

SEMIPHENOMENOLOGICAL KINETIC EQUATION FOR
A SMALL SYSTEM IN A THERMOSTAT WITH A
VARIABLE TEMPERATURE

I. P. Pavlotskii

UDC 532.72

A kinetic equation is obtained for a small system in a thermostat with a variable temperature, the change of temperature being taken into account by a phenomenological nonpotential force of the friction type.

Suppose that the return temperature of a thermostat in energy units $\beta(t)$ changes sufficiently slowly with time t so that the thermostat passes through a sequence of equilibrium states. In this case the single-particle distribution function of the thermostat, consisting of identical particles of mass m , has the form

$$F_1 = \left[\frac{\beta(t)}{2\pi m} \right]^{3/2} \exp \left\{ \frac{-\beta(t) p^2}{2m} \right\},$$

where p is the momentum of the particle. We will call the system small if its effect on the thermostat can be neglected.

Let the small system be in equilibrium with the thermostat. We raise the question of the form of the kinetic equation for such a system taking into account the change of $\beta(t)$ with time. As will be shown below, this effect can be described by introducing an additional nonpotential force Q of the friction type.

1. As a simple example we will consider a gas of identical molecules the bulk of which forms a thermostat with a variable temperature and a small part of which is nonequilibrium, whereby the "internal" interaction in the small system can be neglected. Then the problem reduces to constructing a kinetic equation describing the evolution of the distribution function f of one nonequilibrium particle in the thermostat.

We denote the coordinate and momentum of the nonequilibrium particle by q_1 and p_1 and the coordinates and momenta of the particles of the thermostat by $q_2, p_2, \dots, q_N, p_N$. Let L be the Lagrangian of the complete system "particle and thermostat" and $\alpha Q(p_k, t)$ be forces not having a potential (non-Lagrangian), by means of a suitable selection of which the change of $\beta(t)$ with time will be taken into account. The Lagrangian equations of a system with nonpotential forces have the form

$$\frac{d}{dt} \frac{\partial L}{\partial (dq_k/dt)} - \frac{\partial L}{\partial q_k} = \alpha Q_k(p_k, t); \quad k=1, 2, \dots, 3N. \quad (1)$$

As was shown in [1], in this case the following equation holds

$$\begin{aligned} \frac{\partial f}{\partial t} + \sum_{(1 \leq s \leq 3)} \left[\frac{p_{1s}}{m} \frac{\partial f}{\partial q_{1s}} + \alpha \frac{\partial}{\partial p_{1s}} f Q(p_1, t) \right] \\ = \frac{1}{V} I_B(f, F_1) - \frac{\alpha}{V} \int_{(R)} d^3 q' d^3 p' \left[Q(p_1) f(X_1) \right. \\ \left. \times \frac{\partial}{\partial p_1} F_1(X_2) + Q(p') F_1(X_2) \frac{\partial}{\partial p'} f(X_1) \right]. \quad (2) \end{aligned}$$

Institute of Applied Mathematics, Academy of Sciences of the USSR, Moscow. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 23, No. 6, pp. 1126-1129, December, 1972. Original article submitted June 20, 1972.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

Here V is the specific volume; R is the region of collision in single-particle phase space; $X_1(q_1, q_1', p_1, p', t)$ and $X_2(q_1, q', p_1, p', t)$ are the coordinates and momenta which would be present at time t for particles participating in the collision if these particles were isolated from all others; (q', p') is the coordinate and momentum of the particle of the thermostat participating in the collision. The collision integral in a Boltzmann form is denoted by I_B . We note that by virtue of the assumption of the absence of an effect on the small system on the thermostat the integrand in I_B has a special form:

$$\frac{p_{10} - p'_0}{m} (f'' - f') F_1,$$

where p_{10} and p'_0 are the momenta of the nonequilibrium particle and particle of the thermostat respectively before their collision, and f'' and f' are the function f after and before collision.

Obviously when $\alpha = 0$ Eq. (2) changes to the usual Boltzmann equation; the term proportional to α takes into account the effect of Q in the lower approximation with respect to the parameter α ; the term proportional to the product of the small parameters (α/V) takes into account the lower correlation between the effect of $Q(p)$ and mechanism of collisions.

The equations which should be satisfied by the single-particle distribution function of the thermostat is a particular case of (2). Therefore, substituting F_1 into (2), we obtain the relation determining $Q(p, t)$:

$$\frac{\partial F_1}{\partial t} + \alpha \sum_{(1 \leq s \leq 3)} \frac{\partial}{\partial p_s} (F_1 Q) = 0. \quad (3)$$

As is easy to be convinced by direct substitution, the particular solution of (3) relative to the unknown Q is

$$\alpha Q = -\frac{1}{2} \frac{d \ln \beta(t)}{dt} p. \quad (4)$$

The general solution differs from (4) by an arbitrary additive function $C(t)$. From the requirement $Q = 0$ for $\beta = \text{const}$ we obtain $C = 0$. Thus (4) is a phenomenological force of the friction type which provides heating or cooling of the system. This force is analogous in its content to "systematic friction," which, as Chandrasekhar [2, 3] showed, is experienced by Brownian particles interacting with a thermostat. Since force Q should act equally on all particles of the system, by substituting (4) into (2) and limiting ourselves to terms that are linear with respect to small parameters we obtain the kinetic equation being sought in the form

$$\begin{aligned} \frac{\partial f}{\partial t} + \sum_{(1 \leq s \leq 3)} p_{1s} \left(\frac{1}{m} \frac{\partial f}{\partial q_{1s}} - \frac{1}{2} \frac{d \ln \beta}{dt} \frac{\partial f}{\partial p_{1s}} \right) \\ - \frac{3}{2} \frac{d \ln \beta}{dt} f = \frac{1}{V} I_B(f, F_1). \end{aligned} \quad (5)$$

2. We will make several comments on the equation (5) thus obtained.

It is clear $f = F_1$ is the solution not only of Eq. (5) but also of the more general Eq. (2), which is an obvious consequence of the very method of selecting Q . However, this — one of the particular solutions — is an analog of the equilibrium solution of the Boltzmann equation.

The phenomenological force Q introduced exhibits a particularly formal character. It seems likely to us that in a number of cases it can be interpreted as a time-wise smoothed nonconservative effect on a system, for example, in the mechanism of heating of a gas by radiation. Probably such an interpretation can prove to be admissible also for a gas being heated (cooled) through the walls of a vessel, despite the fact that the kinetic equation is derived at the thermodynamic limit. However, it would not be desirable here to go deeper into this quite difficult matter for an accurate investigation.

The examination of a small system differing in its nature from a thermostat and consideration of the internal interaction in the small system can be conducted without any difficulties by the scheme indicated above if we limit ourselves to lower approximations with respect to small parameters. The form of the equation in this case changes of course.

3. We will establish also the law of the time-wise change of the entropy of the system with a variable temperature. Let $\rho(p_1, q_1, \dots, p_N, q_N, t)$ be the distribution function of the complete system. Then its entropy S is expressed by the formula

$$S = - \int d^3 p_1 \dots d^3 q_N \cdot \rho \ln \rho.$$

whence

$$\frac{dS}{dt} = - \int d^3p_1 \dots d^3q_N (1 + \ln \rho) \frac{d\rho}{dt}. \quad (6)$$

As was shown in [4], for systems obeying dynamic equations (1):

$$\frac{d\rho}{dt} = - \rho \sum_{(1 \leq k \leq 3N)} \frac{\partial Q_k}{\partial p_k},$$

i. e. , in the case being considered

$$\frac{d\rho}{dt} = \frac{3N}{2} \rho \frac{d \ln \beta(t)}{dt}. \quad (7)$$

Substituting (7) into (6), we obtain

$$\begin{aligned} \frac{dS}{dt} &= - \frac{3N}{2} \int d^3p_1 \dots d^3q_N \rho (1 + \ln \rho) \\ &\times \frac{d \ln \beta(t)}{dt} = \frac{3N}{2} \frac{d \ln \beta(t)}{dt} (S-1). \end{aligned} \quad (8)$$

We took into account in (8) the normalization condition

$$\int \rho d^3p_1 \dots d^3q_N = 1.$$

Integrating (8), we obtain finally

$$S(t) = 1 + (S(0) - 1) \left[\frac{\beta(t)}{\beta(0)} \right]^{3N/2}. \quad (9)$$

Thus entropy increases with an increase of temperature and decreases if the temperature decreases.

We can also consider the entropy of the small system

$$h = - \int d^3p_1 d^3q_1 f \ln f.$$

Arguments analogous to those just given (but with the use of Eq. (5) for calculating df/dt) lead to the expression

$$\frac{dh}{dt} = J + \frac{3}{2} \frac{d \ln \beta(t)}{dt} (h-1),$$

where J is a term related with the collision integral in the Boltzmann form. The well-known analysis of this shows [5] that $J \geq 0$. Since $h > 1$, hence it is clear than the entropy of the small system increases when $\beta_t^{-1} > 0$, i. e. , during heating of the thermostat. With a decrease of the temperature of the thermostat the sign of the derivative h with respect to time can be, generally speaking, any.

LITERATURE CITED

1. I. P. Pavlotskii, Dokl. Akad. Nauk SSSR, 190, No. 6 (1970).
2. S. Chandrasekhar, Astrophys. Journ., 97, 255 (1943).
3. S. Chandrasekhar, Rev. Mod. Phys., 15, 1 (1943).
4. I. P. Pavlotskii, Dokl. Akad. Nauk SSSR, 182, No. 4 (1968).
5. G. Uhlenbeck and J. Ford, Studies in Statistical Mechanics [Russian translation], Mir, Moscow (1965).