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# Thermodynamics of Inhomogeneous Systems. II

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By the inclusion of an explicit dependence of the energy on the boundary of the system, the thermodynamic description of inhomogeneous systems is made more complete. In particular, virtual processes can then be defined that determine the measurable stresses everywhere in the system.

## INTRODUCTION

IN an earlier paper,[1] I developed an extension of the thermodynamic methods of Gibbs so that inhomogeneous systems could be described. The treatment of the boundary envelope in that paper seemed to me to be somewhat unsatisfactory, and that point was discussed briefly in the closing paragraphs. A possible alternative description for the boundary was also mentioned, but this was not developed at any length.

The purpose of the present paper is to show that that generalization of the boundary is just what is needed to complete the thermodynamic description of inhomogeneous systems. With this improvement it is possible to define the measurable stress everywhere in the system as well as on the boundaries.

## DEVELOPMENT OF THE THEORY

The notation of the present paper is the same as that of I. Following Eq. (41) of I, we shall let the total energy be augmented by a boundary term. Then

$$E=\int dv\left[Ts+\mu n+\sum_i \omega_i\gamma_i+\nu\lambda-p\right]+\sum_i\int da_i[A_i n+B\gamma_i]. \quad (1)$$

There are now some differences between the equilibrium conditions in I and those which result from the present treatment. These differences of course have to do only with modified boundary terms that result from variations of $\delta n$ and $\delta\gamma_i$ at the boundary. As already noted in Eqs. (20a) and (21a) of I, the boundary conditions of the "chemical equilibrium" equations are simply modified to the form,

$$\sum\nolimits_i da_i(\omega_i-\partial\nu/\partial x_i+A_i)=0, \quad (2)$$

and

$$\nu+B=0. \quad (3)$$

The only other equilibrium conditions which undergo any modification are the boundary terms corresponding to stress equilibrium. We shall follow this in some detail. The inclusion of the generalized boundary interactions enables us to place a more general constraint upon the boundary deformability, corresponding to the necessity of exerting tangential as well as normal tractions on the boundary. The general constraint is then, everywhere on a boundary,

$$\delta x_j=0. \quad (4)$$

For convenience in summing all the constraints given by Eq. (4), we select the Lagrange multipliers in such a form that we obtain a readily recognizable stress tensor. Thus we write

$$\sum_{ij}\int da_i\delta x_j\, P_{ij}=0, \quad (5)$$

where $P_{ij}$ is a tensor function of position on the boundary. The general variational condition to be satisfied is

$$\delta E+\sum_{ij}\int da_i\delta x_j\, P_{ij}=0. \quad (6)$$

The portion of $\delta E$ which corresponds to the volumetric energy contribution is that already given by Eq. (26) of I. It remains to evaluate the portion which depends on our newly introduced boundary contribution to $E$. That portion depends on $\delta n$ and $\delta\gamma_i$ due to the strain deformation, *evaluated at the boundary in its displaced position.* It is readily found that

$$\delta n=-n\frac{\partial}{\partial x_j}\delta x_j,$$

and

$$\delta\gamma_i=-\left[\gamma_j\frac{\partial}{\partial x_i}+\gamma_i\frac{\partial}{\partial x_j}+n\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\right]\delta x_j.$$

Combining the new boundary contribution with Eq. (26), we obtain after some simplification

$$\begin{aligned}\delta E=&\sum_{ij}\int dv\delta x_j\frac{\partial}{\partial x_i}\left[p\delta_{ij}-n\frac{\partial\omega_i}{\partial x_j}-\gamma_i\frac{\partial\nu}{\partial x_j}+n\frac{\partial^2\nu}{\partial x_i\partial x_j}\right]\\&-\sum_{ij}\int da_i\left[\left(p\delta_{ij}+\omega_i\gamma_j+\nu\lambda_{ij}-\gamma_j\frac{\partial\nu}{\partial x_i}\right)\delta x_j\right.\\&+\left(n\omega_i+\nu\gamma_i-n\frac{\partial\nu}{\partial x_i}+nA_i+B\gamma_i\right)\frac{\partial}{\partial x_j}\delta x_j\\&+\left(\nu\gamma_j\frac{\partial}{\partial x_i}+\nu n\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}+B\gamma_j\frac{\partial}{\partial x_i}\right.\\&\left.\left.+Bn\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}\right)\delta x_j\right]\\&+\sum_{ij}\int da_j\delta x_j\frac{\partial}{\partial x_i}\left(n\omega_i+\nu\gamma_i-n\frac{\partial\nu}{\partial x_i}\right).\end{aligned}$$

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[1] Edward W. Hart, Phys. Rev. 113, 412 (1959), hereafter referred to as I.

This expression is further simplified by the use of the boundary conditions given by Eqs. (2) and (3), and by rewriting the last term of the right-hand member. Thus we obtain

$$\delta E=\sum_{ij}\int dv\delta x_j\frac{\partial}{\partial x_i}\left[p\delta_{ij}-n\frac{\partial\omega_i}{\partial x_j}-\gamma_i\frac{\partial\nu}{\partial x_j}+n\frac{\partial^2\nu}{\partial x_i\partial x_j}\right]$$

$$-\sum_{ij}\int da_i\delta x_j\left\{\left[p-\sum_k\frac{\partial}{\partial x_k}\left(n\omega_k+\nu\gamma_k-n\frac{\partial\nu}{\partial x_k}\right)\right]\delta_{ij}+\omega_i\gamma_j+\nu\lambda_{ij}-\gamma_j\frac{\partial\nu}{\partial x_i}\right\}. \tag{7}$$

The substitution of Eq. (7) into Eq. (6) leads to the equilibrium conditions:

$$\sum_i\frac{\partial}{\partial x_i}\left[p\delta_{ij}-n\frac{\partial\omega_i}{\partial x_j}-\gamma_i\frac{\partial\nu}{\partial x_j}+n\frac{\partial^2\nu}{\partial x_i\partial x_j}\right]=0, \tag{8}$$

and

$$P_{ij}=\left[p-\sum_k\frac{\partial}{\partial x_k}\left(n\omega_k+\nu\gamma_k-n\frac{\partial\nu}{\partial x_k}\right)\right]\delta_{ij}+\omega_i\gamma_j+\nu\lambda_{ij}-\gamma_j\frac{\partial\nu}{\partial x_i}. \tag{9}$$

Although the quantity $P_{ij}$ is defined by Eq. (9) only at a boundary, it is convenient to consider that there exists such a tensor defined by that equation throughout the system. It can then be shown that $P_{ij}$ is the *measurable stress* everywhere in the system. This results from the following considerations:

In order to measure the stress somewhere inside the system, it must be possible to introduce a boundary element anywhere in the system in such a way that the density distribution in the system is unaltered by the presence of the boundary element. The stress is then determined from the tractions on that boundary element. We can, for example, introduce a closed cubical boundary somewhere inside the system and remove the matter which was in the region now occupied by volume of the cube. If the boundary is tailored so that its constants $A_i$ and $B$ now satisfy the conditions given by Eqs. (2) and (3) where the boundary is, then clearly the rest of the system will be unperturbed by the replacement that we have effected. The tractions on the boundaries will then be deducible from the tensor $P_{ij}$ as defined by Eq. (9) and we have thereby demonstrated that $P_{ij}$ is the measurable stress everywhere in the system.

We investigate next the equilibrium associated with $P_{ij}$

$$\sum_i\frac{\partial}{\partial x_i}P_{ij}=\sum_i\frac{\partial}{\partial x_i}p\delta_{ij}-\sum_{ik}\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_k}\left(n\omega_k+\nu\gamma_k-n\frac{\partial\nu}{\partial x_k}\right)\delta_{ij}$$

$$+\sum_i\left(\omega_i\frac{\partial\gamma_j}{\partial x_i}+\gamma_j\frac{\partial\omega_i}{\partial x_i}+\nu\frac{\partial\lambda_{ij}}{\partial x_i}-\gamma_j\frac{\partial^2\nu}{\partial x_i^2}\right)$$

$$=\sum_i\frac{\partial}{\partial x_i}\left[p\delta_{ij}-\frac{\partial}{\partial x_j}\left(n\omega_i+\nu\gamma_i-n\frac{\partial\nu}{\partial x_i}\right)\right]$$

$$+\sum_i\left[\omega_i\frac{\partial\gamma_j}{\partial x_i}+\gamma_j\frac{\partial\omega_i}{\partial x_i}+\nu\frac{\partial\lambda_{ij}}{\partial x_i}-\gamma_j\frac{\partial^2\nu}{\partial x_i^2}\right],$$

where the summation indices $i$ and $k$ have been simply interchanged in the term in which they occur. Carrying out the last operations, we obtain directly that

$$\sum_i\frac{\partial}{\partial x_i}P_{ij}=\sum_i\frac{\partial}{\partial x_i}\left[p\delta_{ij}-n\frac{\partial\omega_i}{\partial x_j}-\gamma_i\frac{\partial\nu}{\partial x_j}+n\frac{\partial^2\nu}{\partial x_i\partial x_j}\right],$$

and so, from Eq. (8),

$$\sum_i\frac{\partial}{\partial x_i}P_{ij}=0. \tag{10}$$

This equation can be taken as the stress equilibrium condition instead of Eq. (8).

Now the same type of argument that is used in usual elasticity theory to insure the rotational equilibrium of each element of volume leads to the conclusion that $P_{ij}$ is a symmetric tensor. This leads us to the further conclusions that

$$\omega_i\gamma_j=\omega_j\gamma_i, \tag{11}$$

and

$$\frac{\partial\nu}{\partial x_i}\gamma_j=\frac{\partial\nu}{\partial x_j}\gamma_i, \tag{12}$$

and so the vectors $\omega_i$ and $\partial\nu/\partial x_i$ are parallel to $\gamma_i$. This is not a very surprising conclusion considering the implicit assumption of isotropy in the postulated form of the energy density. It is of course possible to describe *ab initio* systems possessing a lower degree of symmetry, but such extensions will not be pursued in this paper.

## DISCUSSION

Thus, with the modifications presented above, it becomes possible to describe thermodynamically the equilibrium configurations of a wide range of systems. The range of validity of the surface approximation can be evaluated in detail for any particular case by means of the self-consistent phenomenology set forth here.

In the introduction to reference 1 it was mentioned that this method should be useful in treating the phenomena associated with critical point fluctuations. I should like to enlarge slightly upon that idea although the problem is not yet solved. The point here is that the correlation of density fluctuations over macroscopic intervals should depend on the same properties that determine the character of equilibrium macroscopic inhomogeneities. The reason for this is that the "states" which contribute most prominently to the density fluctuations over large regions must be representable as possible thermodynamic states. It now becomes possible to determine the configuration and free energy of those "states" by the methods of this paper, and so to formulate this problem without resort to microscopic statistical mechanics by use of thermodynamic fluctuation theory.

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# Langevin Equation and the ac Conductivity of Non-Maxwellian Plasmas

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The use of the Langevin equation $\{d\mathbf{v}/dt+g\mathbf{v}=(q/m)[\mathbf{E}_0e^{i\omega t}+(\mathbf{v}/c)\times\mathbf{H}]\}$ to describe the electrical conductivity of a non-Maxwellian plasma (a weakly ionized gas in which the average electron collision frequency is temperature dependent) may be in error unless it is understood that the dissipative term, $g$, is complex. In the limiting cases of either high or low pressures the imaginary part of $g$ is negligible. The real and imaginary parts of $g$ are evaluated for these limiting cases, for four different gases; air, helium, Maxwellian gas, and water. The real part of $g$ is shown to be the average collision frequency multiplied by a numerical factor, the size of which depends on the nature of the gas and the pressure limit.

## I. INTRODUCTION

THE conventional description of the ac conductivity of a weakly ionized gas (e.g., Mitra[1]) is based upon the assumption that the average drift velocity of electrons in the gas obeys the Langevin equation[2]:

$$\frac{d\mathbf{v}}{dt}+g\mathbf{v}=\frac{q}{m}\mathbf{E}_0e^{i\omega t},\tag{1}$$

with the steady state solution

$$\mathbf{v}=\frac{1}{i\omega+g}\left(\frac{q}{m}\right)E_0e^{i\omega t},\tag{2}$$

where $\mathbf{v}$ is the average drift velocity, $g$ is a dissipative term which represents the effect of collisions between electrons and molecules of the gas and the symbols $q$, $m$, and $E_0$ have their usual meaning.

The usual approach has been to equate $g$ with $\nu$, the average collision frequency of the electrons. This particular method is, in general, incorrect for real gases. Indeed, it is only for a Maxwellian plasma[3–5] that $g$ is identically equal to $\nu$.

A Maxwellian plasma is a weakly ionized[6] gas for which the cross section for momentum transfer, $Q(V)$, for electron impact on the neutral molecule varies inversely as $V$, the relative velocity between the electron and the molecule.[7]

Now, most real plasmas are non-Maxwellian. For example, the cross section, $Q$, for air[8] or nitrogen[9] is proportional to $V$, the cross section for helium[10] appears to be constant, and the cross section for water, and other molecules possessing permanent electric dipole moments,[11] varies inversely as $V^2$.

It is not to be expected that $g$ is simply related to $\nu$ for these plasmas except under certain limiting circumstances. We proceed to find what form $g$ must take for the above mentioned plasmas.

## II. THE FORM OF $g$ FOR A NON-MAXWELLIAN PLASMA

The average drift velocity for electrons in a gas in the presence of a weak, alternating electric field, may be determined using the relationships presented by Allis[5] and Margenau.[12]

The drift velocity, so determined, is represented, in form, by

$$\mathbf{v}=(q/m)\mathbf{E}_0e^{i\omega t}(B-iD),\tag{3}$$

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[1] S. K. Mitra, *The Upper Atmosphere* (The Asiatic Society, Calcutta, 1952), second edition, pp. 623–629.

[2] W. P. Allis, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 21, p. 392.

[3] T. Kihara, Revs. Modern Phys. **24**, 49 (1952).

[4] S. Altshuler (unpublished).

[5] Reference 2, p. 413.

[6] By "weakly ionized," we mean the only important interactions are those occurring between electrons and neutral particles.

[7] Or equivalently, the collision frequency independent of energy.

[8] Crompton, Huxley, and Sutton, Proc. Roy. Soc. (London) **A218**, 507 (1953).

[9] Phelps, Fundingsland, and Brown, Phys. Rev. **84**, 559 (1951).

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[11] S. Altshuler, Phys. Rev. **107**, 114 (1957).

[12] H. Margenau, Phys. Rev. **69**, 508 (1946).