in Eq. (53) is that the adjoint operator acts on p which represents the source variables, while the field variables p_1 appear only as parameters in the equations—recall that $\phi_{im}(p_1;p)$ is the flux of m-type particles in p_1 due to one i-type source particle in p. This means that Eq. (53) (being linear) can be operated on with respect to the field variables p_1 without changing the equation, except possibly the source term. Herein lies the key to the problem of constructing equations directly for the physical effects. For the latter can invariably be expressed as functionals of the forward flux,

$$R_{im}(\bar{p}_1;p)=\int_{\Delta V_1} dp_1\,\phi_{im}(p_1;p)h(p_1)\ , \tag{54}$$

where ΔV_1 is the volume of phase space over which the response is desired and $\bar{p}_1$ lies in $V_1-\Delta V_1$. We will give an example below of the forms that R_{im} and $h(p_1)$ might typically assume. Operating on Eq. (53) according to the integral in Eq. (54), we obtain an equation for R_{im}

$$\hat{B}_i^{\dagger}R_{im}(\bar{p}_1;p)=\delta_{mi}\Delta_1(p)h(p)\ , \tag{55}$$

where $\Delta_1 p=1$ for p in ΔV_1 and zero otherwise. Equation (55) is the complete backward equation for the desired effect R_{im} and at this stage is an exact equation valid for arbitrary random media. Explicitly, the equation reads

$$\begin{aligned}\left[-\frac{1}{v}\frac{\partial}{\partial t}-\mathbf{\Omega}\cdot\nabla\right]R_{im}=&-S_i\frac{\partial R_{im}}{\partial E}+\sum_{j=1}^{N}\int_{\alpha_{ij}E}^{E}dE'\int d\mathbf{\Omega}'\,\Sigma_{ji}(E\to E';\mathbf{\Omega}'\cdot\mathbf{\Omega})R_{im}(\mathbf{r},E',\Omega',t)\\&+\sum_{j=1}^{N}\int_{0}^{(1-\alpha_{ij})E}dE''\int d\mathbf{\Omega}''\,\Sigma_{ij}^{*}(E\to E'';\mathbf{\Omega}\cdot\mathbf{\Omega}'')R_{jm}(\mathbf{r},E'',\mathbf{\Omega}'',t)\\&+\delta_{mi}\Delta_1(\mathbf{r},E,\mathbf{\Omega},t)h(\mathbf{r},E,\mathbf{\Omega},t)\ .\end{aligned} \tag{56}$$

The operator is still the adjoint operator, but, depending on the form of the source term, the equation will describe different phenomena. The boundary condition for R_{im} can be obtained in a similar manner by replacing the adjoint flux with the forward flux (according to the reciprocity relation) in the adjoint boundary condition Eq. (47) and operating on the latter according to Eq. (54). We obtain finally

$$\mathbf{n}\cdot\mathbf{\Omega}R_{im}(\mathbf{r}_s,E,\mathbf{\Omega},t)+\Theta(E-U_i)\Theta\left[\left[\frac{U_i}{E}\right]^{1/2}-\mathbf{n}\cdot\mathbf{\Omega}\right]\int_0^{\infty}dE'\int_{\mathbf{n}\cdot\mathbf{\Omega}'<0}d\mathbf{\Omega}'\,K_i(\mathbf{r}_s;E\to E';\mathbf{\Omega}\to\mathbf{\Omega}')R_{im}(\mathbf{r}_s,E',\mathbf{\Omega}',t)=0,$$

$$\mathbf{n}\cdot\mathbf{\Omega}>0\ . \tag{57}$$

The other conditions may be similarly adapted from the corresponding adjoint data. As an example, let us consider the sputtering yield of m-type particles at some interior point $\mathbf{r}_1$ at time t_1 due to an i-type source particle in $(\mathbf{r},E,\mathbf{\Omega},t)$. This may be expressed in terms of the forward flux as follows:

$$Y_{im}(\mathbf{r}_1,t_1;\mathbf{r},E,\mathbf{\Omega},t)=\int_{U_1}^{\infty}dE_1\int_{\mathbf{n}\cdot\mathbf{\Omega}_1>\sqrt{U_i/E}}d\mathbf{\Omega}_1|\mathbf{n}\cdot\mathbf{\Omega}_1|\phi_{im}(\mathbf{r}_1,E_1,\mathbf{\Omega}_1,t_1;\mathbf{r},E,\mathbf{\Omega},t)\ . \tag{58}$$

Comparing with Eq. (54), it is clear that R_{im} will represent the sputtering yield if we set

$$h(p_1)=|\mathbf{n}\cdot\mathbf{\Omega}_1|\Theta(E_1-U_i)\Theta\left[\mathbf{n}\cdot\mathbf{\Omega}_1-\left[\frac{U_i}{E}\right]^{1/2}\right] \tag{59}$$

so that in Eq. (55), $\Delta_1(p)$ is just

$$\delta(t-t_1)\delta(\mathbf{r}-\mathbf{r}_1)\ .$$

Thus, the backward equation for the yield may be written as

$$\begin{aligned}\hat{B}_i^{\dagger}Y_{im}=&\,\delta_{mi}\delta(t-t_1)\delta(\mathbf{r}-\mathbf{r}_1)|\mathbf{n}\cdot\mathbf{\Omega}|\\&\times\Theta(E-U_i)\Theta\left[\mathbf{n}\cdot\mathbf{\Omega}-\left[\frac{U_i}{E}\right]^{1/2}\right]\ .\end{aligned} \tag{60}$$

Of course, the actual sputtering yield is the surface value at $\mathbf{r}=\mathbf{r}_s$. The boundary condition is identical to Eq. (57), with R_{im} replaced by Y_{im}. By appropriate choice of $h(p_1)$ in Eq. (54), similar backward equations may be obtained for any effect of interest. In all cases, the operator remains the same, but it is the source term that distinguishes the phenomena.

We are now in a position to establish contact with the Lindhard-type equations, which we expect, in principle, to be identical to the ones derived above [or Eq. (55) in general]. This, however, is not the case, as is readily observed when comparing Eq. (60) for the sputtering yield with the corresponding equation given by Sigmund.[5] The difference resides in the operational variables in the respective operators. In the operator $\hat{B}_i^{\dagger}$ given above [i.e., the adjoint transport operator Eq. (56)], it is the source variables exclusively that are the independent

variables— the field, or final, variables appear only as parameters, a fact was taken advantage of above in generating the complete backward formalism. However, in the Lindhard-type equations, the operational variables are a rather curious mix of source and field variables, which, from a physical point of view, is perhaps a more appealing format than the pure source variable description. As is well known,[7,25] though, this reduction exacts a price, namely a restriction to space and time homogeneous applications. Thus, in the Lindhard description, the complex surface boundary conditions, given for example by Eq. (57), cannot be incorporated, nor can heterogeneities such as multilayered targets be described. It is instructive to consider how the approximate Lindhard formalism emerges conclusively from the exact backward description above. We follow Williams[7] and note that under the assumption of homogeneity, the solution of the backward equation satisfies space-time translational invariance, i.e., the solution depends on the space and time variables only through the combination $|\mathbf{r}-\mathbf{r}_1|$ and t_1-t. In this case it is permissible to replace $\nabla_{\mathbf{r}}$ and $\partial/\partial t$ in the adjoint or backward operator by $-\nabla_{\mathbf{r}_1}$ and $-\partial/\partial t_1$, respectively, i.e., introduce field variables in space and time but retain source variables in energy and direction (or angle). Thus, the equation for the sputtering yield is still Eq. (60) but with the operator $\hat{B}_i^{\dagger}$ replaced by

$$\hat{B}_i^{\dagger} \rightarrow \hat{B}_i^{*} \equiv \hat{L}^{*} - \hat{T}_i^{\dagger} , \tag{61}$$

[cf. Eq. (31)] where $\hat{T}_i^{\dagger}$ is just the adjoint interaction operator and $\hat{L}^{*}$ is given by

$$\hat{L}^{*} \equiv \frac{1}{v}\frac{\partial}{\partial t_1} + \mathbf{\Omega}\cdot\nabla_{\mathbf{r}_1} \tag{62}$$

in contrast to $\hat{L}^{\dagger}$ [see Eq. (21)]. With this transformation, and except for notational differences, the resulting equation for the sputtering yield is identical to that obtained by Sigmund.[5]

We see, thus, that the general form of the Lindhard-type equations is neither fully forward nor fully backward, but a hybrid. The structure appears to follow the laboratory situation more closely by inquiring about spatial distributions (i.e., field quantities) as functions of certain control (i.e., source) variables, but does so only approximately. In order to relax the homogeneity assumption, one must abandon the hybrid approach and resort to either the complete backward or forward description. In this case the forward form is perhaps to be preferred because of its history, but this is purely a matter of preference as the two approaches are entirely equivalent.

Further advantages of the variational approach

The role of the variational principle derived earlier extends beyond providing a pivotal link between the forward, adjoint, and hybrid systems. An important property of a valid VP, shown above, is that a variational estimate of a functional of interest is accurate to second order with respect to errors in the trial functions (see Sec. III). This means that rather accurate estimates of integral quantities such as reflection and sputtering yields, total recoil implantation yields, etc., may be realized from only an approximate knowledge of the distribution functions. This technique is, of course, well known in neutron transport theory[15,26] and the kinetic theory of gases,[15] but appears not to have been exploited in the context of ion-solid interactions.

The general case, described by Eq. (12), is undoubtedly complicated. Trial functions would be required for $5\times N$ functions (N is the number of species) and optimization carried out with respect to free parameters in these functions. However, considerable simplification would ensue if, for example, application were restricted to few species (one or two), if internal reflection were neglected (invariably the case in the literature) and if trial functions were chosen to satisfy the exact boundary and initial conditions. Many terms in Eq. (12) would then vanish identically, but the complication remains of having to determine trial functions for the adjoint flux. Numerous techniques exist for developing approximations for the forward flux[15,17,26,27] and many are physically motivated, but it is difficult to extend these concepts readily and in a meaningful way to generate approximate solutions to the adjoint equations. However, as we have demonstrated a relationship between the adjoint and backward descriptions, there is scope here for using available solutions to the Lindhard-type equations, corresponding to the functional of interest, as trial functions for the adjoint flux. Clearly, much work needs to be done to develop this approach to maturity, but the effort is undoubtedly worthwhile.

V. CONCLUSIONS

A variational technique has been used to establish, for the first time, a rigorous link between the forward and backward Boltzmann equation models of ion-solid interaction phenomena. It was shown that a truly backward formalism is synonymous with the adjoint description if exact geometry and boundary conditions are to be incorporated. Only under the assumption of space and time homogeneity, does the system reduce to the Lindhard-type equations that are so popular in the field. The variational characterization itself demonstrates the duality of the forward and adjoint approaches.

It was also shown that the VP can be used directly to accurately estimate integral quantities (e.g., surface and volume-averaged quantities) using trial functions that need not be known with accuracy. It was proposed that existing solutions of the Lindhard-type equations be considered as trial functions for the adjoint function necessary in this technique.

A result of general applicability in linear transport theory that emerges from this work is that it is not necessary to depend on physical interpretations of the adjoint function in order to assign adjoint boundary conditions, should such a formulation arise in any application. This is particularly so in the neutron context,[19] where the "importance" function is frequently introduced. We have

shown that since the adjoint formalism is problem dependent, one can always express the desired effect as a functional of the forward flux and then use the calculus of variations to systematically generate the adjoint equations and affiliated boundary conditions. Certainly, in situations with complex boundary effects, the physical reasoning commonly employed is likely to prove highly convoluted.

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