Thermodynamic stability of single-phase fluids and fluid mixtures under the influence of gravity

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The equilibrium state attained by a single-phase fluid or fluid mixture when under the influence of gravity and subject to given external constraints differs, as is well known, from its gravity-free counterpart. The thermodynamic stability of single-phase fluids and their mixtures, however, is shown to be uninfluenced by the presence of gravity. Single-phase fluids and their mixtures are thermodynamically stable when under the influence of gravity if, and only if, the gravity-free stability criteria are satisfied everywhere throughout the fluid volume. Gravitational fields, therefore, introduce no additional mechanism whereby spontaneous fluctuations can destabilize an equilibrium state.

INTRODUCTION

The criteria of thermodynamic stability of single-phase fluids and their mixtures were originally derived by Gibbs.[1] In the presence of external fields, an analogous derivation is complicated by the fact that the equilibrium state whose stability is being tested is characterized by spatially varying physical properties. Consequently, there exists no rigorous treatment in the literature on the thermodynamic stability of fluids under the influence of external fields.

Single-component and mixture thermodynamic stability considerations are crucial to the understanding and prevention of a variety of industrial accidents.[2,3] These include catastrophic damage following the mechanical failure or rapid decompression of pressurized vessels for liquefied gas storage,[3,4] water vapor explosions caused by molten aluminum[3,5–7] or smelt spills, sodium–uranium oxide explosions,[8] or cryogen detonation following spills on water.[3,9–12] An investigation into the possible effects of external fields upon the thermodynamic stability of fluids is thus, in principle, of theoretical and practical significance.

In this paper, it is shown that single-phase fluids under the influence of gravitational or centrifugal fields are thermodynamically stable if, and only if, the field-free criteria are satisfied everywhere throughout the system under consideration. Gravitational or centrifugal fields, in other words, are shown not to introduce additional mechanisms whereby spontaneous fluctuations can destabilize an equilibrium state.

The present treatment is limited to gravitational or centrifugal potentials which change over distances which are large when compared to the molecular correlation length. For a gravitational problem, this implies the assumption that it is possible to select a length L, along the direction of gravity, such that physical properties can be considered constant within a "slice" of height L (the slice being perpendicular to the direction of gravity), and such that $Lmg/kT \ll 1$, while at the same time we demand that L be large relative to molecular dimensions (m is a molecular weight, and kT/mg, the characteristic length for variations in the external potential). This means that the conclusions derived here remain valid even in the presence of fields 10^7 times higher than the Earth's gravitational field [if, e.g., we assume a characteristic molecular size of 10 Å, then, for $L = 1\ \mu m$ (i.e., 10^3 molecular lengths), $m = 100$ g/mol, $T = 300$ K, and $g = 10^8$ m/s^2, we obtain $Lmg/kT = 0.004$]. Critical points are possible exceptions to the above statement, since nonlocal effects due to the increase in the correlation length (a phenomenon not considered here) then become important. A detailed analysis of the interaction between gravity and criticality (not including stability) can be found elsewhere.[13–16]

The topic of thermodynamic stability in the presence of gravitational fields, which has not been discussed in the literature, should not be confused with the subject of hydrodynamic stability in gravity-related situations, a venerable field which has attracted the attention of major scientists to situations ranging from the Rayleigh–Bénard problem[17] to the gravitational stability of stars.[18,19] We also mention in this context the work of Dickinson and his colleagues[20,21] on the sedimentation of binary liquid mixtures in the vicinity of a critical point under the action of gravity, an extremely interesting example of the interaction between thermodynamic and hydrodynamic effects.

Because the thermodynamic stability criteria to be derived here are identical to the corresponding field-free counterparts, the present work can be regarded as a proof of the formal independence of thermodynamic stability vis-á-vis the presence of centrifugal or gravitational fields.

PURE FLUIDS

We consider in the first place an isolated pure fluid, in equilibrium under the influence of gravity. As shown by Gibbs,[1] this implies temperature uniformity, a pressure distribution satisfying

$$\frac{dP}{dh} = -mg\rho \tag{1}$$

and a chemical potential distribution satisfying

$$\mu + mgh = \mu^\circ = \text{const}, \tag{2}$$

where h is the relative height with respect to an arbitrary datum, measured along a line parallel to gravity but increasing in the opposite direction, m is the fluid's molecular weight, ρ its number density, μ_0 is the chemical potential at the datum level, and g is the acceleration due to gravity. All intensive properties, therefore, are constant for a given height.

For stable equilibrium we require that all possible variations of the fluid's state which do not alter its entropy lead to an increase in its energy (or, at most, to no change at all in the latter quantity),

$$\Delta(U+\phi)\geqslant 0, \tag{3}$$

$$dS=0, \tag{4}$$

$$dV=0, \tag{5}$$

$$dN=0, \tag{6}$$

where $U=U(S,V,N)$ is the fluid's internal energy, ϕ its potential energy, and Eqs. (4)–(6) describe the constraints imposed on the small variations. Equation (4) simply says that all possible variations of interest here should conserve entropy, whereas Eqs. (5) and (6) imply that the system is closed and surrounded by rigid boundaries. The variations should furthermore be small, and they do not include situations in which parts of the body suffer finite displacements.[1] Expanding energy variations about the equilibrium state in Taylor series,

$$\Delta(U+\phi)=\delta U+\delta\phi+\tfrac{1}{2}\delta^2 U+\tfrac{1}{2}\delta^2\phi+\cdots \tag{7}$$

and taking into account the identical vanishing of $\delta(U+\phi)$ at equilibrium, the stability criterion reads

$$\delta^2 U+\delta^2\phi>0. \tag{8}$$

We now divide the fluid into a large number of horizontal "slices" of height L. If $(Lmg/kT)\ll 1$, the intensive properties can be assumed constant within each slice. Furthermore, we require that L be much larger than the correlation length. Even with $g=10^6$ m/s^2 (i.e., 10^5 times larger than the Earth's gravitational field), $Lmg/kT\sim 10^{-3}$ for $m=10^2$ g/mol, $T=300$ K, and $L=25\,\mu$m, which is of the order of 10^4 molecular lengths, if we take 10 Å as a typical molecular dimension. We therefore write (Fig. 1)

$$\phi=\sum_\gamma \phi_\gamma=mg\sum_\gamma h_\gamma N_\gamma, \tag{9}$$

where N_γ is the number of molecules in slice γ. Therefore,

$$\delta^2\phi=\sum_\gamma \delta^2\phi_\gamma=\left[\sum_\gamma \frac{\partial^2\phi_\gamma}{\partial h_\gamma^2}(\delta h_\gamma)^2+\sum_\gamma \frac{\partial^2\phi_\gamma}{\partial N_\gamma^2}(\delta N_\gamma)^2 + 2\sum_\gamma \frac{\partial^2\phi_\gamma}{\partial N_\gamma \partial h_\gamma}\delta N_\gamma \delta h_\gamma\right]. \tag{10}$$

It follows from Eq. (9) that

$$\frac{\partial^2\phi_\gamma}{\partial h_\gamma^2}=0, \tag{11}$$

$$\frac{\partial^2\phi_\gamma}{\partial N_\gamma^2}=0, \tag{12}$$

$$\frac{\partial^2\phi_\gamma}{\partial h_\gamma \partial N_\gamma}=mg, \tag{13}$$

and therefore

$$\delta^2\phi=2mg\sum_\gamma \delta N_\gamma \delta h_\gamma=0, \tag{14}$$

since, by definition, $\delta h_\gamma=0$. In the light of Eq. (8), the stability criterion now reads

$$\delta^2 U>0 \tag{15}$$

for every possible variation of the fluid's state which does not alter its entropy. We now write, in completely general form,

$$\delta^2 U=\sum_{l=1}^{M}\delta^2 U^l, \tag{16}$$

where the effects of the generic variation (Fig. 2) are computed over M subsystems of fixed height (note that this does not imply constant volume subsystems) which can always be taken to be of such vertical dimensions as to consider all intensive properties constant within each subsystem at equilibrium. Expanding U in terms of its natural variables, we have (Einstein convention implied)

$$\delta^2 U=\sum_{l=1}^{M} U_{ij}^l \delta X_i^l \delta X_j^l \quad (i,j=1,2,3), \tag{17}$$

where X_i^l denotes $S,V,$ or N in subsystem l, and

$$U_{ij}=\frac{\partial^2 U(X_1,X_2,X_3)}{\partial X_i \partial X_j}.$$

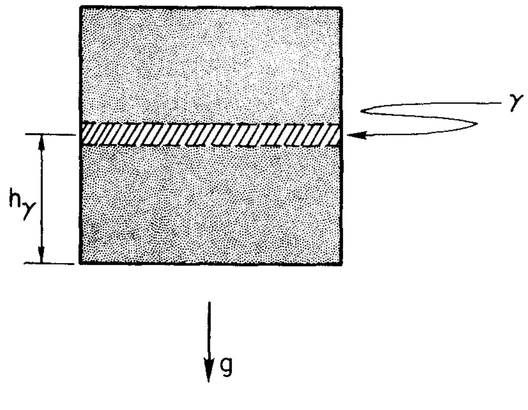

FIG. 1. Subdivision of isolated system into horizontal slices γ.

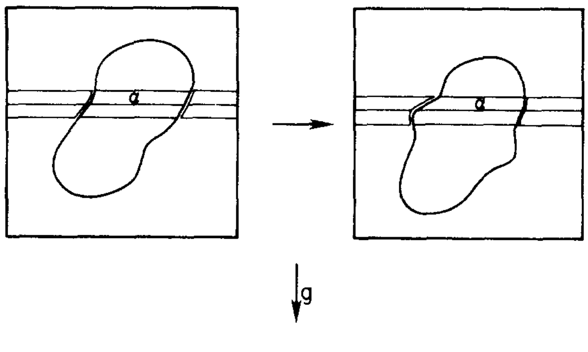

FIG. 2. Construction of elementary horizontal subsystems to study a generic fluctuation.

Because the system is closed and its entropy and volume are constant, we must have

$$\delta X_i^M = -\sum_{l=1}^{M-1} \delta X_i^l \tag{18}$$

and therefore (Einstein convention)

$$\delta^2 U = \sum_{l=1}^{M-1} U_{ij}^l\, \delta X_i^l \delta X_j^l + U_{ij}^M \left[\sum_{l=1}^{M-1} \delta X_i^l\right]\left[\sum_{l=1}^{M-1} \delta X_j^l\right] \tag{19}$$

which differs from Eq. (17) in that all of the δX_i are now independently variable. The quadratic forms can all be diagonalized and we can hence write (see the Appendix for derivation)

$$\begin{aligned}\delta^2 U = {} & (y_{11}^{(0)})_M (\delta Z_1^M)^2 + (y_{22}^{(1)})_M (\delta Z_2^M)^2 \\ & + (y_{33}^2)_M (\delta Z_3^M)^2 \\ & + \sum_{l=1}^{M-1} [(y_{11}^{(0)})_l (\delta Z_1^l)^2 + (y_{22}^{(1)})_l (\delta Z_2^l)^2 \\ & + (y_{33}^{(2)})_l (\delta Z_3^l)^2],\end{aligned} \tag{20}$$

where $(y_{jk}^{(i)})_l$ is the second order partial derivative, with respect to variables j and k ($j,k = 1,2,3$), of the ith Legendre transform of the energy ($y^{(0)}$), in subsystem l [22,23]:

$$\begin{aligned} y^{(i)} &= U - \sum_{j=1}^{i} X_j \left(\frac{\partial U}{\partial X_j}\right)_{X[j]} \\ &= y^{(i)}\left(\frac{\partial U}{\partial X_1},\ldots,\frac{\partial U}{\partial X_i}, X_{i+1},\ldots, X_{n+2}\right).\end{aligned} \tag{21}$$

In the above equation, n is the number of components in the system ($n = 1$ for a pure fluid), and $X[j]$ denotes constancy of all X's except for X_j. Variations in Eq. (20) have the following form:

$$\delta Z_i^l \equiv \delta X_i^l + \sum_{j=i+1}^{3} (y_{ij}^{(i)})_l \delta X_j^l \quad (i = 1,2,3; l = 1,\ldots,M-1), \tag{22}$$

$$\delta Z_i^M \equiv \sum_{l=1}^{M-1} \delta X_i^l + \sum_{j=i+1}^{3} \left[(y_{ij}^{(i)})_M \sum_{l=1}^{M-1} \delta X_j^l\right]. \tag{23}$$

Equations (19)–(23) are mathematical identities. For thermodynamic systems, the partial derivatives $y_{33}^{(2)}$ are identically zero.[22] This is easily shown by choosing any of the possible permutations (S,V,N; S,N,V; etc.) for the ordering of the independent variables of the zeroth-order Legendre transform (i.e., U) and writing down the resulting $y_{33}^{(2)}$ expression. For the ordering (S,V,N), we have

$$y_{33}^{(2)} = \left(\frac{\partial \mu}{\partial N}\right)_{T,P} \tag{24}$$

which is obviously zero. Likewise, for other orderings, $y_{33}^{(2)}$ is always the derivative of an intensive quantity with respect to an extensive quantity, keeping two intensive quantities constant: this is always zero for pure substances. With this simplification, we have, finally,

$$\delta^2 U = \sum_{l=1}^{M} [(y_{11}^{(0)})_l (\delta Z_1^l)^2 + (y_{22}^{(1)})_l (\delta Z_2^l)^2] \tag{25}$$

with variations as per Eqs. (22) and (23). Since each δX_i^l is independently variable, it is necessary in order for $\delta^2 U$ to be positive that

$$\begin{aligned}&(y_{11}^{(0)})_\alpha [\delta X_1^\alpha + (y_{12}^{(1)})_\alpha \delta X_2^\alpha + (y_{13}^{(1)})_\alpha \delta X_3^\alpha]^2 \\ &+ (y_{22}^{(1)})_\alpha [\delta X_2^\alpha + (y_{23}^{(2)})_\alpha \delta X_3^\alpha]^2 \\ &+ (y_{11}^{(0)})_M [\delta X_1^\alpha + (y_{12}^{(1)})_M \delta X_2^\alpha + (y_{13}^{(1)})_M \delta X_3^\alpha]^2 \\ &+ (y_{22}^{(1)})_M [\delta X_2^\alpha + (y_{23}^{(2)})_M \delta X_3^\alpha]^2 > 0\end{aligned} \tag{26}$$

for all α. Since the choice of M is arbitrary, it is necessary in order for $\delta^2 U$ to be positive that the above inequality be satisfied in the particular case when α and M have the same height. When this is the case, $y_{12}^{(1)}$, $y_{13}^{(1)}$, and $y_{23}^{(2)}$, being intensive properties, are equal in α and M. Furthermore, as shown in the Appendix, if two subsystems α and β have equal intensive properties,

$$N^\alpha (y_{11}^{(0)})_\alpha = N^\beta (y_{11}^{(0)})_\beta, \tag{27}$$

$$N^\alpha (y_{22}^{(1)})_\alpha = N^\beta (y_{22}^{(1)})_\beta \tag{28}$$

which means that, when α and M have the same height, Eq. (26) is satisfied, for arbitrary δX_i^α, if, and only if,

$$y_{11}^{(0)} > 0, \tag{29}$$

$$y_{22}^{(1)} > 0. \tag{30}$$

Inequalities (29) and (30) are also necessary conditions of stability when α and M have different heights, since $y_{12}^{(1)}$, $y_{13}^{(1)}$, and $y_{23}^{(2)}$ are now different in α and M, and it is always possible to choose δX_1^α, δX_2^α, and δX_3^α in such a way that δZ_1^α vanishes but δZ_1^M does not (or vice versa), or δZ_2^α vanishes but δZ_2^M does not (or vice versa), where δZ_1^M and δZ_2^M are the third and fourth term in brackets, respectively, in Eq. (26).

Since the choice of α is completely arbitrary, inequalities (29) and (30) must be satisfied throughout the fluid. It follows trivially from Eq. (25) that these conditions are also sufficient with respect to the requirement that $\delta^2 U$ be positive. Inequalities (29) and (30) are simply the familiar gravity-free stability criteria. To see this, we choose any ordering for the independent variables (S,V,N, say), whereupon we have

$$y_{11}^{(0)} = \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,N} = \frac{T}{NC_V},$$

$$y_{22}^{(1)} = \left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial P}{\partial V}\right)_{T,N}$$

and therefore, the inequalities read

$$C_V^{-1} > 0,$$

$$K_T^{-1} > 0.$$

We have thus shown that the necessary and sufficient condition for a pure fluid to be thermodynamically stable when under the influence of gravity is that the gravity-free stability criteria be satisfied everywhere locally throughout the fluid. From this conclusion there follows a futher simplification, which we derive using arguments presented elsewhere[22] in connection with gravity-free stability. It follows from the properties of Legendre transforms[22] that

$$y_{22}^{(1)} = y_{22}^{(0)} - \frac{(y_{12}^{(0)})^2}{y_{11}^{(0)}}. \quad (31)$$

Furthermore, as we approach a limit of stability from a stable region, $y_{11}^{(0)} > 0$ [see Eq. (29)], and $y_{22}^{(0)} > 0$ (since the ordering of the independent variables is arbitrary, and $y_{22}^{(0)}$ becomes $y_{11}^{(0)}$ upon interchanging labels 1 and 2). Therefore, $y_{22}^{(1)}$ always vanishes before $y_{11}^{(0)}$ or $y_{22}^{(0)}$. Thus, the stability criteria reduce to

$$y_{22}^{(1)} > 0 \quad (30)$$

which gives rise to six inequalities, corresponding to 3! ways of ordering the three independent variables (S,V,N). The six inequalities are

$$\left(\frac{\partial P}{\partial V}\right)_{T,N} < 0, \quad (32)$$

$$\left(\frac{\partial T}{\partial S}\right)_{P,N} > 0, \quad (33)$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} > 0, \quad (34)$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{P,S} > 0, \quad (35)$$

$$\left(\frac{\partial T}{\partial S}\right)_{\mu,V} > 0, \quad (36)$$

$$\left(\frac{\partial P}{\partial V}\right)_{\mu,S} < 0. \quad (37)$$

A pure fluid under the influence of gravity is thus thermodynamically stable if, and only if, the six equivalent inequalities (32)–(37) are satisfied everywhere locally throughout said fluid. The above inequalities are equivalent (from a stability point of view) in that they are all satisfied (or violated) simultaneously, a fact which follows from their common origin in the single inequality $y_{22}^{(1)} > 0$, the particular forms of which are obtained via the purely mathematical operation of changing the labels with which the independent variables (S,V,N) are identified.

The above derivation can be generalized to nonuniform fields,[24] in which the body force is a function of position. To illustrate, we consider rigid rotation of a liquid, such as would occur if a tube is placed in a centrifuge and rotated at high speed. Then, we can write

$$\phi = \frac{m\omega^2}{2} \sum_\gamma N_\gamma r_\gamma^2,$$

where ω is the angular velocity and we have divided space into thin concentric cylinders centered at the axis of rotation, with r, the radius measured outwards from the axis of rotation. These cylinders intersect the rotating tube along annular slices, γ. The second order variation then becomes

$$\delta^2\phi = m\omega^2 \sum_\gamma \left(N_\gamma(\delta r_\gamma)^2 + r_\gamma \delta N_\gamma \delta r_\gamma\right)$$

which vanishes identically, since δr_γ is, by definition, zero. Equations (19)–(37) then apply unchanged, provided the horizontal slices in Fig. 2 are replaced by annular slices as described above, within each of which intensive properties, as well as the centrifugal potential $\omega^2 r^2/2$ can be taken as constant.

That a pure fluid must everywhere satisfy the gravity-free stability criteria in order for it to be thermodynamically stable when under the influence of gravity is equivalent to saying that the presence of said external field does not provide for additional mechanisms whereby spontaneous fluctuations can destabilize an equilibrium state. The irrelevance of gravity with respect to thermodynamic stability, though formally demonstrated in the preceding discussion, is more clearly illustrated by considering the simplest elementary fluctuation, namely, one involving just two subsystems (α,β) of the type depicted in Fig. 2. In this case, since the overall system is isolated, we must have $\delta X_i^\alpha = -\delta X_i^\beta$, and, therefore,

$$\delta^2 U = (U_{ij}^\alpha + U_{ij}^\beta)\delta X_i^\alpha \delta X_j^\alpha \quad (38)$$

or equivalently,

$$\delta^2 U = a_{11}\left[\delta X_1^\alpha + \sum_{j=2}^{3} \frac{a_{1j}}{a_{11}} \delta X_j^\alpha\right]^2 + b_{22}\left[\delta X_2^\alpha + \frac{b_{23}}{b_{22}} \delta X_3^\alpha\right]^2 + c_{33}(\delta X_3^\alpha)^2, \quad (39)$$

where (see the Appendix)

$$a_{ij} = U_{ij}^\alpha + U_{ij}^\beta, \quad (40)$$

$$b_{ij} = a_{ij} - \frac{a_{1i}a_{1j}}{a_{11}} \quad (i,j \geqslant 2), \quad (41)$$

$$c_{ij} = b_{ij} - \frac{b_{2i}b_{2j}}{b_{22}} \quad (i,j \geqslant 3). \quad (42)$$

Since all $\delta X_i^\alpha (i = 1,2,3)$ are independently variable, it is necessary and sufficient for stability that

$$a_{11} > 0, \quad (43)$$

$$b_{22} > 0, \quad (44)$$

$$c_{33} > 0. \quad (45)$$

The ordering of the variables being irrelevant, we investigate the consequences that follow from the above inequalities for the particular choice $(1 = S,\ 2 = V,\ 3 = N)$. Inequality (43), upon rearrangement, then reads

$$\frac{1}{c_v^\beta} + \frac{r}{c_v^\alpha} > 0 \quad (r \equiv N^\beta/N^\alpha), \quad (46)$$

where we have used the fact that temperature is uniform throughout the fluid, and the notation c_v^ϵ denotes the isochoric specific heat (per molecule) in subsystem ϵ. Now, if α and β have the same height (or equivalently, in the absence of gravity), Eq. (46) implies $c_v^{-1} > 0$. If, however, α and β have different heights, and in the presence of gravity, c_v being, in general, a function of pressure, is different in both subsystems. Consequently, the above relationship could be satisfied even if c_v^α or c_v^β violated the requirement $c_v^{-1} > 0$. But the subsystem which violates the condition $c_v^{-1} > 0$ cannot possibly participate in fluctuations involving other subsystems having its same height, nor can it participate in fluctuations involving other subsystems of different height which also violate the condition $c_v^{-1} > 0$, for either of these possibilities would violate Eq. (46). Since the choice of subsystems and fluctuations is arbitrary, the criterion $a_{11} > 0$ can only be satisfied if $c_v^{-1} > 0$ everywhere throughout the fluid: gravity does not alter this condition of stability.

Inequality (44), after rearrangement, can be shown to read

$$\left(\frac{\rho}{K_T}\right)^\beta + r\left(\frac{\rho}{K_T}\right)^\alpha > \left[\frac{-rT}{c_v^\alpha + rc_v^\beta}\right]\cdot\lambda^2, \tag{47}$$

where

$$\lambda = \left[\left(\frac{\partial P}{\partial T}\right)_\rho\right]^\alpha - \left[\left(\frac{\partial P}{\partial T}\right)_\rho\right]^\beta. \tag{48}$$

Using an argument identical to the one put forth in connection with inequality (46) (note that λ vanishes for equal height subsystems), and invoking the fact that $c_v > 0$ throughout, it follows that Eq. (47) can only be satisfied for an arbitrary choice of subsystems if $K_T > 0$ throughout the fluid, as in the gravity-free case. From the previous discussion and Eq. (31), it follows that $c_v > 0$ is a necessary (but not sufficient) condition for stability, whereas $K_T > 0$ is both, as in the gravity-free case.

Finally, it remains to be shown that c_{33}, which vanishes identically in the gravity-free case, does not lead [via inequality (45)] to additional stability criteria in the presence of gravity. To this end, we invoke Eqs. (40)–(42); upon substitution into Eq. (45), and after considerable rearrangement, the latter inequality can be expressed as

$$\frac{\Gamma}{K_T^\alpha K_T^\beta} \geqslant \frac{-T}{c_v^\alpha + rc_v^\beta}\left\{\Lambda^2 + \left(\Delta\left[v\left(\frac{\partial P}{\partial T}\right)_v\right] - \Delta s\right)\Delta\left(\frac{\partial p}{\partial T}\right)_v \cdot \left[\frac{1}{K_T^\beta} + \frac{r}{K_T^\alpha}\right]\cdot\Omega\right\}, \tag{49}$$

where v and s are specific quantities, and

$$\Gamma = \frac{\rho^\alpha}{\rho^\beta} + \frac{\rho^\beta}{\rho^\alpha} - 2 \quad (\geqslant 0), \tag{50}$$

$$\Lambda = \left\{\Delta\left[v\left(\frac{\partial P}{\partial T}\right)_v\right] - \Delta s\right\}\left\{\frac{\rho^\beta}{K_T^\beta} + r\frac{\rho^\alpha}{K_T^\alpha}\right\}^{1/2} - \Delta\left(\frac{\partial P}{\partial T}\right)_v \cdot \left[\frac{1}{\rho^\beta K_T^\beta} + \frac{r}{\rho^\alpha K_T^\alpha}\right]^{1/2}, \tag{51}$$

$$\Omega = 2\left\{1 + r\Gamma\left[\left(\frac{K_T^\alpha}{K_T^\beta}\right)^{1/2} + r\left(\frac{K_T^\beta}{K_T^\alpha}\right)^{1/2}\right]^{-2}\right\}^{1/2} - 2 \quad (>0), \tag{52}$$

$$\Delta\psi = \psi^\beta - \psi^\alpha \tag{53}$$

which implies that Eq. (45) is trivially satisfied if

$$\left\{\Delta\left[v\left(\frac{\partial P}{\partial T}\right)_v\right] - \Delta s\right\}\Delta\left(\frac{\partial P}{\partial T}\right)_v > 0. \tag{54}$$

Thus, if Eq. (54) were satisfied without invoking any additional conditions other than the ones derived from Eqs. (43) and (44), it would then follow that no new stability criteria result from the requirement that $\delta^2 U > 0$ for an arbitrary fluctuation involving two subsystems, when the latter are acted upon by the influence of gravity. This is easy to prove. Noting that Δ denotes variations in properties subject to the restriction that the temperature be unchanged, we write, with pressure as an independent variable,

$$\Delta\left[v\left(\frac{\partial P}{\partial T}\right)_v\right] = v\left\{\left[\frac{\partial}{\partial P}(\alpha_p/K_T)\right]_T - \alpha_p\right\}\delta P + O(\delta P)^2, \tag{55}$$

$$\Delta s = -v\alpha_p \delta P + O(\delta P)^2, \tag{56}$$

$$\Delta\left(\frac{\partial P}{\partial T}\right)_v = \left[\frac{\partial}{\partial P}(\alpha_p/K_T)\right]_T \delta P + O(\delta P)^2, \tag{57}$$

where α_p is the thermal expansion coefficient. Invoking Eq. (1), the above expansions can be combined to yield

$$\left\{\Delta\left[v\left(\frac{\partial P}{\partial T}\right)_v\right] - \Delta s\right\}\Delta\left(\frac{\partial P}{\partial T}\right)_v = \rho^\alpha (mg)^2\left[\frac{\partial(\alpha_p/K_T)}{\partial P}\right]_T^2 (\delta h)^2 + O(\delta h)^3. \tag{58}$$

Therefore, inequality (45) is trivially satisfied, and does not imply any new stability criterion. Algebraic manipulations leading from Eqs. (44) and (45) to Eqs. (47) and (49), respectively, are outlined in the Appendix.

FLUID MIXTURES

The preceding treatment can be straightforwardly extended to fluid mixtures. In the first place, we replace Eq. (2) by its mixture analog,[1]

$$\mu_i + m_i gh = \mu_i^0 = c_i$$

with temperature uniformity and Eq. (1) unchanged. Conservation of mass [i.e., Eq. (6)] becomes

$$dN_i = 0, \tag{60}$$

where i denotes the ith mixture component ($i = 1,...,n$). It is clear that for nonreacting mixtures, Eq. (18) applies unchanged to every component,

$$\delta N_i^M = \sum_{l=1}^{M-1} \delta N_i^l \quad (i = 1,...,n) \tag{61}$$

and so, therefore, does Eq. (20), with additional terms up to $y^{(n+1)}_{n+2,n+2}(\delta Z_{n+2})^2$. Likewise, Eqs. (22) and (23) are unchanged, except for the fact that i now runs from 1 to $n+2$, $(S,V,N_1,...,N_n)$, and the upper bound in the j summation is $n+2$. Similarly, it is easy to show that $y^{(n+1)}_{n+2,n+2}$ vanishes identically; Eq. (25) therefore remains unchanged in form, but contains additional terms, up to $y^{(n)}_{n+1,n+1}(\delta Z_{n+1})^2$.

Next, we replace Eqs. (27) and (28) by the identity

$$N^\alpha [y^{(j)}_{j+1,j+1}]_\alpha = N^\beta [y^{(j)}_{j+1,j+1}]_\beta \quad (j \leqslant n) \tag{62}$$

which can be proved by writing $y^{(j)}_{j+1,j+1}$ as a ratio of determinants[22]:

$$y^{(j)}_{j+1,j+1} = \begin{vmatrix} y^{(0)}_{11} & \cdots & y^{(0)}_{1,j+1} \\ \vdots & & \vdots \\ y^{(0)}_{j+1,1} & \cdots & y^{(0)}_{j+1,j+1} \end{vmatrix} \cdot \begin{vmatrix} y^{(0)}_{11} & \cdots & y^{(0)}_{1j} \\ \vdots & & \vdots \\ y^{(0)}_{j1} & \cdots & y^{(0)}_{jj} \end{vmatrix}^{-1} . \tag{63}$$

Now, the generic element in the above determinants has the form

$$y^{(0)}_{kl} = \left(\frac{\partial \xi_k}{\partial X_l}\right)_{X[l]} \quad (k,l \leqslant j+1), \tag{64}$$

where ξ_k is the intensive property conjugate to X_k,

$$\xi_k = \left(\frac{\partial U}{\partial X_k}\right)_{X[k]} .$$

We will now show that $y^{(0)}_{kl}$ can always be expressed as the product of N^{-1} times an intensive property. If X_l is a molecule number, it follows that [since all other molecule numbers are held constant in Eq. (64), along with S and V] $y^{(0)}_{kl}$ can be expressed as

$$y^{(0)}_{kl} = N^{-1}(1 - z_l)\left(\frac{\partial \xi_k}{\partial z_l}\right)_{S,V,N[l]} , \tag{65}$$

where z_l is a mole fraction, and where the product $(1 - z_l)(\partial \xi_k / \partial z_l)$ is an intensive property. If, on the other hand, X_l is S or V, we have [since all N_i are now held constant in Eq. (64)]

$$y^{(0)}_{kl} = N^{-1}\left(\frac{\partial \xi_k}{\partial s}\right)_{v,z_1,...,z_n} \tag{66}$$

for $X_l = S$, and

$$y^{(0)}_{kl} = N^{-1}\left(\frac{\partial \xi_k}{\partial v}\right)_{s,z_1,...,z_n} \tag{67}$$

for $X_l = V$. The partial derivative in Eqs. (66) and (67) is, once again, an intensive property. Equations (65)–(67) imply that the term N^{-1} can be factored out of both determinants in Eq. (63), to obtain

$$y^{(j)}_{j+1,j+1} = N^{-1}|D^{(0)}_{j+1}| \cdot |D^{(0)}_j|^{-1}, \tag{68}$$

where $|D^{(0)}_m|$ denotes the mth order determinant with elements $Ny^{(0)}_{kl}$ which, according to Eqs. (65)–(67), are all intensive properties. Thus, Eq. (62) is indeed satisfied whenever α and β have equal heights.

Using arguments identical to those invoked in the case of pure fluids, therefore, it follows that a single-phase fluid mixture under the influence of gravity is thermodynamically stable if, and only if, the gravity-free stability criteria are satisfied everywhere throughout the mixture. The gravity-free criteria for an n-component mixture can be expressed in Legendre transform notation as[22]

$$y^{(n)}_{n+1,n+1} > 0 \tag{69}$$

of which Eq. (30) is obviously a particular case. Specific examples of the application of Eq. (69) to binary and ternary mixtures can be found elsewhere.[22]

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APPENDIX

In order to prove Eq. (20), we consider the general quadratic form Q,

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{n} u_{ij} x_i x_j . \tag{A1}$$

If u_{11} does not vanish, we can always write

$$Q = u_{11}\left[x_1^2 + 2\frac{x_1}{u_{11}} \sum_{j=2}^{n} u_{1j} x_j\right] + \sum_{i=1}^{n} \sum_{j=2}^{n} u_{ij} x_i x_j \tag{A2}$$

or, equivalently,

$$Q = u_{11}\left[\left(x_1 + \sum_{j=2}^{n} \frac{u_{1j}}{u_{11}} x_j\right)^2 - \left(\sum_{j=2}^{n} \frac{u_{1j}}{u_{11}} x_j\right)^2\right] + \sum_{i=2}^{n}\sum_{j=2}^{n} u_{ij} x_i x_j, \quad \text{(A3)}$$

which, upon rearrangement, reads

$$Q = u_{11}\left[x_1 + \sum_{j=2}^{n} \frac{u_{1j}}{u_{11}} x_j\right]^2 + \sum_{j=2}^{n}\sum_{k=2}^{n} u'_{jk} x_j\, x_k, \quad \text{(A4)}$$

where

$$u'_{jk} = u_{jk} - \frac{u_{1j} u_{1k}}{u_{11}}. \quad \text{(A5)}$$

The double summation on the right-hand side of Eq. (A4) is a quadratic form, formally identical to Q. We may thus apply the procedure leading from Eqs. (A1) to (A4) to it, and, successively, to the remaining quadratic forms, to obtain finally,

$$Q = u_{11}\left[x_1 + \sum_{j=2}^{n}\left(\frac{u_{1j}}{u_{11}}\right)x_j\right]^2 + u'_{22}\left[x_2 + \sum_{j=3}^{n}\left(\frac{u'_{2j}}{u'_{22}}\right)x_j\right]^2 + u''_{33}\left[x_3 + \sum_{j=4}^{n}\left(\frac{u''_{3j}}{u''_{33}}\right)x_j\right]^2 + \cdots + u^{n-1}_{nn} x_n^2, \quad \text{(A6)}$$

where

$$u'_{ij} = u_{ij} - \frac{u_{1i} u_{1j}}{u_{11}}, \quad i,j \geqslant 2, \quad \text{(A7)}$$

$$u''_{ij} = u'_{ij} - \frac{u'_{2i} u'_{2j}}{u'_{22}}, \quad i,j \geqslant 3, \quad \text{(A8)}$$

$$u^{n-1}_{ij} = u^{n-2}_{ij} - \frac{u^{n-2}_{n-1,i} u^{n-2}_{n-1,j}}{u^{n-2}_{n-1,n-1}}, \quad i,j \geqslant n \quad \text{(A9)}$$

and where the validity of Eq. (A6) is only limited by the requirement

$$u^{i}_{i+1,i+1} > 0 \quad (0 \leqslant i \leqslant n-1) \quad \text{(A10)}$$

with the notation $u_{11} = u^0_{11}$ implied. We now relate Eq. (A1) to the $\delta^2 U$ expansion through the correspondence

$$u_{ij} \to U_{ij}, \quad \text{(A11)}$$

$$x_i \to \delta X_i. \quad \text{(A12)}$$

Invoking the properties of Legendre transforms,[22] we can write

$$y^{(1)}_{1j} = \frac{U_{1j}}{U_{11}} \quad (j \neq 1), \quad \text{(A13)}$$

$$y^{(1)}_{ij} = U_{ij} - \frac{U_{1i} U_{1j}}{U_{11}} \quad (i,j \geqslant 2), \quad \text{(A14)}$$

$$y^{(2)}_{ij} = y^{(1)}_{ij} - \frac{y^{(1)}_{2i} y^{(1)}_{2j}}{y^{(1)}_{22}} \quad (i,j \geqslant 3), \quad \text{(A15)}$$

whereupon Eq. (A6) now reads

$$Q = y^{(0)}_{11}[\delta X_1 + y^{(1)}_{12}\delta X_2 + y^{(1)}_{13}\delta X_3]^2 + y^{(1)}_{22}[\delta X_2 + y^{(2)}_{23}\delta X_3]^2 + y^{(2)}_{33}(\delta X_3)^2 \quad \text{(A16)}$$

which agrees with Eqs. (20), (22), and (23).

Next, we prove Eqs. (27) and (28). In the former case, we note that $y^{(0)}_{11}$ can either equal T/NC_v, $-N^{-1}(\partial P/\partial v)_s$, or $(\partial \mu/\partial N)_{S,V}$. That Eq. (27) is satisfied in the former two cases is obvious (α and β have the same height). In the latter case, we invoke the identity

$$\left(\frac{\partial \mu}{\partial N}\right)_{S,V} = \frac{1}{N}\left\{\frac{v}{K_T} + \frac{T}{c_v}\left(\frac{v\alpha_p}{K_T} - s\right)^2\right\}, \quad \text{(A17)}$$

whereupon Eq. (27) follows immediately. As for Eq. (28), $y^{(1)}_{22}$ can be written in six different ways (i.e., 3! permutations of variables 1,2,3) which after rearrangement read

$$-\left(\frac{\partial P}{\partial V}\right)_{T,N} = N^{-1}\left(\frac{1}{vK_T}\right), \quad \text{(A18)}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = N^{-1}\left(\frac{v}{K_T}\right), \quad \text{(A19)}$$

$$\left(\frac{\partial T}{\partial S}\right)_{P,N} = N^{-1}\left(\frac{T}{c_p}\right), \quad \text{(A20)}$$

$$\left(\frac{\partial \mu}{\partial N}\right)_{P,S} = N^{-1}\left(\frac{Ts^2}{c_p}\right), \quad \text{(A21)}$$

$$\left(\frac{\partial T}{\partial S}\right)_{\mu,V} = N^{-1}\left[\frac{cp}{T} + \frac{s^2 K_T}{v} - 2s\alpha_p\right]^{-1}, \quad \text{(A22)}$$

$$-\left(\frac{\partial P}{\partial V}\right)_{\mu,S} = N^{-1}\left[vK_T + \frac{c_p}{T}\left(\frac{v}{s}\right)^2 - \frac{2v^2\alpha_p}{s}\right]^{-1} \quad \text{(A23)}$$

from which Eq. (28) follows trivially (α and β have equal heights).

Finally, we outline the derivation of Eqs. (47) and (49) from Eqs. (44) and (45). In the former case, we start by writing

$$b_{22} = U^{\alpha}_{22} + U^{\beta}_{22} - \frac{[U^{\beta}_{12} + U^{\alpha}_{12}]^2}{U^{\alpha}_{11} + U^{\beta}_{11}} \quad \text{(A24)}$$

or, in Legendre transform notation,

$$b_{22} = (y^{(0)}_{22})_\alpha + (y^{(0)}_{22})_\beta - \frac{[(y^{(0)}_{12})_\alpha + (y^{(0)}_{12})_\beta]^2}{(y^{(0)}_{11})_\alpha + (y^{(0)}_{11})_\beta} \quad \text{(A25)}$$

which, in the light of Eqs. (A13) and (A14), can also be written as

$$b_{22} = (y^{(1)}_{22})_\alpha + (y^{(1)}_{22})_\beta + \frac{(y^{(0)}_{11})_\alpha (y^{(0)}_{11})_\beta}{(y^{(0)}_{11})_\alpha + (y^{(0)}_{11})_\beta}[(y^{(1)}_{12})_\beta - (y^{(1)}_{12})_\alpha]^2. \quad \text{(A26)}$$

Since the ordering of the independent variables is clearly irrelevant, Eq. (44) must be true for any of the 3! ways in which (S,V,N) can be ordered. To illustrate the physical meaning of Eq. (44), we choose the ordering $[1 = S, 2 = V, 3 = N]$, and write (A = Helmholtz energy)

$$y^{(1)}_{22} = A_{VV} = -\left(\frac{\partial P}{\partial V}\right)_{T,N} = \frac{1}{VK_T}, \quad \text{(A27)}$$

$$y^{(1)}_{12} = A_{TV} = A_{VT} = -\frac{\alpha_p}{K_T}, \quad \text{(A28)}$$

$$y_{11}^{(0)} = U_{SS} = \frac{T}{NC_v}. \tag{A29}$$

Equation (47) then follows immediately upon substitution of Eqs. (A27), (A28), and (A29) into Eq. (A26), and invoking the starting inequality (44).

In order to derive Eq. (49) from Eq. (45), we invoke Eqs. (41) and (42), and rewrite Eq. (45) as

$$\left(a_{33} - \frac{a_{13}^2}{a_{11}}\right) - \frac{(a_{23} - a_{12}a_{13}/a_{11})^2}{(a_{22} - a_{12}^2/a_{11})} > 0. \tag{A30}$$

The quantities in brackets can be expressed, after rearrangement, as follows:

$$a_{33} - \frac{a_{13}^2}{a_{11}} = \left\{\left(\frac{1}{\rho K_T}\right)^\beta + \frac{r}{(\rho K_T)^\alpha} + \frac{rT}{c_v^\alpha + rc_v^\beta}\left[\Delta\left(\frac{v\alpha_p}{K_T} - s\right)\right]^2\right\}(N^\beta)^{-1}, \tag{A31}$$

$$a_{23} - \frac{a_{12}a_{13}}{a_{11}} = \left\{-\left[\left(\frac{1}{K_T}\right)^\beta + \frac{r}{(K_T)^\alpha}\right] - \frac{rT}{c_v^\alpha + rc_v^\beta}\left[\Delta\left(\frac{v\alpha_p}{K_T} - s\right)\right] \times\left[\Delta\left(\frac{\alpha_p}{K_T}\right)\right]\right\}(N^\beta)^{-1}, \tag{A32}$$

$$a_{22} - \frac{a_{12}^2}{a_{11}} = \left\{\left(\frac{\rho}{K_T}\right)^\beta + r\left(\frac{\rho}{K_T}\right)^\alpha + \frac{rT}{c_v^\alpha + rc_v^\beta}\left[\Delta\left(\frac{\alpha_p}{K_T}\right)\right]^2\right\}(N^\beta)^{-1}. \tag{A33}$$

Equation (49) then follows after straightforward, if tedious, algebra.

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[24] The author is grateful to a referee for pointing this out.