Kinetic Equations

III. Difficulties in the Derivation of Kinetic Equations

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Die von verschiedenen Autoren bei der Ableitung von kinetischen Gleichungen festgestellten Schwierigkeiten in Form von Säkularitäten und Divergenzen können durch geeignete Partialsummationen überwunden werden. Damit ist die Anwendung der Störungstheorie in der klassischen Statistik gerechtfertigt. Aus dem Auftreten von Divergenzen wurden in der Literatur verschiedene physikalische Schlußfolgerungen (logarithmische Dichteabhängigkeit der Transportkoeffizienten, Ungültigkeit der Bogoljubovschen Synchronisationsannahme) gezogen. Das ist nicht gerechtfertigt, da sich die Schwierigkeiten streng überwinden lassen.

1. Introduction

Using perturbation-theoretical methods in different fields of physics difficulties will appear owing to divergent terms of the perturbation expansion. A detailed discussion of these difficulties shows them to be due to the occurrence of secular terms. The investigation in this paper concerns the perturbation expansion of the classical **S**-operator. These difficulties may be overcome by adequate partial summations. In principle, this is a method to avoid the non-physical divergences also in other fields of physics.

Already in celestial mechanics [1, 2] the perturbation theory was applied by using the exactly soluble two-body system sun-planet as a zeroth approximation for a perturbation expansion in terms of the masses of the other disturbing planets. In the representation of the orbital elements by perturbation series there occur temporal terms of the n-th order, i. e. terms growing proportional t^n. However, STERNE [2] emphasized that from these secularities no conclusions can be drawn as to the long-time behaviour of the sun-system and the stability of the planet motions. In celestial mechanics the method of slowly variable parameters has been used since Lagrange. In it the motion of planets is described by weakly time-dependent orbital elements. Here two essential points of view are already indicated:

1. Summarizing the secular terms in terms of time-functions and
2. approximating the explicit time-dependence of the desired quantities by an implicit time-dependence with the aid of a functional dependence on variable parameters of the undisturbed solution.

The difficulties of celestial mechanics are analogous to those involved in the theory of nonlinear vibrations [3]. For instance the equation

$$\ddot{x} + \omega^2 x + \varepsilon x^3 = 0 \qquad (1)$$

has only restricted solutions $x(t)$, which can be represented by the series

$$x(t) = A\cos(\omega t + \varphi) + \varepsilon\left[\frac{A^3}{32\,\omega^2}\cos 3(\omega t + \varphi) - \frac{3\,A^3}{8\,\omega}\,t\sin(\omega t + \varphi)\right] + \dots \qquad (2)$$

with the aid of a perturbation expansion in the small parameter $\varepsilon > 0$. It is no use trying to find the asymptotic behaviour of the solutions of (1) for $t \to \infty$ from Eq. (2). In the theory of nonlinear vibrations the difficulties of secular terms can also be overcome either by summing up the terms of (2)

$$x = A\,\mathrm{cn}(\sqrt{E}\,a\,t, K)\,,$$
$$a = \frac{\omega^2}{E} + \varepsilon\frac{1}{2\,\omega^2} + O(\varepsilon^2)\,, \quad K = \varepsilon\frac{1}{2\,\omega^2} + O(\varepsilon^2) \qquad (3)$$

(E = energy, cn = cosinus amplitudinis) or by assuming the amplitude A and the phase-factor φ of the undisturbed solution to vary slowly in time.

[1] D. BROUWER and G. M. CLEMENS, Methods of Celestial Mechanics, Academic Press, New York, London 1961.

[2] T. E. STERNE, An Introduction to Celestial Mechanics, Interscience Publ., Inc., New York 1960.

[3] N. N. BOGOLJUBOW and J. A. MITROPOLSKI, Asymptotische Methoden in der Theorie nichtlinearer Schwingungen, Akademie-Verlag, Berlin 1965.

In quantum mechanics [4, 5], secularities and divergences also appear. So WIGNER [4] started from the free electron, treated the Coulomb potential $-\varepsilon\, e^2/r$ as perturbation, and tried to gain by this the lowest energy-level of the hydrogen atom with $\varepsilon = 1$. However, it turned out that the expansion led to divergent expressions in Schrödinger's perturbation series. As HAUSMANN [5] showed these divergences do not appear when the electron is treated as bound in a large, but finite volume V. The terms of Schrödinger's perturbation series become secular, i. e. the n-th term is of the order V^n. Although the series is badly convergent, the desired energy can be determined as a function $E(\varepsilon)$ of the perturbation parameter ε as in Fig. 1 a. However, in the limit $V \to \infty$ for $\varepsilon \leqq 0$ the lowest energy level is always $E = 0$, so that the function $E(\varepsilon)$ becomes non-analytical at $\varepsilon = 0$ (Fig. 1 b).

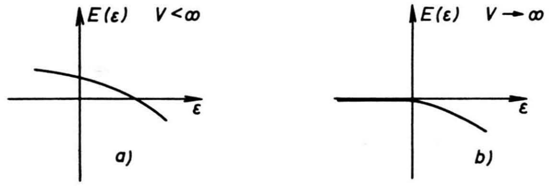


Fig. 1. Analytic and nonanalytic form of the function $E(\varepsilon)$ for finite and infinite volume.

HAUSMANN avoids these difficulties by summing up the secular terms in

$$E = \Theta(\varepsilon)\, E(\varepsilon) = \Theta(0)\, E(0) + \frac{\varepsilon}{1!}\left(\Theta(0)\, E'(0) + \delta(0)\, E(0)\right) + \dots \tag{4}$$

preceding the limit $V \to \infty$ and he gets

$$E = \Theta(\varepsilon)\left[E(0) + \frac{\varepsilon}{1!}\, E'(0) + \dots\right]. \tag{5}$$

In this case no divergences appear at the limit $V \to \infty$.

Secularities of this kind also cause the difficulties in quantum field-theory [5a], where nonphysical divergences appear because of an infinite four-dimensional normalization-volume. The method of renormalization used there can be regarded as a special kind of partial summation.

The appearance of secular terms in a perturbation expansion is not restricted to a special system. It is a general phenomenon which can be deduced only in some special cases from a nonanalytical behaviour of the solutions relative to the perturbation parameter ε at $\varepsilon = 0$. At the corresponding limits the divergences follow from the secularities. Their occurrence cannot be used for physical conclusions. These difficulties may be overcome by the general method of partial summation performing a "modified Taylor expansion"

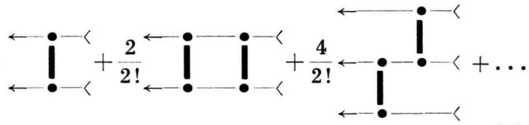
$$f(\varepsilon, t) = \sum_{\nu=0}^{\infty} \varepsilon^\nu f^{(\nu)}(\varepsilon, t)\,; \quad \left|f^{(\nu)}(\varepsilon, t)\right| \leqq M < \infty \tag{6}$$

analogous to (5). Of course only such partial summations lead to reasonable results in which the partial sums, i. e. $f^{(\nu)}$ in (6), are nonsecular. This knowledge will be used in the following parts of the paper for a solution of the difficulties in classical statistics involved in the derivation of kinetic equations.

2. Secularities and Divergences in the Perturbation Expansion of Classical Statistics

In classical statistics divergences in the derivation of kinetic equations and the calculation of transport coefficients [6–10] have already been noticed for a long time. Particularly DORFMAN and COHEN [11] and GOLDBERG and SANDRI [12] showed the divergences to be caused at the limit $\tau \to \infty$ by secular terms of the perturbation expansion (I.3.2, 3.3, 3.5) for the **S**-operator and the linked-cluster sum resp. dealt with in the preceding paper [13]

$$\mathbf{S}_\tau = \mathbf{1} + (-i)\int_0^\tau \mathrm{d}t_1\, \tilde{\mathbf{L}}^{\mathrm{v}}{}_{t_1} + (-i)^2 \int_0^\tau \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2\, \tilde{\mathbf{L}}^{\mathrm{v}}{}_{t_1} \tilde{\mathbf{L}}^{\mathrm{v}}{}_{t_2} + \dots = N_{\eta,\, \delta/\delta\eta} \exp\{\mathbf{\Gamma}_\tau\}\,,$$

$\mathbf{\Gamma}_\tau =$  (7)

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5 K. HAUSMANN, Ann. Phys. Leipzig **17**, 368 [1966].

5a G. HEBER and G. WEBER, Grundlagen der modernen Quantenphysik, II, Verlag Teubner, Leipzig 1963. — S. O. AKS, Fortschr. Phys. **15**, 661 [1967].

6 J. V. SENGERS, Phys. Rev. Letters **15**, 515 [1965].

7 J. V. SENGERS, Phys. Fluids **9**, 1333, 1685 [1966].

8 M. S. GREEN, Proc. Intern. Seminar on Transport Properties of Gases, Brown University Press, Providence, Rhode Islands 1964.

9 S. FUJITA, Phys. Letters **A 24**, 235 [1967].

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11 J. R. DORFMAN and E. G. D. COHEN, J. Math. Phys. **8**, 282 [1967].

12 P. GOLDBERG and G. SANDRI, Phys. Rev. **154**, 188, 199 [1967].

13 U. BAHR, P. QUAAS, and K. VOSS, Z. Naturforsch. **23 a**, 633 [1968]; hereafter referred to as I.

Here the n-th term of the perturbation series for $\mathbf{S}_\tau$ again contains a secularity of the n-th order as caused by the n time-integrations which occur there. For an investigation of secularities SANDRI's procedure is particularly convenient, because it does not require a transition from the phase-space-description of statistical mechanics to the kinetic theory of single dynamical collisions. This transition can only be treated exactly in the so-called pair-collision term, because only the two-body problem is exactly soluble. As a kinetic model the collisional events used by DORFMAN and COHEN [11], SENGERS [7], HAINES and DORFMAN, and ERNST [14] are only an approximation for the exact temporal behaviour of the phase-space distribution.

In order to overcome the difficulties in the derivation of kinetic equations and in the calculation of transport coefficients in (1), partial summations may be performed as explained in the introduction. This will be described in more detail in part 3 of this paper. The divergence of generalized Boltzmann terms (secularity of the quadrupole collision term) which was found by DORFMAN and COHEN [11] in spite of partial summation, are presumably caused by the fact that the kinetic considerations of dynamic collisions of particles undertaken in order to evaluate the collision-integrals are merely approximate ones. Hence the term

$$\begin{aligned} &n^2 \int \mathrm{d}x_2\, U_2(x_1, x_2; t)\, D_1(x_1; t)\, D_1(x_2; t) \\ &= n^2 \int \mathrm{d}x_2 [D_2(x_1, x_2; t) - D_1(x_1; t)\, D_1(x_2; t)] \end{aligned} \tag{2}$$

of formula (2.9) in [11] is claimed to be secular. However, the integral with the distribution functions $D_2(x_1, x_2; t)$ and $D_1(x_1; t)\, D_1(x_2; t)$ is limited for all times, because the functions D_2 and D_1 satisfy the corresponding Liouville equations which follow from formula (2.1) in [11] (vid. part 3).

The divergences found by SENGERS [6, 7] in the density expansion of transport coefficients also seem to be caused by the considerations of dynamical collisions for evaluating the collision-integrals, which is inappropriate for the statistical description. However they may be possibly caused also by the special model used (hard disks). In every case physical conclusions cannot be drawn from the occurrence of secular terms.

Thus it was deduced, that BOGOLJUBOV's functional assumption [15] is not allowed [11] and that the transport coefficients have a logarithmic density dependence [6, 7, 16] at $\mathcal{N} = 0$, which causes the invalidity of a density expansion. But according to FUJITA [9] the investigations of KAWASAKI and OPPENHEIM contain a mistake, so that there is no logarithmic singularity of the transport coefficients at $\mathcal{N} = 0$. Similar facts are suggested by the experiments [17] which show a linear density-dependence of the transport coefficients (Fig. 2).

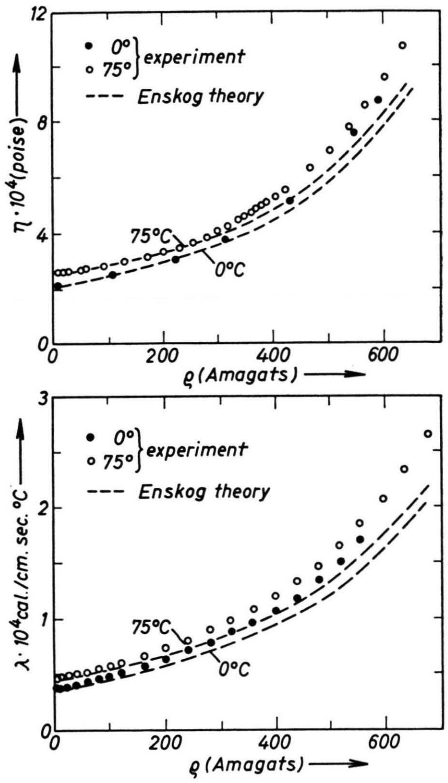

Fig. 2. Viscosity η and thermal conductivity λ of Argon as function of density $\varrho = m\,\mathcal{N}$ [18].

Moreover, the results of the theory by CHAPMAN and ENSKOG [19] for low densities agree very well with the experimental data of Fig. 2. Hence discussions

[14] L. K. HAINES, J. R. DORFMAN, and M. H. ERNST, Phys. Rev. **144**, 207 [1966].

[15] N. N. BOGOLJUBOW, J. Phys. USSR **10**, 256, 265 [1946]; english transl. in "Studies in Statistical Mechanics. I", Amsterdam 1961.

[16] K. KAWASAKI and I. OPPENHEIM, Phys. Rev. **139 A**, 1763 [1965].

[17] N. J. TRAPPENIERS, A. BOTZEN, C. A. TEN SELDAM, H. R. VAN DEN BERG, and J. VAN OSTEN, Physica **31**, 1681 [1966].

[18] S. A. RICE and P. GRAY, The Statistical Mechanics of Simple Liquids, Interscience Publ., Inc., New York 1965 (see Fig. 6.4.2 and 6.4.3).

[19] See p. e. J. U. HIRSCHFELDER, C. F. CURTISS, and R. BIRD, Molecular Theory of Gases and Liquids, John Wiley & Sons, Inc., New York, London 1954, Chapters 7/8.

of a logarithmic singularity relative to the density cannot be exact. BOGOLJUBOV's functional assumption is further justified by the fact that phenomenological closed equations are good approximations also in dense systems. Therefore it will be shown in part 3 that the partial summations performed in a preceding paper [20] are nonsecular, so that the program to derive kinetic equations given there continues to be valid.

However, in the derivation of kinetic equations there are divergences of another kind. They are caused by the molecular chaos in which higher distribution functions are replaced by products of one-particle distribution functions. The integrand of collision-integrals then takes the form $\boldsymbol{l}_{12} f_{12} \rightarrow \boldsymbol{l}_{12} f_1 f_2$, and with strongly singular forces the integrand becomes infinite at $\mathfrak{r}_1 = \mathfrak{r}_2$. This problem can be solved either by a cut-off of the lower integration limit $r \equiv |\mathfrak{r}_1 - \mathfrak{r}_2|$ or by introducing the radial distribution function of equilibrium [21]. However, these questions only refer to the numerical evaluation of the integrals.

3. Partial Summation in Classical Statistics

All physical quantities of classical statistics can be obtained from the reduced distribution functions with the linked-cluster sum (I.3.7, 3.8). With the dimensional analysis (II.2.2) the linked graphs may be represented by

$$\boldsymbol{\Gamma}_\tau = N \sum_{\alpha}^{1\ldots\infty} \sum_{\beta}^{2\ldots\alpha+1} \sum_{\gamma}^{0\ldots\alpha} \left(\frac{u_0}{k\,T}\right)^{\alpha} (\mathcal{N} r_0^3)^{\beta-1} \left(\frac{\tau}{\tau_0}\right)^{\gamma} \boldsymbol{\Gamma}_\tau'^{(\alpha,\beta,\gamma)} \tag{1}$$

where the dimensionless graphs $\boldsymbol{\Gamma}_\tau'^{(\alpha,\beta,\gamma)}$ are of the order one. Here $\mathcal{N}$ is the mean particle density, r_0 the effective range of the potential $u(r)$, u_0 its effective strength and τ_0 the characteristic interaction time-interval of the system. GOLDBERG and SANDRI [12] already investigated what kinds of secularities marked by γ appear in the terms.

When we perform the partial summation of row-graphs in II, part 2 by summing over all α and γ we get (II.2.8)

$$\begin{aligned}\boldsymbol{\Gamma}_\tau &= \sum_{\beta}^{2\ldots\infty} (\mathcal{N} r_0^3)^{\beta-1} \boldsymbol{\Gamma}^{(\beta)} \\ &= \sum_{n}^{2\ldots\infty} \int \frac{\mathrm{d}1\ldots\mathrm{d}n}{n!} \eta_1 \ldots \eta_n \, \boldsymbol{k}_{1\ldots n,\tau} \frac{\delta}{\delta\eta_1} \cdots \frac{\delta}{\delta\eta_n}.\end{aligned} \tag{2}$$

The operators $\boldsymbol{k}_{12\ldots n,\tau}$ lead to the generalized Boltzmann terms. Since according to I, part 5, every functional derivation $\delta/\delta\eta_\nu$ may be replaced by a one-particle distribution function n_{ν,t_0} the temporal behaviour of the quantities

$$k^{(n)} \equiv \boldsymbol{k}_{12\ldots n,\tau}\, n_{1,t_0} \ldots n_{n,t_0} \tag{3}$$

has to be investigated in the limit $\tau \rightarrow \infty$. Analogous to the calculations of II, part 3, it can be shown that the $\boldsymbol{k}_{1\ldots n,\tau}$ are constructed as finite sums of finite products like

$$\begin{aligned}k_{1\ldots s} \equiv \exp\{i\tau(\boldsymbol{l}_1 + \ldots + \boldsymbol{l}_s)\} \\ \cdot \exp\{-i\tau\,\boldsymbol{l}_{1\ldots s}\}\, n_{1,t_0} \ldots n_{s,t_0}.\end{aligned} \tag{4}$$

If the expressions in (4) are finite, non-secular terms, the same is valid for their sums and products, i. e. for the $k^{(n)}$ from (2). The operator $\exp\{i\tau(\boldsymbol{l}_1 + \ldots + \boldsymbol{l}_s)\}$ is a simple displacement-operator because of $\boldsymbol{l}_n \equiv -i(\mathfrak{p}_n/m)(\partial/\partial\mathfrak{r}_n)$, which only causes a transformation of variables in the function

$$g_{1\ldots s,\tau} \equiv \exp\{-i\tau\,\boldsymbol{l}_{1\ldots s}\}\, n_{1,t_0} \ldots n_{s,t_0}. \tag{5}$$

In this, however, the function remains restricted so that this operator does not cause any secularities or divergences. The same is valid for the evolution operator $\exp\{-i\tau\,\boldsymbol{l}_{1\ldots s}\}$ which because of Liouville's theorem does not change the density of the phase-space distribution along a trajectory and therefore cannot lead to secularities.

We assume for all phase-space points $\{1\ldots s\}$ the inequality

$$g_{1\ldots s,0} = n_{1,t_0} \ldots n_{s,t_0} \leqq M < \infty \tag{6}$$

for the non-negative phase-space distribution $g_{1\ldots s,0}$ to be valid. And we assume further that the expression (5) is secular and leads to divergences at $\tau \rightarrow \infty$. Then for $\tau_1 > \tau_0$ with a certain $\tau_0 = \tau_0(M)$ the inequality (6) would be violated at least for one particle-tupel $\{1' \ldots s'\}$ so that in this case

$$g_{1'\ldots s',\tau_1} > M \tag{7}$$

is valid. However, this phase-space point $\{1' \ldots s', \tau_1\}$ according to the Liouville equation has developed from an initial state $\{1' \ldots s', 0\}$ for which Eq. (6) is generally valid. Then the phase-space density $g_{1'\ldots s',\tau}$ must have changed for this system-state. But this is a contradiction to the Liouville theorem.

[20] U. BAHR, P. QUAAS, and K. VOSS, Z. Naturforsch. **23 a**, 638 [1968]; herafter referred to as II.

[21] W. POMPE, Ann. Phys. Leipzig **20**, 326 [1968].

The conclusion to be drawn from these considerations is that the operators in $k_{1 \ldots s}$ from (4) do not produce secularities and that accordingly the collision-terms $\boldsymbol{k}_{1 \ldots n, \tau}$ from (2) do not lead to divergent expressions for $\tau \to \infty$ either. Therefore the partial summations performed in II satisfy the condition that the expressions thus obtained must be nonsecular. On this basis it is possible to overcome the difficulties in the derivation of kinetic equations and also to get nondivergent expressions for transport coefficients.

Bedingungen für das Auftreten von Ferromagnetismus in realen Gasen

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We consider a gas consisting of particles (molecules) with spin 1/2 and vanishing electrical charge. We assume the existence of spin-dependent two-body-potentials of interaction between these particles. Our aim is to establish conditions for the appearance of ferromagnetism in such systems.

Calculations are done for a modified Lennard-Jones-type two-body-potential. The sum-over states is expanded with respect to cluster-integrals which are approximately calculated up to the fourth order. Cluster of higher order seem to give only uniportant contributions to the conditions mentioned. The conditions for ferrmagnetism are fulfilled, if the density of the gas is higher and the temperature lower than some critical values. The dependence of magnetization on temperature is given and some considerations regarding the equation of state are made. It is supposed that liquids of the same composition and interaction will also show ferromagnetism. The results seem to hold also for potentials which are not of the Lennard-Jones-type, but have the appropriate spin-dependence.

I. Einleitung

Der Ausgangspunkt für unsere Überlegungen war der experimentelle Befund, daß Ferromagnetismus in Festkörpern ohne kristalline Fernordnung auftreten kann [1]. Das führt natürlich zu der Frage, ob auch in Flüssigkeiten eine ferromagnetische Ordnung möglich ist. Es besteht nämlich kein Unterschied zwischen der Art der Anordnung der Atome (bzw. Moleküle) in einem amorphen Festkörper und in einer Flüssigkeit. Für alle bekannten Materialien ist jedoch die Wechselwirkung, die die magnetische Ordnung erzeugt, kleiner als die Wechselwirkung, die die kristalline Ordnung hervorruft. Dieser Umstand führt zu der Regel:

$$T_{\text{Curie}} < T_{\text{Schmelz}}, \tag{1}$$

die, soweit wir wissen, für alle kristallinen Substanzen gilt. Es ist nun interessant zu untersuchen, welche Art von Wechselwirkung das Auftreten der entgegengesetzten Relation:

$$T_{\text{Curie}} > T_{\text{Schmelz}} \tag{2}$$

gestattet.

Im folgenden geben wir uns solch eine hypothetische Art von Wechselwirkung vor.

Die heutigen uns bekannten mikroskopischen Flüssigkeitstheorien basieren darauf, daß man die Theorien der Festkörper bzw. Gase (die beide selbständige ausgearbeitete Theorien darstellen) im Sinne der Beschreibung einer Flüssigkeit abändert. Diese Näherungen sind unbefriedigend, da sie die gleichzeitige Beschreibung aller Spezifika einer Flüssigkeit nicht gestatten. Weil man schwer überschauen kann, ob ein evtl. auftretender ferromagnetischer Effekt von der Verwandtschaft der Theorie mit den entsprechenden Festkörper- bzw. Gastheorien herrührt oder nicht, haben wir die Untersuchung von Flüssigkeiten vorerst aufgegeben und uns einem Gasmodell zugewandt. Unsere Begründung hierfür ist folgende: Wenn in einem Gas eine ferromagnetische Ordnung möglich ist, dann wird sie sicherlich auch in der zugehörigen Flüssigkeit auftreten können.

[1] S. MADER u. A. S. NOWICK, Appl. Phys. Lett. **7**, 57 [1965]. — B. ELSCHNER u. H. GÄRTNER, Z. Angew. Phys. **20**, 342 [1966].