Communications

On the Concept of Local Equilibrium in Irreversible Thermodynamics

R. P. RASTOGI & BYAS MISHRA
Department of Chemistry, University of Gorakhpur
Gorakhpur

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The concept of local equilibrium of irreversible thermodynamics has been examined. It is concluded that local equilibrium is not disturbed when external fields are present. However, it may be doubtful for a rotating gas.

It has been pointed out in a number of research papers that formal thermodynamics of irreversible processes can be justified on statistical mechanical grounds if equilibrium is assumed to be valid locally at microscopic level. When a system is separated by a membrane, there are greater chances of existence of local equilibrium separately in the two chambers although pressure, temperature, concentration and potential may be different in different chambers. This expectation has been experimentally justified in thermoosmotic and electrokinetic phenomena where it is observed that linear laws and thermodynamic results are valid for a large range of differences of thermodynamic parameters in the two chambers. The recent work of Rastogi and coworkers shows that the non-linearity which is observed in electrokinetic experiments is due to the change in the character of the electrical double layer and not due to any weakness of the concept of local equilibrium.

However, it is still necessary to examine the concept from different angles, since there is considerable interest? The thermodynamic relation for thermal transpiration has been proved from kinetic theory when Maxwell-Boltzmann distribution of velocities is assumed to be valid. It should be noted that near the pores of the capillary rotational velocity and screw motion may become significant enough to affect the Boltzmann distribution. The distribution would also be expected in the presence of external fields. It is worth while to examine whether predictions of irreversible thermodynamics would still be valid.

Velocity distribution in an external field — According to Maxwell-Boltzmann statistics, the velocity distribution function at equilibrium is given by the relation

\[ f(0) = n_0 \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mV^2}{2kT}} \]  

where \( m \) is the molecular mass, \( k \) is the Boltzmann constant, \( n_0 \) is the number-density, \( T \) is the absolute temperature and \( c \) is the velocity. The average velocity \( \bar{c} \) is \( \int c f(c) dc \) and is given by expression

\[ \bar{c} = \left( \frac{8kT}{\pi m} \right)^{1/2} \]  

When we consider the system in the presence of an external field \( mF \) (\( F \), the force per unit mass, being independent of velocity of the molecule), the form of distribution function \( f \) is given by Eq. (3)

\[ f = n_0 \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m(c-Ft)^2}{2kT}} \]

where \( \Psi \) is the potential possessed by the field of force, which in the steady state is given by expression

\[ \Psi = \frac{kT}{m} \log n + \text{constant} \]

The number-density \( n \) in the presence of external field is given in terms of \( \Psi \) by Eq. (5)

\[ n = n_0 e^{-\frac{m\Psi}{kT}} \]

where \( n_0 \) is the number-density when \( \Psi = 0 \). Now the average velocity \( \bar{c} \) in the presence of the external field following the usual procedure would be given by Eq. (6)

\[ \bar{c}' = \int c f(c) dc = \left( \frac{8kT}{\pi m} \right)^{1/2} \]

so that \( \bar{c}' = \bar{c} \)

Thermoosmosis in an external field — When two compartments, separated by a membrane or a barrier, are maintained at different temperatures, transport of matter takes place from one compartment to another and in the steady state a fixed pressure difference, \( \Delta P \), corresponding to temperature difference \( \Delta T \) is set up. Thermoosmosis is a non-equilibrium phenomenon which has been satisfactorily interpreted using the methods of irreversible thermodynamics. We shall try to examine how the results are modified when an external field is imposed on the system. The conclusions would be relevant in the context of irreversible thermodynamics of highly charged membranes including ion-exchange membranes.

Consider an orifice of negligible thickness, the diameter of which is comparable to mean-free path. Now the total number of molecules striking the orifice per unit time whose velocities lie between 0 to \( \infty \) in the presence of an external field would be given by

\[ \frac{dn}{dt} = \frac{1}{4} n \bar{c} \]

Therefore using Eqs. (5) and (7), we get

\[ \frac{dn}{dt} = \frac{1}{4} n_0 e^{-\frac{m\Psi}{kT}} \]

Now, mass flow per unit time would be given by the expression

\[ \frac{dn}{dt} = P \phi \int(2\pi MRT)^{1/2} e^{-\frac{m\Psi}{kT}} \]

where \( M \) is the molecular weight of the gas. If there are two chambers at temperatures \( T_1 \) and \( T_2 \),
and pressures $P_1$ and $P_2$ and separated by a membrane, the mass flow $J_m$ would be given by Eq. (11)

$$J_m = \frac{P_1}{(2\pi MRT_1)^{1/2}} e^{-\frac{M^2}{RT_1}} - \frac{P_2}{(2\pi MRT_2)^{1/2}} e^{-\frac{M^2}{RT_2}}, \quad \ldots (11)$$

On rearrangement we get

$$J_m = \left[ \frac{P_1}{(2\pi MRT_1)^{1/2}} - \frac{P_2}{(2\pi MRT_2)^{1/2}} \right] \times \frac{M^2}{RT_1} \cdot \frac{1}{(P_1^{1/2} - P_2^{1/2})(\sqrt{P_1^{1/2}} + \sqrt{P_2^{1/2}})} \ldots (12)$$

where $\Delta T = T_1 - T_2$.

In the steady state when we have $J_m = 0$, Eq. (12) yields the usual thermal transpiration relation (13)

$$\frac{P_1}{(T_1)^{1/2}} = \frac{P_2}{(T_2)^{1/2}} \quad \ldots (13)$$

**Velocity distribution and thermal transpiration during screw motion** — Now, we consider the case when the fluid particles passing through the cylindrical container are in a steady rotatory motion along with streamline motion. Let the direction of the axis of rotation be $Z$ axis. Let the motion of the boundary be defined by $U$, $V$, the transational velocities in $x$ and $y$ direction and by $\omega$, the angular velocity, as shown in Fig. 1.

Components of the velocity at any point $P$ (whose cartesian coordinate are, $x$, $y$, and $z$) parallel to the axis of coordinates, are $U = \omega r \sin \theta$ and $V = \omega r \cos \theta$ or $U = -\omega y$ and $V = \omega x$. Applying boundary condition, i.e. at $P$ the normal velocity of the boundary is equal to the normal velocity of the fluid situated at that point, and considering the motion of the boundary uniform, $\Phi$, the stream function or current function is given by

$$\Phi = Ux - Uy + \frac{1}{2} \omega (x^2 + y^2) + \text{constant} \quad \ldots (14)$$

It is possible however for the orthogonal surfaces to exist without a velocity potential. Take for instance $u = -\omega y$, $v = \omega x$, $w = 0$, $u$, $v$ and $w$ being the fluid velocities in $x$, $y$ and $z$ directions, where $w$ is the specific volume. It also follows that Eq. (16) would remain valid in the presence of external field. The phenomenological coefficients $L_{14}$ and $L_{12}$ would be a function of $\omega$ and external field. However $L_{14}/L_{11}$ would remain the same at a fixed temperature and the relation

$$\Delta P/\Delta T = -Q^* \nu^* T \quad \ldots (17)$$

where $Q^*$ is the heat of transport would still be satisfied.

It follows that the concept of local equilibrium remains valid even in the presence of external field. This finding adds further confidence to the fact that irreversible thermodynamics of membranes can be expected to have far greater range of validity.

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**References**


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**Fig. 1**