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Hierarchy in Variational Principles of Irreversible Processes

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Dynmaical processes in macroscopic systems can be categorized tipycally into three hierarchial stages. First the initial dynamical stage is concerned with the precise information of microscopic level, to which the Liouville or von Neumann equation is relevant. Secondly the kinetic stage is described on the basis of the Boltzmann equation, where the microscopic basis of the second law of thermodynamics was elucidated as well as irreversibility. Thirdly the thermo-hydordynamical stage comes, which is described in terms of hydrodynamics and thermodynamics. Variational principles relevant to these three stages are presented, which shows that the dynamical basis of irreversibility comes about as a result of the information contraction of the state of the system.

§1.Introduction

Corresponding to the hierarchy of development of dynamical systems, we have three sorts of variational principles, which are converted into one another by contracting informatons of the state of the system, as shown in the table below. We begin with the kinetic theories of conduction electrons in solids based on the Boltzmann equation, for which a varitional principle we call the Umeda-Kohler-Sondheimer (abbreviated as UKS) principle[1)] is presented as an extremum problem in §2, whose thermodynamical meaning is given on the basis of the entropy production. The extremum gives such a transport coeffcents as electrical conductivity.

Contracting the informaton of the distribution function, we can derive the hydrothermodynamical variational principle which was obtaied by Onsager[2] many years ago by applying the theory of stochastic processes to the system at thermal equilibrium.

In §3 we investigate the dynamical stage on the basis of the von Neumann equation, for which a variational principles[3] formulated as a stationarity problem. By means of the information contraction the stationarity problem is converted into an extremum problem. This contraction is presented in §4, where the variational principle is reduced to the UKS principle in a more rectified form[4]. In §5 it is summarized how the contracton of information of the densiity matrix and distribution function convert the variational principle of reversible dynamical processes into the one of irreversibile thermodynamical processes.

Successive information contraction---------------→

Our V.P. Dynamical stage	UKS V.P. Kinnetic stage	Onsager's V.P. Hydro-Thermodynamical stage

von Neumann eq.→→→Boltzzmann eq.→→Navier-Stokes eq.

time developing-----------------------------------→

§2. UKS and thermodynamical variational principles

The Boltzmann equation in the kinetic theory is written

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_C + \left(\frac{\partial f}{\partial t}\right)_D, \tag{1}$$

as the sum of the collision and drift terms, which are given by

$$\left(\frac{\partial f}{\partial t}\right)_D = -e\mathbf{E}\cdot\frac{\partial f}{\partial \mathbf{p}} - \frac{\mathbf{p}}{m}\cdot\frac{\partial f}{\partial \mathbf{r}}, \tag{2}$$

$$\left(\frac{\partial f}{\partial t}\right)_C = \sum_{k'} W_{k,k'}\,\delta(\varepsilon_k - \varepsilon_{k'})(f_{k'} - f_k), \tag{3}$$

respectively, for the system of conduction electrons in solids scattered by static impurities, where the transition probability is written

$$W_{k,k'} = 2\pi|\langle k|V|k'\rangle|^2/\hbar \tag{4}$$

in terms of the impurity potential V.

Assuming

$$f_k(\mathbf{r},t) = f_0 - \frac{\partial f_0}{\partial \varepsilon}\,\Phi_k \tag{5}$$

in terms of the Fermi distribution

$$f_0(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon-\mu)]+1}, \tag{6}$$

we obtain

$$\left(\frac{\partial f}{\partial t}\right)_C = \frac{\partial f_0}{\partial \varepsilon}\,L\Phi, \tag{7}$$

from (3), where the collision operator L is defined by

$$L\Phi(\mathbf{k}) = \sum_{k'} W_{k,k'}\,\delta(\varepsilon_k - \varepsilon_{k'})(\Phi_k - \Phi_{k'}). \tag{8}$$

The drift term (1) is written as

$$\left(\frac{\partial f}{\partial t}\right)_D = -\frac{\partial f_0}{\partial \varepsilon}\,(\mathbf{j}_k \cdot \mathbf{X}_1 + \mathbf{q}_k \cdot \mathbf{X}_2), \tag{9}$$

in terms of the flows and forces

$$\mathbf{j}_k = e\mathbf{v}_k, \qquad \mathbf{q}_k = (\varepsilon_k - \mu)\mathbf{v}_k, \qquad (\mathbf{v}_k = \hbar\mathbf{k}/m) \tag{10}$$

$$X_1 = E-(\nabla\mu/e), \quad X_2 = -(\nabla T)/T. \tag{11}$$

Substituting (7) and (9) into (1), we get the linearized Boltzmann equation

$$L\Phi = X, \quad X = j_k \cdot X_1 + q_k \cdot X_2 \tag{12}$$

in the wave number **k**-space.

With respect to the inner product defined as

$$(\Phi, \psi) = (\psi, \Phi) = -\sum_k \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \Phi_k \psi_k, \tag{13}$$

$$(\psi, L\Phi) = -\sum_k \sum_{k'} \frac{\partial f_0}{\partial \varepsilon_k} W_{k,k'} \, \delta(\varepsilon_k - \varepsilon_{k'})(\psi_k - \psi_{k'})(\Phi_k - \Phi_{k'}), \tag{14}$$

satisfies the self-adoint and positive definite relations

$$(\Phi, L\psi) = (\psi, L\Phi), \tag{15}$$

$$(\Phi, L\Phi) \geq 0. \tag{16}$$

Thus observed values of the electric and heat currents are expressed as

$$J_i = \sum_k f_k (j_i)_k = (\Phi, j_i) \qquad (i=1,2), \tag{17}$$

where we rewrite $j_1 \equiv j$, $j_2 \equiv q$. Puttng the solution of (12) as

$$\Phi = X_1 \cdot \varphi_1 + X_2 \cdot \varphi_2, \tag{18}$$

we get

$$L\varphi_i = j_i. \tag{19}$$

Thus we can rewrite (16) as

$$J_i = \sum_{j=1}^{2} L_{i,j} \cdot X_j \qquad (i=1,2), \tag{20}$$

confining ourselves to an isotropic or cubic system, where

$$L_{ij} = L_{ji} = (\phi_i, L\phi_j) = (j_i, L^{-1} j_j) = \int_0^\infty (j_i, j_j(t))dt \quad (i,j=1,2), \tag{21}$$

$$j_j(t) = e^{-Lt} j_j . \tag{22}$$

which show Onsager's reciprocity relation.

Based on the relations (15) and (16), the Umeda-Kohler-Sondheimer(UKS) variatiional principle[1] is presented as follows.

[I] $(\psi, L\psi) = \mathrm{Max.}$ on the condition $(\psi, L\psi) = (\psi, X)$. (23)

[II] $2(\psi, X) - (\psi, \psi L\psi) = \mathrm{Max.}$ (24)

[III] $\dfrac{(\psi, X)^2}{(\psi, L\psi)} = \mathrm{Max.}$ (25)

The maximum gives the entropy production, which is equal, if X is an orthogonal component of the electric current, to the electrical conductivity. Changes of entropy with time due to collisions and drift are written as

$$\left(\frac{\partial S}{\partial t}\right)_C = \frac{(\phi, L\phi)}{T}, \tag{26}$$

$$\left(\frac{\partial S}{\partial t}\right)_D = -\frac{(\phi, X)}{T} \tag{27}$$

repectively. The entropy production (25) is intrinsic to the system. Using (18) and (19), we can rewrite (26) and (27) as

$$\left(\frac{\partial S}{\partial t}\right)_C = \sum_i \sum_j (L^{-1})_{ij} J_i J_j \tag{28}$$

$$\left(\frac{\partial S}{\partial t}\right)_D = \sum_i J_i X_i , \tag{29}$$

in terms of the flows and forces. The UKS principle, when reproposed merely with respect to J_i's, is much contracted, and we obtain the thermodynamical variation principle, which was obtained by Onsager based on a probabilistic augument and stated as

$$2\sum_i J_i X_i - \sum_i\sum_j (L^{-1})_{ij} J_i J_j = \mathrm{Max}. \tag{30}$$

with respect to J_i's without reference to Φ as in UKS.

§3.Dynamical or quantum-statistical variational principle

The von-Neumann equation for the system exposed to an electric field $\mathbf{E}(t)$ is expressed as

$$i\hbar \frac{\partial \rho}{\partial t} = [H-\mathbf{P}\cdot\mathbf{E}(t),\rho], \tag{31}$$

in terms of the Hamiltonian H and the polarization operator $\mathbf{P}$ of the system and a time dependent external electric field $\mathbf{E}(t)$. We assume

$$\rho(t)=\rho_c+\rho_1(t), \tag{32}$$

$$\rho_c=K\exp(-\beta H-\xi N) \tag{33}$$

$$\rho_1(t)=\int_0^\beta d\lambda\, \rho_c \exp(\lambda H)\Phi(t)\exp(-\lambda H), \tag{34}$$

which correspond to (5) for the Boltzmann equation. Substituting (31) into (30) with (32) and (33), we get

$$\partial\Phi/\partial t+L\Phi=\mathbf{j}\cdot\mathbf{E}(t), \tag{35}$$

where we have defined L by

$$L\Phi = -i[H,\Phi]/\hbar, \quad j = i[H,P]/\hbar. \tag{36}$$

Assuming for the appliied electric field in analogy with incoming and outgoing waves in the scattering theory[5] as

$$E(t) = E\exp(st) \quad (t<0), \quad \lim_{t\to-\infty} \rho(t) = \rho_C, \tag{37}$$

$$E(t) = E\exp(-st) \quad (t>0), \quad \lim_{t\to\infty} \rho(t) = \rho_C, \tag{38}$$

in terms of an adiabatic parameter s(>0), and also

$$\Phi(t) = \Phi^{(+)}\exp(st) \quad (t<0), \tag{39}$$

$$\Phi(t) = \Phi^{(-)}\exp(-st) \quad (t>0). \tag{40}$$

Substituting (39) and (40) with (37) and (38) into (45), we obtain

$$L_s\Phi^{(+)} = j\cdot E, \tag{41}$$

$$L_{-s}\Phi^{(-)} = j\cdot E, \tag{42}$$

defining a superoperator

$$L_s = L+s, \quad L\Phi = i[H,\Phi]/\hbar. \tag{43}$$

Let us define the inner product

$$(\Phi,\Psi) = (\Psi,\Phi) = \int_0^\beta \mathrm{Tr}\{\Phi\rho_C \exp(\lambda H)\Psi\exp(-\lambda H)d\lambda. \tag{44}$$

Then the superoperator L_s satisfies

$$(\Phi, L_s\Psi) = -(\Psi, L_{-s}\Phi). \tag{45}$$

for any pair of operators Φ and Ψ. The quantum variational principle is presented as follows. Let us make

$$W(\Phi^{(+)},\Phi^{(-)})=(\Phi^{(+)}-\Phi^{(-)},E\cdot j)+(\Phi^{(-)},L_s\Phi^{(+)}) \tag{46}$$

stationary with respect to $\Phi^{(+)}$ and $\Phi^{(-)}$. Then the solutions satisfiy (55) and (56), respectively, and gives the Joule heat

$$W = J_s\cdot E = -J_{-s}\cdot E, \tag{47}$$

to (46), where J_s and J_{-s} are the current at t=0 for the states governed by (41) and (42), respectively. If $\mathbf{E}$ is a unit vector parallel to the μ-axes, the stationary value of

$$\sigma(\Phi_+,\Phi_-)=(\Phi_+-\Phi_-,j_u)+(\Phi_-,L_s\Phi_+), \tag{48}$$

gives the electrical condctivity

$$\sigma=\int_0^\infty dt \int_0^\beta d\lambda\ \mathrm{Tr}\{\rho_c j_u(t-i\hbar\lambda)j_u\}. \tag{49}$$

§4. Reduction of variational principle from the quantum to UKS

Let us write $\Phi^{(+)}$ and its time reversal $\Phi^{(-)}$ as

$$\Phi^{(+)}=\Phi=\Phi'+\Phi'',\quad \Phi^{(-)}=\overline{\Phi}=-\Phi'+\Phi'', \tag{50}$$

where Φ' and Φ'' are odd and even components of Φ with respect to inversion of time. Eliminating Φ'' in (46) into which (50) are substituted, we get

$$W(\Phi')=2(\Phi',j\cdot E)-(\Phi',\Lambda\Phi'), \tag{51}$$

where Λ is defined by

$$(\Phi,\Lambda\Psi)=\sum_m\sum_n \frac{\rho_n-\rho_m}{E_m-E_n}\,\frac{\hbar^2s^2+(E_m-E_n)^2}{\hbar^2 s}(m|\Phi|n)(n|\Psi|m) \tag{52}$$

including a singular term inverse to s and satisfies

$$(\Phi,\Lambda\Psi)=(\Psi,\Lambda\Phi), \tag{53}$$

$$(\Phi,\Lambda\Phi)\geq 0. \tag{54}$$

Thus we get the UKS type principle. Maximizing (65) as to Φ', we get a master equation

$$\Lambda\Phi'=\mathbf{j}\cdot\mathbf{E}. \tag{55}$$

The maximum is the Joule heat generated in the system and the electrical conductivity for a special case. So as to remove such a singular term as in (52), we decompose $\Phi^{(+)}$, $\Phi^{(-)}$ into diagonal and offdiagonal parts in the scheme of diagonalizing the unperturbed Hamiltonian H_0 as

$$\Phi^{(+)}=\Phi_d{}^{(+)}+\Phi_c{}^{(+)}, \qquad \Phi^{(-)}=\Phi_d{}^{(-)}+\Phi_c{}^{(-)}, \tag{56}$$

and then introduce decompositions

$$\Phi_d{}^{(+)}=\Phi_d{}'+\Phi_d{}'', \quad \Phi_d{}^{(-)}=-\Phi_d{}'+\Phi_d{}'', \tag{57}$$

as to time reversal into odd and even components. Contracting (46) in these terms, we get

$$W(\Phi_d{}')=2(\Phi',\mathbf{j}\cdot\mathbf{E})-(\Phi',\mathrm{L}\Phi_d{}'), \tag{58}$$

where L is defined for any diagonal operator D by

$$\mathrm{L}D=\frac{2\pi}{\hbar}\sum_a|a\rangle\langle a|\ \sum_b|\langle a|T(E_a+i\varepsilon)|b\rangle|^2\,\delta(E_a-E_b)(D_a-D_b), \tag{59}$$

and satisfies

$$(\Phi',\mathrm{L}\Psi')=(\Psi',\mathrm{L}\Phi'), \tag{60}$$

$$(\Phi',\mathrm{L}\Phi')\geq 0. \tag{61}$$

Thus we get the variational principle maximizing (58), which is similar to but more complex than the UKS case.

If we redefine the inner product as

$$(\Phi,\Psi)=(\Psi,\Phi)=\int_0^\infty \mathrm{Tr}\{\Phi\rho_0 \exp(\lambda H_0)\Psi \exp(-\lambda H_0)d\lambda, \tag{62}$$

in terms of the thermal weight

$$\rho_0 = K_0 \exp[-\beta(H_0-\mu N)] \tag{63}$$

for the unperturbed Hamiltonian H_0, we can rewrite (58)

$$W(\Phi_d')=2(\Phi_d',\mathbf{j}\cdot\mathbf{E})-(\Phi_d',\mathfrak{L}\Phi_d'), \tag{64}$$

which is the most fundamental, rectified form of the UKS principle. Maximizing (64) with Φ_d' gives a sort of master equation

$$\mathfrak{L}\Phi_d'=\mathbf{j}\cdot\mathbf{E}, \tag{65}$$

which reduces to the Boltzmann equation for conductiion electrons with the collision term written in terms of the T-matrix.

§5.Conclusion

The quantum variational principle concerning the von Neumann equation in the system of conduction electrons exposed to an applied electric field presented as a stationarity problem was transformed into the UKS maximum principle by means of information contractions. The maximization demands that diagonal elements of the odd component of density matrix or the distribution function of electron with respect to time reversal should satisfy the rectified Boltzmann equation with the collision term given in terms of the T-matrix. Further the UKS principle is reduced to the thermodynamical variation principle first due to Onsager.[2]

That is to say, through successive contractions the quantum, kinetic and thermodynacal variational principles, which governs the three typical hierarchial stages of the thermodynamical system are converted from one to another, exhibiting that irreversibility comes about through contractions.

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