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FLOW IN GEOTHERMAL WELLS:
PART I. FUNDAMENTALS OF TWO-PHASE
FLOW BY THE METHOD OF IRREVERSIBLE
THERMODYNAMICS

Z. Bilicki and J. Kestin

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Flow by the Method of
Irreversible Thermodynamics

By

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1. Introduction

The assessment of the economic value of a geothermal resource must be based on a thermodynamic analysis. It is certain that the best criterion for judgment is the value of the exergy (available work) of the geofluid [1] at the wellhead. The exergy is a function of the thermodynamic properties and the parameters assigned to the reference or dead state. Hence it is necessary to know the temperature (or saturation pressure) together with the dryness fraction and chemical composition of the mixture of liquid and vapor at the wellhead. Since in most wells the geofluid flashes before it reaches the wellhead, it is necessary to base the calculation on a suitable "model" for two-phase (or even multi-phase) flow.

The fundamentals of two-phase flow through channels are still in dispute. A study of the contemporary literature of the subject [2-8] shows that the systems of equations now in use can be classified under two broad headings: *homogeneous diffusion models* and *two-fluid models*. In this report we wish to provide a careful derivation of the equations of the homogeneous model and to base it on the formalism of so-called irreversible thermodynamics. In this respect we shall follow the exposition of J. Meixner and H.G. Reik [9], noting that certain other presentations [10,11] are entirely equivalent to it. This will be done in the present Part I.

Since the nomenclature in this subject has not yet become uniform, we emphasize that the equations of the homogeneous diffusion model do not exclude the occurrence of slip between the phases. We also do not claim that the model presented here is the "true" one and should always be preferred over the two-fluid model. The former is certainly simpler than the latter, but we hold the view that the domain of preference of either has

yet to be established.

Part II of this study will specialize the considerations of Part I to the case of a vertical well. Part III will describe the results of numerical calculations based on a computer algorithm developed on the basis of Part II together with comparisons with field data.

As far as the basic approach is concerned, we shall take account of the inherently inhomogeneous nature of the flow system and replace it by a physically equivalent continuum through the application of the Euler-MacLaurin approximation of a sum by an integral. We formulate the conservation laws in terms of this model-continuum. The Gibbs equation for the system is written for the accompanying equilibrium state of a physical element, as proposed by J. Bataille and J. Kestin [12,13]. A physical analysis of the properties of an elementary subsystem allows us to determine the thermodynamic variables which describe the accompanying equilibrium state as well as the original nonequilibrium state. The explicit expression for the rate of entropy production per unit volume identifies the dissipative mechanisms and suggests the forms of the phenomenological relations to be adopted.

The general model is too complex to form a basis for numerical calculations. For this reason we further simplify it and substitute for it a one-dimensional or "engineering" approximation. This is achieved by the introduction of lumped or mean values of the appropriate quantities in a cross-section.

As far as possible, we perform space-averaging with respect to *extensive* and *deformation* variables which are additive and can be summed over the system. At this stage we ignore turbulent fluctuations (as is done when the laminar form of the Navier-Stokes equations is derived) and will rely on heuristic assumptions introduced at a later stage to account for them.

It is perhaps useful to point out that the essential difference between the homogeneous model and the two-fluid model resides in the magnitude of the elements of volume, V , chosen for the description. The homogeneous model chooses much larger elements than the two-fluid model. This has a direct effect on the remainder R in eqn. (13) and opens up the unanswered question about the conditions under which the two descriptions become equivalent.

2. Nature of the two-phase system

The two-phase system which we explore here consists of regions of liquid and its vapor which exist side by side so that the thermodynamic properties change discontinuously when a phase boundary is crossed. This feature is common to all flow regimes even though the latter may be significantly different from case to case. For example, in a vertical pipe we encounter a succession of four topologically different patterns: bubble flow, plug flow, unstable froth flow and annular-mist flow [2-8].

The sketch in Figure 1 represents an element of small volume, V , of a two-phase system. Such an element constitutes a thermodynamic system, and the sum total of the liquid and vapor in it, respectively, can be regarded as two co-existing thermodynamic subsystems. In this respect the two phases represent a weakly interaction mixture as defined by J. Bataille and J. Kestin [14]. If we neglect the energy of surface tension, we can describe the state of an element of volume V in a unified manner and regardless of the particular flow pattern present at a given instant, as suggested by Figure 2. Without loss of generality, we shall assume that the liquid fills a simply connected space. The tabulated (i.e. necessarily equilibrium) properties of the liquid will be denoted by a prime (density ρ' , specific

Figure 1. An element of small volume V of a two-phase system.

Figure 2. Description of thermodynamic state in unified manner.

volume v' , specific energy u' , specific enthalpy h' , specific entropy s'), whereas those for the vapor (which may or may not fill a simply connected space) will be denoted by a double prime.

The motion of a two-phase element is governed by the action of surface forces as well as of body forces. In the terrestrial gravitational field g , the intensity of the sum of the body forces acting on the liquid ($\rho'g$) is larger than that acting on the vapor ($\rho''g$). Thus the vapor element is acted upon by a buoyancy force

$$F = -(\rho' - \rho'') V''g, \quad (1)$$

where V'' is the total volume occupied by the vapor. In addition, the masses m' and m'' of the two subsystems do not remain constant even if the total mass $m = m' + m''$ is conserved. This is due to the evaporation and condensation which occur during the motion. The dynamic situation is illustrated in Fig. 3 which suggests that the element is equivalent to two interacting, variable masses $m'(t)$ and $m''(t)$ whose centers move with different velocities w' and w'' . The center of the combined mass $m = m'(t) + m''(t)$, whose value does not change ($m = \text{const}$), moves with a velocity w . This *difference in the velocities of the two centers of mass*, the vector

$$s = w'' - w' \quad (2)$$

is referred to as *slip*. In practical applications, the three velocities are parallel, and the quantity

$$\beta_s = |w''| / |w'| \quad (2a)$$

is called *slip ratio*. Evidently

$$mw = m'(t)w' + m''(t)w'' \quad (2b)$$

Figure 3. Equivalent dynamic system.

The term "slip" does not imply a discontinuity of velocity at the phase boundary. The formation of a boundary layer along it, and on a scale small compared with the linear dimensions of V , must be expected.

The process of phase transition causes one subsystem to lose mass which is gained by the other, and each, therefore, is the seat of sources or sinks of matter.

3. Thermodynamic state

In order to base our analysis on a secure foundation, we pay special attention to the description of the state of the system of volume V and clearly distinguish between the nonequilibrium state, Fig. 4a, and its accompanying equilibrium state, Fig. 4b. The latter arises from the former by a hypothetical adiabatic, no-work process during which the velocity w of the center of mass as well as the extensive and deformation variables retain their values [13]. The original nonequilibrium state and the accompanying equilibrium state are thus characterized by identical values of the extensive and deformation variables, but the same cannot be said about the conjugate intensive variables. The volumes V , V' , V'' , the masses m , m' , m'' , as well as the energies U , U' , U'' of the system and subsystems in nonequilibrium can be measured (or "defined") in a physically unambiguous way. By contrast, the intensive variables such as temperature T or pressure tensor P_{ij} which have clearly defined values ($P_{ij}^o = \delta_{ij} P^o$ with $P^o = \frac{1}{3} P_{ii}$, and T^o) in the equilibrium case do not retain this characteristic in the nonequilibrium case. The same remark concerns the values of entropy S , S' and S'' which are not defined in the nonequilibrium state. In our two-phase system we must also recognize the existence of an internal deformation variable, the mass transferred inside the system between the two phases. The chemical

$\Phi, \mathcal{V}, m, U$
 $\mathcal{V}', m, U'$
 $\mathcal{V}'', m'', U''$
 T, P_{ij}

a

nonequilibrium

$\Phi, \mathcal{V}, m, U, S$
 $\mathcal{V}', m', U', S', \mu^{o'}$
 $\mathcal{V}'', m'', U'', S'', \mu^{o''}$
 T^o, P^o

b

accompanying
 equilibrium
 state

Figure 4. Accompanying equilibrium state.

work expressed as the product of the chemical potential acting on the "disappearing", as well as "appearing" masses dm' and dm'' , must be included in the balance. In the hypothetical process of creating the accompanying state from the nonequilibrium state the internal deformation variable is assumed to have been constrained by an outside agent, and the mass exchange is assumed performed reversibly at the cost of transferring work to the surroundings [11, Chaps. 21 and 22].

The proportions of vapor and liquid present in the system can be described either by the volumetric fractions

$$\phi' = V'/V \text{ and } \phi'' = V''/V \text{ with } \phi' + \phi'' = 1, \quad (3a)$$

or by the mass fractions

$$\gamma' = m'/m \text{ and } \gamma'' = m''/m \text{ with } \gamma' + \gamma'' = 1. \quad (3b)$$

In the theory of two-phase flow, volumetric fractions are preferred and

$$\phi \equiv \phi'' \text{ with } \phi' = 1 - \phi \quad (4)$$

is called the *void fraction*. We favor the notation of eqn. (3a) because subsequent equations acquire a more symmetric form. We shall make the substitution (4) only in the working equations. It is clear that the void fraction $\phi \equiv \phi''$ and the frequently employed *dryness fraction*

$$x \equiv \gamma'' \text{ with } \gamma' = 1 - x \quad (5)$$

are not independent. It is easy to show that

$$x = \frac{\phi \rho''}{\rho' (1 - \phi) + \rho'' \phi} \quad \text{or} \quad = \frac{1}{1 + (1 - x) \rho'' / x \rho'} \quad (6)$$

Here

$$\rho' = \frac{m'}{V'} \quad \text{and} \quad \rho'' = \frac{m''}{V''} \quad (6a)$$

are tabulated equilibrium densities of the substance, and not the ratios

m'/V and m''/V used in [9].

All extensive quantities of the system V can be expressed in terms of the properties of the two co-existing subsystems. In this connection it is usual to introduce specific quantities per unit mass. In particular,

$$\rho = \phi' \rho' + \phi'' \rho'' , \quad (7)$$

or for any specific quantity $\psi = \Psi/m$ per unit mass

$$\rho \psi = \rho' \phi' \psi' + \rho'' \phi'' \psi'' , \quad (8)$$

because

$$\Psi = m' \psi' + m'' \psi'' . \quad (8a)$$

Thus,

$$\Psi = m \psi = \rho \psi V = (\rho' \phi' \psi' + \rho'' \phi'' \psi'') V . \quad (8b)$$

Here ψ may be interpreted as u , h , s , etc. As far as the nonequilibrium state is concerned, the properties ρ and ψ calculated above represent *mean values* taken over the volume V . It is emphasized that the same procedure *cannot be applied to the intensive properties*. However, in the expression for the Second Part of the Second Law (Clausius-Duhem inequality), the equilibrium values of temperature and entropy must be employed [11,13].

We are now in a position to write the Biggs equation for the system V :

$$T^\circ dS = dU + P^\circ dV - \mu^\circ' dm' - \mu^\circ'' dm'' . \quad (9)$$

The last two terms describe the reversible transfer of masses, dm' and dm'' with

$$dm' + dm'' = 0 , \quad (10)$$

between the two subsystems, the symbols μ°' and μ°'' denoting the *equilibrium*

chemical potentials of the two phases. These two quantities may or may not be equal. If we approximate the system by one in which surface tension and the possible appearance of metastable states are neglected, we may equate the two chemical potentials. Then the last two terms cancel each other in view of eqn. (10). In our working model we shall make this simplification, but retain the last terms in our equation to preserve generality.

The Gibbs equation (9) clearly identifies the thermodynamic variables which enter the system's *equation of state*. The extensive variables S and U are assumed expressed in terms of the subsystems by eqn. (8b). Compared with a standard thermodynamic equilibrium system, the equation of state has acquired one additional variable, the void fraction ϕ (or dryness fraction x). In the absence of surface tension and metastability, the pressure P° is a unique function of the temperature T° in view of the condition that

$$\mu^{\circ'} = \mu^{\circ''} , \text{ (Clausius-Clapeyron) } .$$

The Gibbs equation per unit mass becomes

$$T^\circ ds = du + P^\circ d(1/\rho) - \mu^{\circ'} d\gamma' - \mu^{\circ''} d\gamma'' , \quad (11)$$

where the mass fractions from eqn. (3) have been introduced.

The original system of volume V is not in equilibrium because it interacts with its surroundings by exchanging heat and work. Furthermore, it moves with a center-of-mass velocity w . Due to the difference in body forces acting on the subsystems (gas and liquid, respectively), as well as to the exchange of mass between them by evaporation or condensation, the centers of mass of the latter move with respect to each other, and their absolute center-of-mass velocities w' and w'' differ, as already mentioned earlier. Finally it is worth noticing that the system is compressible due to the compressibility of the vapor as well as to the exchange of mass

between the phases. In most cases the two phases taken separately are either practically incompressible (liquid) or compressible with very short relaxation times (saturated vapor or metastable vapor). However, the whole system exhibits a relaxation time which may become long if the rate of evaporation or condensation is not very large, or is significantly affected by surface tension. This means that the system as a whole may become the seat of viscoelastic effects which can manifest themselves in the form of a non-zero bulk viscosity.

4. Continuum model

The local discontinuities in our two-phase system and its stochastic topological structure make it impossible to analyze its dynamics in any detail. This becomes feasible by the introduction of a continuum model of our system in motion, Fig. 5. We subdivide the whole system of volume V into k elements V_i , and ascribe to each of them the properties of the system V discussed earlier. The *instantaneous* value of any extensive property $\Psi(t)$ for the whole system is equal to the sum

$$\Psi(t) = \sum_{i=1}^k \bar{\rho}_i \bar{\psi}_i V_i, \quad (12)$$

where $\bar{\rho}_i$ and $\bar{\psi}_i$ are the *instantaneous* mean specific quantities introduced in Section 3. Each specific quantity is the mean of some extensive or deformation parameter but not of an intensive property.

We now apply the Euler-MacLaurin formula to equation (13) and obtain

$$\Psi(t) = \int_{V(t)} \rho(x,y,z,t) \psi(x,y,z,t) dV + R, \quad (13)$$

where R is the remainder. The functions $\rho(x,y,z,t)$ and $\psi(x,y,z,t)$ are continuous at every point (x,y,z) of a hypothetical, or transformed, space $V(t)$,

Figure 5. Transformation of real space of a two-phase system into a continuum.

except possibly for a subspace of measure zero (shock fronts). The mean values $\bar{\rho}_i$, $\bar{\psi}_i$ of element i correspond to some interior point of the element V_i in the transformed space, and the property of being continuous is associated with the functions $\rho(x,y,z,t)$, $\psi(x,y,z,t)$ rather than with the real fields in the physical space.

It is assumed that the volumes V_i have been so chosen that the description on the scale V is adequate to allow us to neglect the remainder and to accept the approximation

$$\Psi(t) \approx \int_{V(t)} \rho(x,y,z,t) \psi(x,y,z,t) dV . \quad (14)$$

The accuracy of such an approximation can only seldom be calculated mathematically with any assurance. It is clear, however, that the scale must be related to the flow structure and must contain an adequate number of stochastically equivalent elements such as bubbles, droplets or plugs with V_i of order $V \ll V$. The continuous functions $\rho(x,y,z,t)$ and $\psi(x,y,z,t)$ have the obvious property that

$$\bar{\rho}_i \bar{\psi}_i = \frac{1}{V_i} \int_{V_i} \rho(x,y,z) \psi(x,y,z) dV , \quad (15)$$

and by the mean value theorem we are assured that the instantaneous value $\rho\psi = \bar{\rho}_i \bar{\psi}_i$ corresponds to at least one point in the interior of V_i , as already stated earlier. Thus, the field functions are not unique in a given situation.

Using the above approximation we have not replaced the physical system by a continuum which can be thought of as a juxtaposition of the fields $\rho(x,y,z,t)$, $\psi(x,y,z,t)$, $w(x,y,z,t)$, $w'(x,y,z,t)$, $w''(x,y,z,t)$, etc. The fields ρ, ψ, w are well known from fluid mechanics, but in the present case every point of the continuum has assigned to it a value of

$$\rho'(x,y,z,t), \rho''(x,y,z,t), \phi'(x,y,z,t), \phi''(x,y,z,t) \text{ etc.}$$

as well. We shall examine the number of equations which determine these fields in Section 11.

The continuum model of our system does not differ from that of a mixture treated in the classical theory [9,14], and the obvious assumption is made that the conservation laws apply. The only difference now is that we shall write separate momentum conservation equations for the vapor and liquid in order to introduce their densities and volume fractions explicitly.

When the local instantaneous equations are written down for the two-fluid model (e.g. Chap. 5 in [2]), it is implied that the elementary volume V chosen for the description is much smaller than the scale on which our description is based. Transition to a coarser scale of description is achieved later by *averaging*. It is thus clear that there is no difficulty in working out the correspondence between the extensive properties of the two levels of description. The intensive properties may, however, be entirely different. The situation is rather like that which connects the description of a fluid on the molecular scale with that on the accepted continuum level.

5. Notation

In order to write down the conservation laws for the model-continuum, it is convenient to introduce the indicial notation and to adopt the Einstein summation convention. The two phases will be distinguished by a prime or a double prime, as before, but to avoid repetition we shall use the superscript α to denote any one of them. No summation convention is implied with respect to the superscripts, and a summation sign will always

be displayed. Thus, for example, $\gamma^\alpha w_i^\alpha$ means *either* $\gamma' w_i'$ or $\gamma'' w_i''$, but

$$\Sigma \gamma^\alpha w_i^\alpha \text{ means } \gamma' w_i' + \gamma'' w_i'' .$$

6. Conservation laws

The conservation laws for the continuum model can be written, equivalently, in integral or differential form. The integral form is usually written for a volume $V(t)$ whose boundary deforms in the barycentric velocity field $w_i(x_j, t)$ of the center of mass of an element defined in eqn. (26) or by

$$w_i = \Sigma \gamma^\alpha w_i^\alpha = (\Sigma \rho^\alpha \phi^\alpha w_i^\alpha) / \rho . \quad (16)$$

This is done to ensure that the system is one of constant mass, and that the conservation laws apply to it. Taken separately, the boundaries of the subsystems α deform in velocity fields $w_i^\alpha(x_j, t)$ and this is equivalent to the appearance of material fluxes

$$J_i^\alpha = \rho^\alpha \phi^\alpha (w_i^\alpha - w_i) . \quad (17)$$

The change in phase gives rise to two scalar source terms $\Gamma^\alpha(x_i, t)$ in our model-continuum. Evidently

$$\Sigma J_i^\alpha = 0 \quad \text{and} \quad \Sigma \Gamma^\alpha = 0 . \quad (18)$$

The *conservation of mass* in subsystem α can thus be written either as

$$\frac{\partial \rho^\alpha \phi^\alpha}{\partial t} + \frac{\partial (\rho^\alpha \phi^\alpha w_i^\alpha)}{\partial x_i} = \Gamma^\alpha \quad (19)$$

or as

$$\rho \frac{d\gamma^\alpha}{dt} + \frac{\partial J_i^\alpha}{\partial x_i} = \Gamma^\alpha , \quad (20)$$

where

$$\frac{d}{dt} \equiv \frac{\partial}{\partial t} + w_i \frac{\partial}{\partial x_i} \quad (21)$$

is referred to the center-of-mass velocity w_i of the whole element. Equation (21) arises from eqn. (19) by the substitution of eqns. (16) and (17).

A global equation of mass conservation arises from the summation of the terms in eqn. (20) over α subject to (18). This is

$$\frac{d\rho}{dt} + \rho \frac{\partial w_i}{\partial x_i} = 0, \quad (22)$$

as might have been expected.

In order clearly to derive the equation of *momentum conservation* it is convenient to revert to the representative system V shown in Fig. 4. The external forces acting on each system consist of body forces $\rho^\alpha g_i$ and of surface forces represented by the pressure tensors $\pm \Lambda_{ij}$ acting on surface A_1 and P_{ij} acting on surface A . The former is internal to V , whereas the latter is the result of the interaction between system V and the rest of the fluid. In order to bring out the difference in the body forces and center-of-mass velocities, we write for the liquid

$$\frac{d}{dt} \int_{V(t)} \phi' \rho' w_i' dV = \int_{V(t)} \phi' \rho' g_i dV - \int_{A(t)} P_{ji} n_j dA - \int_{A_1(t)} \Lambda_{ji} n_j dA,$$

whereas for the vapor, we have

$$\frac{d}{dt} \int_{V(t)} \phi'' \rho'' w_i'' dV = \int_{V(t)} \rho'' \phi'' g_i dV + \int_{A_1(t)} \Lambda_{ji} n_j dA.$$

Adding both sides, we are led to the equation

$$\frac{d}{dt} \int_{V(t)} \rho w_i dV = \int_{V(t)} (\Sigma \phi^\alpha \rho^\alpha g_i) dV - \int_{A(t)} P_{ji} n_j dA. \quad (23)$$

It is seen that the internal, interphase surface tractions described by the tensors $\pm \Lambda_{ij}$ cancel. This, however, should not be interpreted as meaning that the pressure tensor P_{ij} is the negative of the familiar

stress tensor for the liquid from the Navier-Stokes equations. This pressure tensor is associated with the nonequilibrium state depicted in Fig. 4 and must be presumed measured when a two-phase system is deformed. This measurement must be performed on a system of a volumetric scale which is large compared with V . Such a measurement would fully account for all the dissipative mechanisms internal to V . Clearly, one-third of the trace of this tensor is *not* equal to the equilibrium pressure P° , as intimated at the beginning of Section 3. In particular, the interpretation of the entropy balance equation, Section 7, will reveal that the deviator of this non-equilibrium tensor depends on more variables than just the rate of shear deformation in the velocity field $w_i(x_j, t)$, and that the system possesses a bulk viscosity.

From a mathematical point of view it is possible to regard eqn. (23) as a *definition* of the pressure tensor, that is a thermodynamically justified definition of an intensive parameter represented by the field $P_{ij}(x_k, t)$ in our continuum. This definition gives us a prescription for the measurement of P_{ij} , in the same way as the constitutive law for a Newtonian fluid leads to a prescription for the measurement of viscosity which defines the stress tensor. In our case the fluid is inhomogeneous, and the inhomogeneities are distributed in it in a random manner. Thus, it is impossible to guarantee that all samples on which measurements might be performed will reproduce each other, as a pure and homogeneous fluid would. Rather, we must think in terms of an ensemble of replicas which are topologically equivalent and interpret P_{ij} as an *ensemble average*. Alternatively, we may construct regular models of vapor bubbles distributed throughout a liquid and accept that a calculation performed on one of them from first principles, or averaged over an ensemble of regular sys-

tems, constitutes a heuristic approximation to be verified or refuted by experiment.

Equation (23) is also valid in our model-continuum and can be referred to any volume $V(t)$. By the further use of Gauss's theorem we obtain the local form

$$\rho \frac{dw_i}{dt} = - \frac{\partial P_{ji}}{\partial x_j} + \rho g_i \quad (24)$$

Upon reflection we conclude that eqn. (24) could have been written at once for the model continuum. Nevertheless, the preceding derivation is considered useful in that it clarifies the physical meaning of the pressure tensor P_{ij} .

A special form of the momentum equation - the mechanical energy equation - is obtained when the components of the vector equation (24) are multiplied by w_i and added. We thus obtain

$$\rho \frac{d}{dt} (w_i w_i) = \rho g_i w_i - w_i (\partial P_{ji} / \partial x_j) \quad (24a)$$

Evidently, this is not the same as the energy conservation equation embodied in the First Law of thermodynamics.

In order to write the equation of *energy conservation* we again temporarily refer to the representative system V shown in Fig. 4 in its non-equilibrium state. Even though the writing of the equation presents no difficulties, it is useful first to write down the work rate W_b of the body forces bearing in mind the existence of slip between the two centers of the variable masses $m'(t)$ and $m''(t)$, Fig. 3. The basic expression is

$$W_b = \int_{V(t)} g_i (p' d' w'_i + p'' d'' w''_i) dV \quad (25)$$

which we transform to

$$W_b = \int_{V(t)} g_i \left\{ (w_i' - w_i) \phi' \rho' + (w_i'' - w_i) \phi'' \rho'' + (\rho' \phi' + \rho'' \phi'') w_i \right\} dV .$$

This contributes the term

$$W_b = g_i \int_{V(t)} (\Sigma J_i^\alpha + \rho w_i) dV \quad (26)$$

to the energy balance.

We assume that the transfer of heat can be described by the vector field $q_i(x_j, t)$ of heat flux, and recognize that the rate of work performed by the tractions $P_{ji} n_j$ is

$$W_t = \int_{A(t)} P_{ji} n_j w_i dA . \quad (27)$$

Special care must be exercised in writing the expression for internal energy in view of the fact that the centers of mass of the vapor and liquid move with respect to the centers of mass of the element and thus add two terms of internal kinetic energy to the thermodynamic internal energy ρu measured in the accompanying equilibrium state. These terms are equivalent to the kinetic energy of diffusion introduced by de Groot and Mazur ([10]p.28). Thus the energy per unit mass of system V is

$$e = \Sigma \rho^\alpha \phi^\alpha u^\alpha + \Sigma \frac{1}{2} \rho^\alpha \phi^\alpha w_i^\alpha w_i^\alpha \quad (28a)$$

or

$$e = \rho u + \frac{1}{2} \rho w_i w_i + \Sigma \frac{1}{2} \rho^\alpha \phi^\alpha (w_i^\alpha - w_i) (w_i^\alpha - w_i) , \quad (28b)$$

in which the fluxes from eqn. (17) have been introduced explicitly. Bearing this in mind, we can write that

$$\begin{aligned} \frac{d}{dt} \int_{V(t)} \rho \left(u + \frac{1}{2} w_i w_i \right) dV + \frac{d}{dt} \int_{V(t)} \Sigma \frac{1}{2} \rho^{\alpha\alpha} \phi^{\alpha} (w_i^{\alpha} - w_i) (w_i^{\alpha} - w_i) dV = \\ = g_i \int_{V(t)} (\rho w_i + \Sigma J_i^{\alpha}) dV - \int_{A(t)} P_{ji} n_j w_i dA - \int_{A(t)} q_i n_i dA . \end{aligned} \quad (29a)$$

By the use of Reynolds's transport theorem, Gauss's theorem and performing the transition to a point in the continuum, we derive the local form

$$\begin{aligned} \rho \frac{d}{dt} \left(u + \frac{1}{2} w_i w_i \right) + \Sigma J_i^{\alpha} \frac{d}{dt} (w_i^{\alpha} - w_i) = \\ = - \frac{\partial (P_{ji} w_i)}{\partial x_j} - \frac{\partial q_i}{\partial x_i} + g_i (\rho w_i + \Sigma J_i^{\alpha}) . \end{aligned} \quad (29b)$$

In the course of this derivation we made use of the identity

$$\Sigma \frac{1}{2} (w_i^{\alpha} - w_i) (w_i^{\alpha} - w_i) \left(\frac{d}{dt} \rho^{\alpha\alpha} \phi^{\alpha} + \rho^{\alpha\alpha} \phi^{\alpha} \frac{\partial w_i}{\partial x_i} \right) = 0 . \quad (30)$$

Readers familiar with the subject will recall that a more convenient form of eqn. (29b) arises when we subtract from it the equation of mechanical energy, eqn. (24a). This yields

$$\begin{aligned} \rho \frac{du}{dt} = - \frac{\partial q_i}{\partial x_i} - P_{ji} \frac{\partial w_i}{\partial x_j} + g_i \Sigma J_i^{\alpha} + \\ - \Sigma J_i^{\alpha} \frac{d}{dt} (w_i^{\alpha} - w_i) . \end{aligned} \quad (31)$$

A preferred alternative form of energy conservation arises by the elimination of internal energy in favor of the enthalpy

$$h = u + P^{\circ}/\rho . \quad (32)$$

The form of eqn. (32) emphasizes the fact that the enthalpy is a thermodynamic property defined in equilibrium and, like temperature and entropy,

must be measured in the accompanying equilibrium state. The result of this transformation is

$$\rho \frac{d}{dt} \left(h + \frac{1}{2} w_i w_i \right) = - \frac{\partial (P_{ji} - P^\circ \delta_{ij}) w_i}{\partial x_j} - \frac{\partial q_i}{\partial x_i} +$$

$$+ g_i \left(\rho w_i + \sum J_i^\alpha \right) + \frac{\partial P^\circ}{\partial t} - \sum J_i^\alpha \frac{d}{dt} (w_i^\alpha - w_i) . \quad (33)$$

The somewhat unorthodox appearance of the terms $P^\circ \delta_{ij}$ and $\partial P^\circ / \partial t$ compared with standard texts [10,15] is a direct result of the distinction made between the trace P_{ii} of P_{ji} and $3P^\circ$. The often-made assumption that they are equal is not justified in the case of two-phase flow.

7. Entropy production

The last equation which we must introduce is the entropy balance equation, that is the local form of the Gibbs equation (11). This is

$$\frac{ds}{dt} = \frac{1}{T^\circ} \frac{du}{dt} + \frac{P^\circ}{T^\circ} \frac{d(1/\rho)}{dt} - \sum \frac{\mu^{\circ\alpha}}{T^\circ} \frac{d\gamma^\alpha}{dt} . \quad (34a)$$

We now eliminate du/dt , $d(1/\rho)/dt$ and $d\gamma^\alpha/dt$ with the aid of equations (20), (22) and (28b) and obtain

$$\frac{ds}{dt} = - \frac{1}{T^\circ} \frac{\partial q_i}{\partial x_i} + \frac{g_i}{T^\circ} \sum J_i^\alpha - \frac{1}{T^\circ} \sum J_i^\alpha \frac{d}{dt} (w_i - w_i) - \frac{1}{T^\circ} P_{ji} - \delta_{ij} P^\circ \frac{\partial w_i}{\partial x_j} +$$

$$- \sum \frac{\mu^{\circ\alpha}}{T^\circ} \left(\Gamma^\alpha - \frac{\partial J_i^\alpha}{\partial x_i} \right) . \quad (34b)$$

In order to identify the local rate of entropy production, it is necessary to accept the physical hypothesis advanced by proponents of "classical" irreversible thermodynamics [9-11]. This we do in spite of objections raised on grounds of "logic", because we accept it as a statement justified by experience. This is to the effect that the entropy flux is

$$J_i^S = \frac{1}{T^0} \left(q_i - \sum \mu^{\alpha} J_i^{\alpha} \right) . \quad (35)$$

Adding the divergence of J_i^S to both sides of equation (34b), we obtain the classical form of the entropy balance equation

$$\rho \frac{ds}{dt} + \frac{\partial J_i^S}{\partial x_i} = \sigma , \quad (36)$$

where the local volumetric rate of entropy production is

$$\begin{aligned} \sigma = & q_i \frac{\partial(1/T^0)}{\partial x_i} - \frac{1}{T^0} P_{ji} - \delta_{ij} P^0 \frac{\partial w_i}{\partial w_j} + \\ & + \sum J_i^{\alpha} \left[\frac{g_i}{T^0} - \frac{\partial}{\partial x_i} \left(\frac{\mu^{\alpha}}{T^0} \right) \right] - \frac{1}{T^0} \sum J_i^{\alpha} \frac{d}{dt} (w_i^{\alpha} - w_i) - \sum \Gamma^{\alpha} \mu^{\alpha} / T^0 . \end{aligned} \quad (37)$$

The second part of Second Law of thermodynamics imposes the condition that

$$\sigma \geq 0 . \quad (38)$$

It was shown in [9] that the expression for entropy production given in eqn. (37), and resulting from the hypothesis of eqn. (35), is mathematically consistent with the requirement of eqn. (38).

At this stage it is necessary to write down the equation of *conservation of moment of momentum* which will decide whether the pressure tensor P_{ji} is symmetric. It appears that this will depend on whether the steam bubbles perform their rigid-body rotation with or without dissipation. We leave a more detailed analysis of this point to a future date, and concentrate on cases where symmetry of P_{ji} prevails.

As a final step, we separate the pressure tensor P_{ji} into its deviator Π_{ji} and trace $3P^* = P_{ii} \neq 3P^0$ and represent the velocity gradient $\partial w_i / \partial x_j$ in the form of the sum of the symmetric rate-of-strain tensor

$$S_{ij} = \frac{1}{2} \left(\frac{\partial w_i}{\partial x_j} + \frac{\partial w_j}{\partial x_i} \right) = S_{ji} \quad (39a)$$

and the antisymmetric part

$$\Omega_{ij} = \frac{1}{2} \left(\frac{\partial w_i}{\partial x_j} - \frac{\partial w_j}{\partial x_i} \right) = - \Omega_{ji} . \quad (39b)$$

Noting that for a symmetric pressure tensor P_{ij}

$$P_{ij} = P_{ji} \quad (39c)$$

we must have

$$P_{ij} \Omega_{ij} \equiv 0 ,$$

we are led to the form

$$\begin{aligned} \sigma = & \frac{P^\circ - P^*}{T^\circ} \frac{\partial w_i}{\partial x_i} - \Sigma \Gamma^\alpha \mu^{\circ\alpha} / T^\circ + \\ & + q_i \frac{\partial(1/T^\circ)}{\partial x_i} + \Sigma J_i^\alpha \left[\frac{g_i}{T^\circ} - \frac{\partial}{\partial x_i} \left(\frac{\mu^{\circ\alpha}}{T^\circ} \right) \right] - \frac{1}{T^\circ} \Sigma J_i^\alpha \frac{d}{dt} (w_i^\alpha - w_i) + \\ & - \Pi_{ij} S_{ij} / T^\circ . \end{aligned} \quad (40)$$

The preceding form is still inadequate to identify the generalized forces and fluxes which depend on them, because not all terms in it are independent in view of condition (10) which implies conditions (18). In order to take them into account, we introduce the notation

$$\Gamma' = - \Gamma'' = \quad \text{and} \quad J_i' = - J_i'' = J_i , \quad (41)$$

which yields

$$\sigma = \sigma_0 + \sigma_1 + \sigma_2 , \quad (42)$$

where

$$\sigma_0 = \frac{P^\circ - P^*}{T^\circ} \frac{\partial w_i}{\partial x_i} + \Gamma \frac{\mu^{\circ''} - \mu^{\circ'}}{T^\circ} , \quad (42a)$$

$$\sigma_1 = q_i \frac{\partial(1/T^\circ)}{\partial x_i} + J_i \left[\frac{\partial}{\partial x_i} \left(\frac{\mu^{\circ''} - \mu^{\circ'}}{T^\circ} \right) + \frac{1}{T^\circ} \frac{d}{dt} (w_i'' - w_i') \right] , \quad (42b)$$

$$\sigma_2 = - \Pi_{ij} S_{ij} / T^0 . \quad (42c)$$

8. The phenomenological assumptions

The final form of the entropy production rate contained in eqns. (42a-c) allows us to identify physically justified generalized forces and their conjugate fluxes. We make the assumption that our model-continuum is isotropic, and this signifies that the generalized fluxes depend only on forces of equal tensorial rank, given that our second-order tensors are traceless. The first term, σ_0 , contains only products of scalar quantities, the second term, σ_1 , contains scalar products of vectors, and the last term, σ_2 , is the scalar product of two traceless second-order tensors.

In physical terms, this denotes the absence of coupling between the forces and fluxes of the three categories, and eqn. (3) implies

$$\sigma_0 \geq 0 ; \quad \sigma_1 \geq 0 ; \quad \sigma_2 \geq 0 , \quad (43)$$

separately.

We shall assume that linear phenomenological rate-equations are justified in our case. We can represent them by the following homogeneous equations:

$$\frac{\partial w_i}{\partial x_i} = L_{01} \frac{P^0 - P^*}{T^0} + L_{02} \frac{\mu^{0''} - \mu^{0'}}{T^0} , \quad (44a)$$

$$= L_{03} \frac{P^0 - P^*}{T^0} + L_{04} \frac{\mu^{0''} - \mu^{0'}}{T^0} , \quad (44b)$$

$$q_i = L_{11} \frac{\partial(1/T^0)}{\partial x_i} + L_{12} \left[\frac{\partial}{\partial x_i} \left(\frac{\mu^{0''} - \mu^{0'}}{T^0} \right) + \frac{1}{T^0} \frac{d}{dt} (w_i'' - w_i') \right] , \quad (44c)$$

$$J_i = L_{13} \frac{\partial(1/T^0)}{\partial x_i} + L_{14} \left[\frac{\partial}{\partial x_i} \left(\frac{\mu^{0''} - \mu^{0'}}{T^0} \right) + \frac{1}{T^0} \frac{d}{dt} (w_i'' - w_i') \right] , \quad (44d)$$

$$S_{ij} = - L_2 \Pi_{ij} / T^0 . \quad (44e)$$

The forces in eqns. (44a-d) are even, and for this reason the Onsager reciprocal relations impose the conditions

$$L_{02} = L_{03} \quad \text{and} \quad L_{12} = L_{13} . \quad (45)$$

In eqn. (44e) the force Π_{ij} is odd, but its symmetry causes the reciprocal relations to be satisfied automatically.

Equation (44a) shows that the dilatation rate depends on pressure as well as on the difference $\mu^{o''} - \mu^{o'}$ in the chemical potentials of the vapor and liquid. Since only the equilibrium values $\mu^{o''}$ and $\mu^{o'}$ appear in the entropy production term, it is clear that the second effect will exist only in the presence of surface tension, even though the energy stored in the capillary surface has been neglected. Similarly, this generalized force will be different from zero and will affect the normal stress for a given rate of strain in the presence of undercooling or supersaturation. The same remarks apply to the effect on the rate of evaporation Γ and to the influence of the gradient of the difference in chemical potentials on the heat flux, q_i , and the mass flux due to slip, J_i , which is analogous to diffusion in a mixture.

The relative acceleration

$$\frac{d}{dt} (w_i'' - w_i')$$

represents a generalized force generated by slip, which in turn is produced by a combination of buoyancy and change of phase.

In more familiar terms, the thermal conductivity in the absence of mass diffusion is

$$\lambda = - L_{11} / T^{o2} , \quad (46)$$

and the "constitutive relation" for stress is

$$\Sigma_{ij} = - P_{ij} = \mu(1 - \delta_{ij}) S_{ij} + \zeta \delta_{ij} (\partial w_i / \partial x_i) . \quad (47)$$

Here μ plays the same role as the ordinary viscosity, but must be measured in a two-phase system of appropriate configuration, and ζ plays the part of a bulk viscosity.

9. Simplified form

In a drastically simplified version of the theory, we shall completely neglect surface tension or the occurrence of metastable states and assume that $\mu^{\circ'} = \mu^{\circ''}$, as was done in eqn. (11). Without this assumption, the vapor-pressure relation must be modified, at least in principle, it being known that the departures introduced by surface tension and governed by the Kelvin-Helmholtz formula (see ref. [11]) are not very large. It must, however, be realized that an experimentally determined "constitutive law" of the form of eqn. (47) will account for both slip and change of phase. Similarly, a constitutive law derived as an ensemble average should include both effects even if the energy of the capillary layers has not been included explicitly in the energy equation. In any case, all coefficients $L_{\alpha\beta}$ which appear in the rate equation will change their values, at least in principle, as the two-phase flow pattern changes.

We record the simplified form of eqns. (44a-e) and (47) for future reference:

$$\frac{\partial w_i}{\partial x_i} = L_{01} \frac{P^{\circ} - P^*}{T^{\circ}} , \quad (48a)$$

$$q_i = L_{11} \frac{\partial(1/T^{\circ})}{\partial x_i} + L_{12} \frac{1}{T^{\circ}} \frac{d}{dt} (w_i'' - w_i') , \quad (48b)$$

$$J_i = L_{13} \frac{(1/T^\circ)}{x_i} + L_{14} \frac{1}{T^\circ} \frac{d}{dt} (w_i'' - w_i') , \quad (48c)$$

$$S_{ij} = - L_2 \Pi_{ij}/T^\circ . \quad (48d)$$

The "constitutive law"

$$\Sigma_{ij} = \mu(1 - \delta_{ij}) S_{ij} + \zeta \delta_{ij} (w_i/x_i) \quad (49a)$$

with

$$\mu = - \frac{T^\circ}{L_2} , \quad (49b)$$

$$\zeta = \frac{T^\circ}{L_{01}} \quad (49c)$$

remains unaltered, and the entropy-production terms are

$$\sigma_0 = \frac{P^\circ - P^*}{T^\circ} \frac{\partial x_i}{\partial x_i} , \quad (50a)$$

$$\sigma_1 = q_i \frac{\partial(1/T^\circ)}{\partial x_i} + J_i \frac{1}{T^\circ} \frac{d}{dt} (w_i' - w_i'') , \quad (50b)$$

$$\sigma_2 = - \Pi_{ij} S_{ij}/T^\circ . \quad (50c)$$

From eqn. (50a) with $\sigma_0 \geq 0$, we note that

$$P^\circ > P^* \text{ implies } \partial w_i/\partial x_i > 0 \text{ (expansion)} , \quad (51a)$$

whereas

$$P^\circ < P^* \text{ implies } \partial w_i/\partial x_i < 0 \text{ (compression)} . \quad (51b)$$

10. Note on surface tension

At this stage it is useful once again to stress the fact that our Gibbs equations (11) and (34a) do not contain the work of surface tension, even though the distinction between the chemical potentials $\mu^{\circ'}$ and $\mu^{\circ''}$ has been retained. This difference is, evidently, caused by surface tension. The situation is compounded by the fact that in expansion the system

may develop internal constraints and produce metastable states either in the liquid or in the vapor. In such cases the properties of the accompanying equilibrium state will differ from those along the saturation line thus causing complications. We have glossed over all those phenomena for the sake of simplicity, recognizing that their effect on engineering calculations is probably considerably smaller than their inevitable uncertainty.

11. Summary of variables and equations

We leave the further consideration of the case when $\mu^{\circ'} \neq \mu^{\circ''}$ to a future date and concentrate on the simple case represented by eqns. (48a-d) and (50a-c). In this simplified case, the nonequilibrium state is described by the following 25 fields:

. the barycentric velocity	$w_i(x_j, t)$	or 3 scalar variables
. the center-of-mass velocity of the liquid phase	$w_i'(x_j, t)$	or 3 " "
. the center-of-mass velocity of the vapor phase	$w_i''(x_j, t)$	" 3 " "
. the diffusion flux of the liquid phase	$J_i'(x_j, t)$	" 3 " "
. the diffusion flux of the vapor phase	$J_i''(x_j, t)$	" 3 " "
. the symmetric pressure tensor field (P^* , $P_{12}=P_{21}$, $P_{13}=P_{31}$, $P_{23}=P_{32}$)	$P_{ij}(x_k, t)$	" 4 " "
. the heat flux	$q_i(x_j, t)$	" 3 " "
. the void fraction	$\phi(x_i, t)$	" 1 " "
. the thermodynamic pressure	$P^{\circ}(x_i, t)$	" 1 " "
. the thermodynamic temperature	$T^{\circ}(x_i, t)$	" 1 " "
Total:		25 dependent variables

The conservation laws contain additional thermodynamic properties which we have omitted from the above count because their values are determined by the thermodynamic pressure P° , the thermodynamic temperature T° , and the void fraction ϕ . In particular, the following functional relations exist:

$$\rho' = \rho'(T^\circ); \rho'' = \rho''(T^\circ); \rho = \rho(T^\circ, \phi); u = u(T^\circ, \phi);$$

$$h = h(T^\circ, \phi); s = s(T^\circ, \phi); \text{ etc.}$$

To solve for the above twenty-five fields we have at our disposal the following twenty-five partial differential equations:

. relation between center-of-mass velocities, eqn. (16)	3	scalar	equations
. relations between diffusion flux and velocities, eqn. (17)	6	"	"
. conservation of mass, eqn. (22)	1	"	"
. conservation of momentum, eqn. (24)	3	"	"
. conservation of energy, eqn. (28a)	1	"	"
. Clausius-Clapeyron equation ($\mu^{\circ'} = \mu^{\circ''}$ or vapor-pressure line)	1	"	"
. phenomenological relation, eqn. (44e) (stress versus rate of strain)	3	"	"
. phenomenological relation, eqn. (44a) (pressure versus dilatation)	1	"	"
. phenomenological relation, eqn. (44c) (Fourier's law for conduction)	3	"	"
. phenomenological relation, eqn. (44d) (diffusion flux versus slip velocity)	3	"	"
<hr/>			
25 scalar equations			

As expected, the system of equations, though complicated, is a closed one. At least in principle, it is possible to determine all dependent field variables as functions of position and time by solving the full set of partial differential equations, subject to the approximate boundary and initial conditions.

The phenomenological coefficients $L_{\alpha\beta}$ introduced in eqns. (44a-e) represent unknown quantities, because all past experimentation has been carried out in terms of more heuristic theories. Consequently, at this stage, nothing can be said about them, except for repeating the remarks made earlier in Section 6 {after eqn. (23)} and for noting that their values, all functions of the thermodynamic parameters of the accompanying equilibrium state, must vary from flow pattern to flow pattern. Strictly speaking, they must vary even for a class of flows characterized by the same topological configuration, except that here we may expect that a suitably conceived ensemble average will provide us with an adequate approximation.

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Figure Captions

- Fig. 1. An element of small volume V of a two-phase system.
- Fig. 2. Description of thermodynamic state in unified manner.
- Fig. 3. Equivalent dynamic system.
- Fig. 4. Accompanying equilibrium state.
- Fig. 5. Transformation of real space of a two-phase system into a continuum.