precisely to the fact that $f$ is *different* from the Maxwellian equilibrium distribution.

Similarly, one can write down the flux of other molecular quantities. For example, consider a monatomic gas at rest so that $\boldsymbol{u} = 0$. The entire energy of a molecule is then its kinetic energy $\frac{1}{2}mv^2$, and the heat flux (or energy flux) $\mathcal{Q}_z$ in the $z$ direction is by (13·1·13) simply

$$\mathcal{Q}_z = n\langle v_z(\tfrac{1}{2}mv^2)\rangle = \tfrac{1}{2}nm\langle v_z v^2\rangle \qquad (13\cdot1\cdot20)$$

## 13 · 2 *Boltzmann equation in the absence of collisions*

In order to find the distribution function $f(\boldsymbol{r},\boldsymbol{v},t)$, we should like to know what relations this function must satisfy. Let us assume that each molecule of mass $m$ is subject to an external force $\boldsymbol{F}(\boldsymbol{r},t)$ which may be due to gravity or electric fields. (For simplicity we assume that $\boldsymbol{F}$ does *not* depend on the velocity $\boldsymbol{v}$ of the molecule. We thus exclude magnetic forces from the present discussion.) We begin by considering the particularly simple situation when interactions between molecules (i.e., collisions) can be completely neglected. What statements can one make about $f(\boldsymbol{r},\boldsymbol{v},t)$ under these circumstances?

Consider the molecules which at time $t$ have positions and velocities in the range $d^3\boldsymbol{r}\,d^3\boldsymbol{v}$ near $\boldsymbol{r}$ and $\boldsymbol{v}$, respectively. At an infinitesimally later time $t' = t + dt$ these molecules will, as a result of their motion under the influence of the force $\boldsymbol{F}$, have positions and velocities in the range $d^3\boldsymbol{r}'\,d^3\boldsymbol{v}'$ near $\boldsymbol{r}'$ and $\boldsymbol{v}'$, respectively. Here

$$\boldsymbol{r}' = \boldsymbol{r} + \dot{\boldsymbol{r}}\,dt = \boldsymbol{r} + \boldsymbol{v}\,dt \qquad (13\cdot2\cdot1)$$

and

$$\boldsymbol{v}' = \boldsymbol{v} + \dot{\boldsymbol{v}}\,dt = \boldsymbol{v} + \frac{1}{m}\boldsymbol{F}\,dt \qquad (13\cdot2\cdot2)$$

The situation is illustrated schematically in Fig. 13·2·1. In the absence of collisions this is all that happens; i.e., all molecules in the range $d^3\boldsymbol{r}\,d^3\boldsymbol{v}$ near $\boldsymbol{r}$

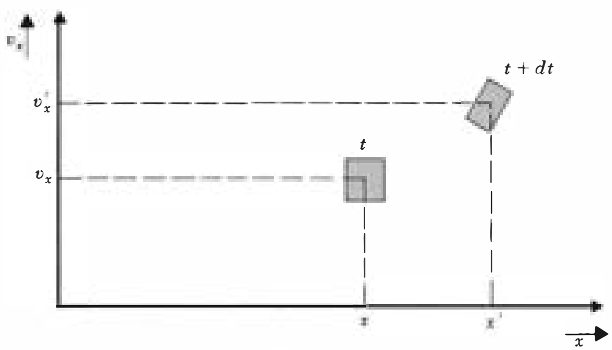


***Fig. 13·2·1*** ***Figure illustrating the motion of a particle in one dimension in a two-dimensional phase space specified by the particle position $x$ and its velocity $v_x$.***

and $\boldsymbol{v}$ will, after the time interval $dt$, be found in the new range $d^3\boldsymbol{r}'\, d^3\boldsymbol{v}'$ near $\boldsymbol{r}'$ and $\boldsymbol{v}'$. In symbols,

$$f(\boldsymbol{r}',\boldsymbol{v}',t')\, d^3\boldsymbol{r}'\, d^3\boldsymbol{v}' = f(\boldsymbol{r},\boldsymbol{v},t)\, d^3\boldsymbol{r}\, d^3\boldsymbol{v} \tag{13·2·3}$$

***Remark*** The element of volume $d^3\boldsymbol{r}\, d^3\boldsymbol{v}$ in the six-dimensional $(\boldsymbol{r},\boldsymbol{v})$ phase space may become distorted in shape as a result of the motion. But its new volume is simply related to the old one by the relation

$$d^3\boldsymbol{r}'\, d^3\boldsymbol{v}' = |J|\, d^3\boldsymbol{r}\, d^3\boldsymbol{v} \tag{13·2·4}$$

where $J$ is the Jacobian of the transformation (13·2·1) and (13·2·2) from the old variables $\boldsymbol{r}$, $\boldsymbol{v}$ to the new variables $\boldsymbol{r}'$, $\boldsymbol{v}'$. The partial derivatives appearing in $J$ are (for the various components $\alpha$, $\gamma$ = 1, 2, 3)

$$\frac{\partial x_\alpha'}{\partial x_\gamma} = \delta_{\alpha\gamma}; \qquad \frac{\partial x_\alpha'}{\partial v_\gamma} = \delta_{\alpha\gamma}\, dt \qquad \text{by (13·2·1)}$$

$$\frac{\partial v_\alpha'}{\partial x_\gamma} = \frac{1}{m}\frac{\partial F_\alpha}{\partial x_\gamma}\, dt; \qquad \frac{\partial v_\alpha'}{\partial v_\gamma} = \delta_{\alpha\gamma} \qquad \text{by (13·2·2)}$$

where we have used the fact that $\boldsymbol{F}$ is independent of $\boldsymbol{v}$. Hence $J$ is given by

$$J = \frac{\partial(x',y',z',v_x',v_y',v_z')}{\partial(x,\,y,\,z,\,v_x,\,v_y,\,v_z)} = \left|\begin{array}{ccc:ccc} 1 & 0 & 0 & dt & 0 & 0 \\ 0 & 1 & 0 & 0 & dt & 0 \\ 0 & 0 & 1 & 0 & 0 & dt \\ \hdashline \frac{1}{m}\frac{\partial F_x}{\partial x}\, dt & \cdots & \cdots & 1 & 0 & 0 \\ \cdots & \cdots & \cdots & 0 & 1 & 0 \\ \cdots & \cdots & \cdots & 0 & 0 & 1 \end{array}\right|$$

where all nine terms in the lower left corner of the determinant are proportional to $dt$. Hence

$$J = 1 + \mathcal{O}\,(dt^2)$$

so that $J = 1$ is correct up to and including first-order terms in the infinitesimal time interval $dt$. Hence it follows by (13·2·4) that

$$d^3\boldsymbol{r}'\, d^3\boldsymbol{v}' = d^3\boldsymbol{r}\, d^3\boldsymbol{v} \tag{13·2·5}$$

By (13·2·5) the relation (13·2·3) becomes simply*

$$f(\boldsymbol{r}',\boldsymbol{v}',t') = f(\boldsymbol{r},\boldsymbol{v},t) \tag{13·2·6}$$

or

$$f(\boldsymbol{r} + \dot{\boldsymbol{r}}\, dt,\ \boldsymbol{v} + \dot{\boldsymbol{v}}\, dt,\ t + dt) - f(\boldsymbol{r},\boldsymbol{v},t) = 0$$

By expressing this in terms of partial derivatives, one obtains

$$\left[\left(\frac{\partial f}{\partial x}\dot{x} + \frac{\partial f}{\partial y}\dot{y} + \frac{\partial f}{\partial z}\dot{z}\right) + \left(\frac{\partial f}{\partial v_x}\dot{v}_x + \frac{\partial f}{\partial v_y}\dot{v}_y + \frac{\partial f}{\partial v_z}\dot{v}_z\right) + \frac{\partial f}{\partial t}\right] dt = 0$$

* Since $J$ in (13·2·4) differs from 1 only by terms of second order in $dt$, it follows that (13·2·5) and (13·2·6) hold actually for *all* times and not merely for infinitesimal times.

More compactly, this can be written

$$Df = 0 \tag{13·2·7}$$

where
$$Df \equiv \frac{\partial f}{\partial t} + \dot{\boldsymbol{r}} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \dot{\boldsymbol{v}} \cdot \frac{\partial f}{\partial \boldsymbol{v}} = \frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \frac{\boldsymbol{F}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{v}} \tag{13·2·8}$$

Here $\partial f/\partial \boldsymbol{r}$ denotes the gradient with respect to $\boldsymbol{r}$, i.e., the vector with components $\partial f/\partial x$, $\partial f/\partial y$, $\partial f/\partial z$. Similarly, $\partial f/\partial \boldsymbol{v}$ denotes the gradient with respect to $\boldsymbol{v}$, i.e., the vector with components $\partial f/\partial v_x$, $\partial f/\partial v_y$, $\partial f/\partial v_z$.

Equation (13·2·7) is a linear partial differential equation satisfied by $f$. The relations (13·2·6) or (13·2·7) assert that $f$ remains unchanged if one moves along with the molecules in phase space. (This is a special case of Liouville's theorem proved in Appendix A·13.) Equation (13·2·7) is the Boltzmann equation without collisions. (In plasma physics it is sometimes called the "Vlasov equation.")

******Alternative derivation*** Instead of following the motion of an element of volume of phase space as we did in Fig. (13·2·1), one can focus attention on a *fixed* element of volume. Thus, consider a *given* range of molecular positions between $\boldsymbol{r}$ and $\boldsymbol{r} + d\boldsymbol{r}$ and of velocities between $\boldsymbol{v}$ and $\boldsymbol{v} + d\boldsymbol{v}$ (see Fig. 13·2·2). The number of molecules in this element of volume $d^3\boldsymbol{r}\, d^3\boldsymbol{v}$ of phase space changes as the positions and velocities of the molecules change. The increase in the number of molecules in this range in time $dt$ is given by $(\partial f/\partial t)\, d^3\boldsymbol{r}\, d^3\boldsymbol{v}\, dt$. This change is due to the number of molecules entering and leaving this range $d^3\boldsymbol{r}\, d^3\boldsymbol{v}$ as a result of their motion.

In the absence of collisions, the molecular positions and velocities change simply in accordance with (13·2·1) and (13·2·2). The number of molecules entering the "volume" $d^3\boldsymbol{r}\, d^3\boldsymbol{v}$ in time $dt$ through the "face" $x$ = constant is then just the number contained in the volume $(\dot{x}\, dt)\, dy\, dz\, dv_x\, dv_y\, dv_z$, i.e., equal to $f(\dot{x}\, dt)\, dy\, dz\, dv_x\, dv_y\, dv_z$. The number leaving through the "face"

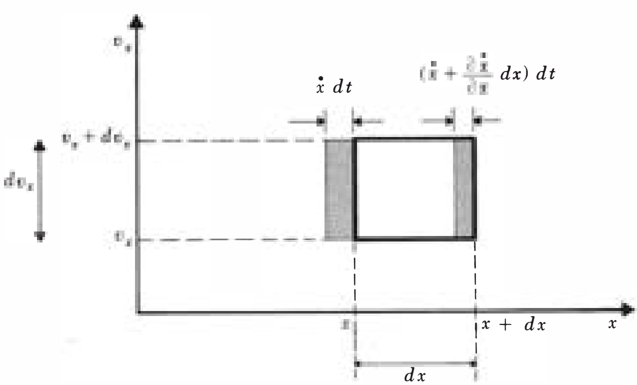


***Fig. 13·2·2 Figure illustrating a fixed element of volume of phase space for a particle moving in one dimension and specified by its position $x$ and velocity $v_x$.***

$x + dx =$ constant is given by a similar expression except that both $f$ and $\dot{x}$ must be evaluated at $x + dx$ instead of at $x$. Hence the net number of molecules entering the range $d^3\boldsymbol{r}\, d^3\boldsymbol{v}$ in time $dt$ through the faces $x$ and $x + dx$ is

$$f\dot{x}\, dt\, dy\, dz\, dv_x\, dv_y\, dv_z - \left[f\dot{x} + \frac{\partial}{\partial x}(f\dot{x})\, dx\right] dt\, dy\, dz\, dv_x\, dv_y\, dv_z = -\frac{\partial}{\partial x}(f\dot{x})\, dt\, d^3\boldsymbol{r}\, d^3\boldsymbol{v}$$

Summing similar contributions for molecules entering through the faces labeled by $y$, $z$, $v_x$, $v_y$, and $v_z$, one obtains

$$\frac{\partial f}{\partial t}\, dt\, d^3\boldsymbol{r}\, d^3\boldsymbol{v} = -\left[\frac{\partial}{\partial x}(f\dot{x}) + \frac{\partial}{\partial y}(f\dot{y}) + \frac{\partial}{\partial z}(f\dot{z}) + \frac{\partial}{\partial v_x}(f\dot{v}_x) + \frac{\partial}{\partial v_y}(f\dot{v}_y) + \frac{\partial}{\partial v_z}(f\dot{v}_z)\right] dt\, d^3\boldsymbol{r}\, d^3\boldsymbol{v}$$

Thus
$$\frac{\partial f}{\partial t} + \sum_{\alpha=1}^{3}\left[\frac{\partial f}{\partial x_\alpha}\dot{x}_\alpha + \frac{\partial f}{\partial v_\alpha}\dot{v}_\alpha\right] + \sum_{\alpha=1}^{3} f\left[\frac{\partial \dot{x}_\alpha}{\partial x_\alpha} + \frac{\partial \dot{v}_\alpha}{\partial v_\alpha}\right] = 0 \qquad (13\cdot2\cdot9)$$

where
$$x_1 = x,\ x_2 = y,\ x_3 = z$$
and
$$v_1 = v_x,\ v_2 = v_y,\ v_3 = v_z$$
But
$$\frac{\partial \dot{x}_\alpha}{\partial x_\alpha} = \frac{\partial v_\alpha}{\partial x_\alpha} = 0$$

since the variables $\boldsymbol{v}$ and $\boldsymbol{r}$ are independent, and

$$\frac{\partial \dot{v}_\alpha}{\partial v_\alpha} = \frac{1}{m}\frac{\partial F_\alpha}{\partial v_\alpha} = 0$$

since $\boldsymbol{F}$ does not depend on velocity. Hence the last bracket in (13·2·9) vanishes so that this equation reduces to

$$\frac{\partial f}{\partial t} + \dot{\boldsymbol{r}} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \dot{\boldsymbol{v}} \cdot \frac{\partial f}{\partial \boldsymbol{v}} = 0$$

which is identical to (13·2·7).

***Remark*** This last derivation is, of course, similar to that used in the derivation of Liouville's theorem in Appendix A·13. This also suggests how one would generalize the discussion to include magnetic forces which *are* velocity dependent. Since the force could still be derived from a Hamiltonian $\mathcal{H}$, one could introduce a distribution function $f'(\boldsymbol{r},\boldsymbol{p},t)$ involving the momentum $\boldsymbol{p}$ instead of the velocity $\boldsymbol{v}$. By Liouville's theorem this would satisfy the equation

$$\frac{\partial f'}{\partial t} + \dot{\boldsymbol{r}} \cdot \frac{\partial f'}{\partial \boldsymbol{r}} + \dot{\boldsymbol{p}} \cdot \frac{\partial f'}{\partial \boldsymbol{p}} = 0$$

(Here $\boldsymbol{p} = m\boldsymbol{v} + (e/c)\boldsymbol{A}$ if the magnetic field is given in terms of a vector potential $\boldsymbol{A}$.)