

Negative Entropy, Energy, and Heat Capacity in Connection with Surface Tension: Artifact of a Model or Real?

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Received January 14, 1987

It is only by *neglecting* self-adsorption (a treatment referred to as “pure-energy,” PE) that one gets textbook thermodynamics of a surface, based upon the tension \mathcal{S} as a function of temperature T , and one finds negative specific heat for hot water. Any lower critical point and PE provides the other exciting negatives: nicotine-and-water is an example. In order to *include* adsorption, \mathcal{S} must be known in terms of T and chemical potentials as *independent* variables; this forces measurement of the tension of curved menisci. Will the minus signs remain?

1. MOTIVATIONS

1.1. Pure Energy (PE) or Not?

Two systems stand out as unusually and similarly simple, in each having but two dimensions, only one of which is intensive, in standard, elementary thermodynamics (e.g., Zemansky and Dittman, 1981): these are blackbody radiation, and a surface between two fluids. For Planck’s blackbody radiation, the entropy S is a function $S(U, V)$ of energy U and volume V only, with no independent coordinate to signify number of photons N —such a third coordinate can be usefully managed to discuss, for example, what astrophysicists call Comptonization, but that is another story. The usual version of Planck’s story is in a context where the chemical potential μ for photons is zero, which does validate the simple account.²

For the surface, entropy S is again presented as a function of energy U and now area A only, in the treatment I call here the model of *pure*

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²Departing from $\mu = 0$ for light is a topic in my unpublished notes, Thermodynamics for Beginners and Mathematicians.

energy, *PE*. Yet thermodynamics of either adjacent bulk informs us that here the chemical potential is *not* usually zero, hence that *PE* may be oversimple. Accordingly, I sketch a more complete story using $S(U, A, N)$, parallel to a bulk's $S(U, V, N)$. Here N is an amount of chemical associated with the surface *per se*; for lack of a better term, I call this complication "self-adsorption." *Are the extra terms needed to treat N indeed negligible, justifying *PE*, or, if not, just what more needs measurement to properly organize the thermodynamics of a surface empirically?*

I will find no reason to regard the extra terms negligible; that will complicate the usual study of $\mathcal{S}(T)$ to a study of $\mathcal{S}(T, \mu)$, the surface tension \mathcal{S} as a function of temperature T and chemical potential μ as independent variables. Since for flat surfaces T and μ are *dependent*, this will force us to generalize to curved surfaces.

Indeed, chemical potentials appear very much in this way already in Gibbs (1948). The main point here, then, is the negative quantities suggested by *PE*, and whether these will remain in the full treatment.

1.2. Inequalities

The root of thermodynamics is the second law, an inequality; hence, our deepest concern is with inequalities.³ From Boltzmann's statistical interpretation of entropy S as a sum $\sum p \ln(1/p)$ of nonnegative terms, we have

$$S \geq 0 \tag{1}$$

an inequality simpler than the second law. But this positivity of entropy applies to a "complete system". Is (1) yet true for that *part* of entropy due to a surface, or may the impossibility of parting the surface physically from bulks allow *the entropy s per unit area to sometimes be negative?*

Is the energy u per unit area sometimes negative?

A standard argument (given later) which uses the second law informs us that, for the function S that gives the entropy of a bulk chemical system, the body

$$x^0 \leq S(x^1, \dots, x^v)$$

where x^1, \dots, x^v are v independent additive extensive variables, is convex. This is usually called "stability"; I will use "convexity." *Is there an analogous fact of convexity for surfaces?*

³Indeed, if the equations be viewed as identities, they are without content: as we may always doubt our model, this is of course an overstatement!

1.3. Water, Nicotine

I will show that assuming PE for the interface between hot water and steam is *not* consistent with convexity. And near a lower critical point, PE will also give negative entropy and energy per unit area; an example is nicotine and water.

1.4. Flatland?

Were we to imagine a surface as a universe complete unto itself, “Flatland” (Abbott, 1953), then entropy and energy *would* be positive, and even the proof of convexity for bulks would go through, with “area” in place of “volume.” Examples where these inequalities are reversed would then reject Flatland even if the thermodynamic treatment of a surface in formal mathematical isolation might otherwise suggest it.

If only the 2-sphere leading to (15) below is replaced by a sphere of some other dimension, the terms “volume” and “area” here could be taken as referring to any adjacent dimensions; hence our topic bears on whether or not our own universe can be modeled as a surface between one-higher-dimensional “bulks”—a first step toward fractal models. The possibility of telltale negative quantities shows a way to distinguish Flatland-like models from others. Yet where these negatives appear—possibly near a lower critical point between two fluids—may be so unusual as to put such “telldales” out of reach for models of our own universe.

2. THE MODEL

Quantities pertaining to the surface will be unsubscripted; hence, total quantities are subscripted “tot”; 1 and 2 refer to the two bulks:

$$\begin{aligned} S_{\text{tot}} &= S_1 + S_2 + S \\ N_{\text{tot}} &= N_1 + N_2 + N \\ U_{\text{tot}} &= U_1 + U_2 + U \\ V_{\text{tot}} &= V_1 + V_2 \end{aligned} \tag{2}$$

(no volume being assigned to the surface, which “instead” has area A) and

$$\begin{aligned} dS_1 &= \frac{1}{T} dU_1 + \frac{P_1}{T} dV_1 - \frac{\mu}{T} dN_1 \\ dS_2 &= \frac{1}{T} dU_2 + \frac{P_2}{T} dV_2 - \frac{\mu}{T} dN_2 \\ dS &= \frac{1}{T} dU - \frac{\mathcal{F}}{T} dA - \frac{\mu}{T} dN \end{aligned} \tag{3}$$

the P 's are pressures; other symbols are as already set. Each N is easily generalized to a list N^i or vector of c independent "chemicals."

2.1. Justification

Associated with a 1-2 difference in pressure, I have drawn the surface in Fig. 1 curved. I imagine the edge of this surface to adhere to some ring, which is to provide a countervailing force. Figure 1 suggests bulk 1, "surface," and bulk 2 separated by two thin waists, these waists symbolizing the possibility of arbitrarily low conductances connecting the hence almost separate parts. I wish to begin this way, so that we may imagine either 1, or surface, or 2 to attain a private equilibrium, independent of the other two parts, characterized, then, by independent functions $S_1(U_1, V_1, N_1)$, $S(U, A, N)$, $S_2(U_2, V_2, N_2)$, although the middle, "pure surface" is something of a fiction; indeed, the middle part should really have "a little $U_1, V_1, N_1, U_2, V_2,$ and N_2 also." I wish such separation, so that at first, we may consider nine independent partial derivatives

$$\begin{aligned} \frac{1}{T_1} &= \left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1}, & \frac{1}{T} &= \left(\frac{\partial S}{\partial U} \right)_{A, N}, & \frac{1}{T_2} &= \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} \\ \frac{P_1}{T_1} &= \left(\frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1}, & -\frac{\mathcal{P}}{T} &= \left(\frac{\partial S}{\partial A} \right)_{U, N}, & \frac{P_2}{T_2} &= \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2, N_2} \\ -\frac{\mu_1}{T_1} &= \left(\frac{\partial S_1}{\partial N_1} \right)_{U_1, V_1}, & -\frac{\mu}{T} &= \left(\frac{\partial S}{\partial N} \right)_{U, V}, & -\frac{\mu_2}{T_2} &= \left(\frac{\partial S_2}{\partial N_2} \right)_{U_2, V_2} \end{aligned}$$

But then I wish to imagine *large* conductances for energy and for chemicals, installed between the chambers; e.g., let the walls be made of a "highly conducting metal," and let the trapped chemical(s) easily diffuse through these walls, so that $T_1 = T_2 = T$ and $\mu_1 = \mu_2 = \mu$, while yet there is a jump

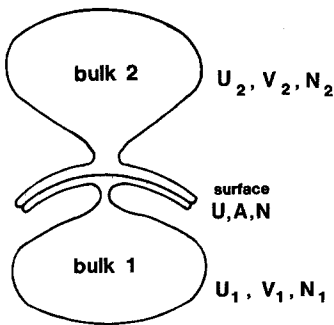


Fig. 1. Waists

in pressure,

$$\left(\frac{\partial S_1}{\partial V_1}\right)_{U_1, N_1} \neq \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2, N_2}$$

because pure transfer of volume between 1 and 2 is forbidden by the geometry linking dV_1 , dV_2 , and dA . My newly installed large conductances destroy the need for narrow waists, which served only to illuminate the prior independent meaning of T_1 , T_2 , and T , and the possibility of having them unequal, as a context in which the specialization of equation (3) to a uniform $T = T_1 = T_2$ is physically clear; similarly for $\mu = \mu_1 = \mu_2$: I have dwelled on this point because having a jump $P_1 \neq P_2$ in the pressure while yet temperature and chemical potential are taken exactly uniform looks funny! But my story of the two waists has for the moment reconciled me with this conventional asymmetry between P on the one hand and T and μ on the other.

I now present a derivation of the usual relation

$$P_1 - P_2 = 2\mathcal{F}/r \tag{4}$$

where r is the radius of curvature of the surface, based only on the present thermodynamic model, that is, this derivation makes no direct reference to Newtonian force. Expressions (2) and the T , μ uniformity of (3) give us

$$dS_{\text{tot}} = \frac{1}{T} dU_{\text{tot}} - \frac{\mu}{T} dN_{\text{tot}} + \frac{P_1}{T} dV_1 + \frac{P_2}{T} dV_2 - \frac{\mathcal{F}}{T} dA \tag{5}$$

Our 1-2-surface totality is to be isolated from yet other systems, hence $dU_{\text{tot}} = 0$, $dN_{\text{tot}} = 0$. Equilibrium demands that S_{tot} be maximum, hence that $dS_{\text{tot}} = 0$ for the d 's a variation from that three-system equilibrium consequent upon exchanges of shared quantities between the three components 1, 2, and surface. So (5) becomes

$$0 = \frac{P_1}{T} dV_1 + \frac{P_2}{T} dV_2 - \frac{\mathcal{F}}{T} dA \tag{6}$$

I now impose as part of isolation that $V_{\text{tot}} = V_1 + V_2$ is fixed. Thus,

$$dV_2 = -dV_1$$

and so

$$(P_1 - P_2) dV_1 = \mathcal{F} dA \tag{7}$$

Scaling (3) up from zero quantities at fixed intensives gives us $S_1 = (U_1 + P_1 V_1 - \mu_1 N_1)/T_1$ from

$$dS_1 = \frac{dU_1}{T_1} + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1$$

Similarly, $S_2 = (U_2 + P_2 V_2 - \mu_2 N_2)/T_2$ and $S = (U - \mathcal{F}A - \mu N)/T$, which for

T, μ uniform add to

$$S_{\text{tot}} = (U_{\text{tot}} - \mu N_{\text{tot}} + P_1 V_1 + P_2 V_2 - \mathcal{S}A) / T \quad (8)$$

At fixed $U_{\text{tot}}, N_{\text{tot}}$, the total entropy is maximized, then, by maximizing

$$(P_1 V_1 + P_2 V_2 - \mathcal{S}A) / T \quad (9)$$

If \mathcal{S}/T were negative, then A would grow indefinitely, causing the surface to ramify so as to produce complete mixing, rather than two bulks separated by a surface. *Existence* of a surface, then, requires

$$\mathcal{S}/T \geq 0 \quad (10)$$

I will drop the $=0$ alternative in the sequel, and if negative T is ignored, we have simply $\mathcal{S} > 0$. Then, for given V_1, V_2 , the area A is to be minimized. This gives us the classic problem of finding the shape of a given volume, say V_1 , that minimizes its bounding area; I take over the commonly known result, that the answer is a sphere. Since the problem is one in the calculus of variations, it is also local, so that even if our concern is not with the complete boundary of a finite volume V_1 , but only with a small neighborhood of that portion of the boundary that separates 1 from phase 2, the spherical shape of the small neighborhood is still a valid result.⁴ And now our “radius r ” becomes legitimate.

I now verify that r indeed satisfies (4), even if the surface is only the curved cap of a sector of a sphere, rather than a whole sphere, even though this is redundant with Gibbs’ argument.

Let the circular ring to which the surface of radius r is supposed to adhere have radius ρ , and let h be the extent of linear intrusion of phase 1 into phase 2, i.e., let h be the height of the sector (Fig. 2).

We had equation (7), or

$$P_1 - P_2 = \mathcal{S} \frac{dA}{dV_1} = -dV_2 \quad (11)$$

⁴Denbigh (1966, p. 85) gives $1/r_1 + 1/r_2$ in place of $2/r$ for surfaces with two principal radii of curvature. The relevant variational problem, of minimizing the area of a two-sided but single surface with a given fixed edge but with no net transfer of volume from one side to the other, will have nonspherical solutions if, e.g., the given edge or “ring” cannot itself lie on a sphere—but a nonplanar edge that lies on a sphere *of the wrong radius* shows that the problem has more depth than I am reaching here. I will assume that the given ring is a circle, and that hence I will have only spheres! Denbigh refers to Gibbs (1948), who gives the following argument on p. 299: Transposing his equation (499) to my symbols, it reads $\mathcal{S} dA - P_1 dV_1 - P_2 dV_2 = 0$, my equation (7). Then, continuing in my symbols, “If all parts of the dividing surface move a uniform normal distance δD , we shall have $\varepsilon dA = (c_1 + c_2)A \delta D$, $\delta V_1 = A \delta D$, $\delta V_2 = -A \delta D$; whence $\mathcal{S}(c_1 + c_2) = P_1 - P_2$, (500).” Here $c_1 = 1/r_1$ and $c_2 = 1/r_2$ are the principal curvatures. Unfortunately, a uniform δD violates fixity of the bounding ring; this can be mended by having δD uniform over a small patch, small so that c_1 and c_2 are sensibly constant there, having δD decay to zero in a thin band around that patch, and zero elsewhere.

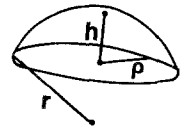


Fig. 2. Sector of a sphere.

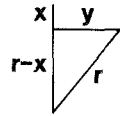


Fig. 3. $y^2 = 2rx - x^2$.

I now go through the calculus of evaluating dA/dV_1 , to get the answer $2/r$, equation (15) (Fig. 3):

$\Delta V_1 =$ volume of sector

$$\begin{aligned} &= \int \pi y^2 dx_0^h = \pi \int (2rx - x^2) dx_0^h \\ &= \pi \left(rx^2 - \frac{x^3}{3} \right)_{x=0}^h = \pi \left(rh^2 - \frac{h^3}{3} \right) \end{aligned} \tag{12}$$

The area A is easily found by $d/d\varepsilon$ upon $r \rightarrow r + \varepsilon$, $h \rightarrow h + \varepsilon$ or

$$A = \pi \frac{d}{d\varepsilon} \left(rh^2 - \frac{h^3}{3} \right)$$

with $dr/d\varepsilon = dh/d\varepsilon = 1$, which gives

$$A = 2\pi rh \tag{13}$$

Next, $(r - h)^2 + \rho^2 = r^2$ (Fig. 4), gives

$$r = (h^2 + \rho^2)/2h \tag{14}$$

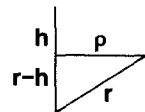


Fig. 4. $r = (h^2 + \rho^2)/2h$.

which is useful as ρ is to be held fixed, not r . Thus,

$$dV_1 = \pi d \left(\frac{h^2 + \rho^2}{2h} h^2 - \frac{h^3}{3} = \frac{1}{6} h^3 + \frac{1}{2} \rho^2 h \right), \quad dA = 2\pi d \frac{h^2 + \rho^2}{2}$$

$$dV_1 = \pi \left(\frac{1}{2} h^2 + \frac{1}{2} \rho^2 \right) dh, \quad dA = 2\pi h dh$$

So

$$\frac{dA}{dV_1} = \frac{2\pi h}{\pi(\frac{1}{2}h^2 + \frac{1}{2}\rho^2)}$$

whence, by (14),

$$dA/dV_1 = 2/r \quad (15)$$

From (15) our conclusion (4) follows.

2.2. The Function $\mathcal{S}(T, \mu)$

Much as knowledge of the PE's function $S(U, A)$ is interchangeable through a Legendre transformation with the empirically more accessible $\mathcal{S}(T)$, so our $S(U, A, N)$ may be had through $\mathcal{S}(T, \mu)$; the details:

$$dS = \frac{1}{T} dU - \frac{\mathcal{S}}{T} dA - \frac{\mu}{T} dN$$

implies that

$$dQ \equiv d \left(S - \frac{1}{T} U + \frac{\mu}{T} N \right) = -Ud \frac{1}{T} - \frac{\mathcal{S}}{T} dA + Nd \frac{\mu}{T} \quad (16)$$

where

$$Q \equiv S - \frac{1}{T} U + \frac{\mu}{T} N \quad (17)$$

is a modified entropy.⁵

Integrating (16) in a scaling process where T and μ are fixed but the area goes from 0 to A gives

$$Q = -(\mathcal{S}/T)A \quad (18)$$

or

$$q = -\mathcal{S}/T \quad (19)$$

⁵If the surface were regarded as directly open to a bath of energy and matter, then it is Q whose maximization would be equivalent to maximization of the entropy of the surface's universe, which is perhaps reason enough for looking at Q : in fact, the surface is so intimately linked to bulks 1 and 2 that it is Q_{tot} below, not Q , that is to be maximized.

in the convention that lowercase letters that refer to surfaces stand for quantities per unit area; thus, $q = Q/A$. Then (18) in (16) yields

$$d\frac{\mathcal{S}}{T} = ud\frac{1}{T} + nd\frac{-\mu}{T} \quad (20)$$

where of course $u = U/A$ and $n = N/A$.

If T and μ are independent variables, then (20) could give the energy per unit area u and the matter per unit area or self-adsorption n as the partial derivatives of $(\mathcal{S}/T)(1/T, -\mu/T)$; thus, $\mathcal{S}(T, \mu)$ would determine u and n . Furthermore, (17) gives us $S = Q + (1/T)U - (\mu/T)N$, so $s = q + (1/T)u - (\mu/T)n$, or

$$s = \frac{u - \mathcal{S} - \mu n}{T} = \frac{1}{T} \left(\frac{\partial(\mathcal{S}/T)}{\partial(1/T)} \right)_{-\mu/T} - \frac{\mu}{T} \left(\frac{\partial(\mathcal{S}/T)}{\partial(-\mu/T)} \right)_{1/T} - \frac{\mathcal{S}}{T} \quad (21)$$

which reaches also to s from knowledge of $\mathcal{S}(T, \mu)$. With s, u, n all thus parameterized by T and μ , the dependence of s on u and n , hence $U, A, N \rightarrow S(U, A, N) = As(U/A, N/A)$, are implicitly also defined, and so the whole thermodynamics of the surface is determined by the function $\mathcal{S}(T, \mu)$.⁶

2.3. Reduction to PE

Putting either μ or N arbitrarily to zero—in the sense that also $d\mu = 0$, or $dN = 0$, etc.; the idea is that one or the other of these two quantities is *identically* zero—produces the cardinal equations of PE. For example, our

$$u = \left(\frac{\partial(\mathcal{S}/T)}{\partial(1/T)} \right)_{-\mu/T}$$

simplifies in PE to

$$u = \frac{d(\mathcal{S}/T)}{d(1/T)} = \mathcal{S} - T \frac{d\mathcal{S}}{dT} \quad (\text{PE}) \quad (22)$$

But μ is set by either bulk, 1 or 2, and is usually *not* zero. The wild thought of studying an interface between liquid and vapor for *pure light* would indeed have μ infinitesimal, but that is not the case for water, helium, etc.! With μ not 0, justification for PE must rest on the self-adsorption n being small. If N abbreviates N^1, \dots, N^c , a *list* of chemicals, the “self”-adsorption encompasses ordinary adsorption, known often to be large, but even for $c = 1$ chemical only, there is no certitude that n is small.

For the rest, then, I consider how to manage with the extra terms.

⁶I call such a function a *master function*; correspondingly, Gibbs (1948; Denbigh, 1966) calls the equation that defines such a function a *fundamental equation*. On p. 86 Gibbs (1948) informs us that Massieu’s term is *characteristic function*. Technically, the preservation of mastery in passing from $s(u, n)$ to $\mathcal{S}(T, \mu)$ is identical with the invertibility of a Legendre transformation.

3. STABILITY OF THE CURVED SURFACE FOR SECTORS LESS THAN A HEMISPHERE

Equation (8),

$$S_{\text{tot}} = \frac{1}{T} U_{\text{tot}} - \frac{\mu}{T} N_{\text{tot}} + \frac{P_1}{T} V_1 + \frac{P_2}{T} V_2 - \frac{\mathcal{S}}{T} A$$

when diminished by reservoir entropies, gives us

$$Q_{\text{tot}} \equiv S_{\text{tot}} - \frac{1}{T} U_{\text{tot}} + \frac{\mu}{T} N_{\text{tot}} = \frac{P_1 V_1 + P_2 V_2 - \mathcal{S} A}{T}$$

as what is to be maximized for equilibrium of our tripartite system 1-surface-2, in contact with a (T, μ) reservoir. This is *not* just $-(\mathcal{S}/T)A$, the quantity Q dealt with earlier. So at fixed T, μ , hence fixed \mathcal{S} , we maximize

$$Q_{\text{tot}} = (P_1 V_1 + P_2 V_2 - \mathcal{S} A) / T \tag{9}$$

I note the similarity of this to an earlier conclusion by repeating the old relation's number! Then, fixing $V_{\text{tot}} = V_1 + V_2$ and $T > 0$ gives us maximization of $(P_1 - P_2) V_1 - \mathcal{S} A$. Since T, μ are given, intensives \mathcal{S}, P_1 , and P_2 are also fixed, so V_1, A are the only variables! For given V_1, A is to be minimum, which again gives us the spherical shape; if the surface is assumed attached to a given ring of radius ρ , then both V_1 and A are determined by the height h , say, or by the radius r . Equilibrium, to first order, is $(P_1 - P_2) dV_1 = \mathcal{S} dA$, which already gave us $P_1 - P_2 = 2\mathcal{S}/r$. *The reason for this section is to decide when this is stable or not by whether a spherical sector of varied r gives us a smaller Q_{tot} or not.* From equations (9), (12), and (13) we must study the function

$$(P_1 - P_2)\pi(rh^2 - h^3/3) - \mathcal{S}2\pi rh$$

for fixed radius ρ of our assumed ring of attachment; more explicitly, then, (14) gives us the study of this function of h :

$$(P_1 - P_2)\pi \left(\frac{h^2 + \rho^2}{2} h - \frac{h^3}{3} \right) - \mathcal{S}2\pi \frac{h^2 + \rho^2}{2} \equiv \phi(h) \tag{23}$$

in the neighborhood of $\phi'(h) = 0$.

Now,

$$\phi'(h) = (P_1 - P_2)\pi(h^2 + \rho^2)/2 - 2\pi\mathcal{S}h \tag{24a}$$

$$\phi''(h) = (P_1 - P_2)\pi h - 2\pi\mathcal{S} \tag{24b}$$

For our entropy to be maximum at h_0 such that $\phi'(h_0) = 0$, we must have $\phi''(h_0)$ negative. Let "1" label the bulk at higher pressure, so

$$P_1 - P_2 \geq 0$$

Negative h into (24a) produces a positive answer, hence $\phi'(h_0) = 0$ requires $h_0 > 0$; then $\phi''(h_0) < 0$ requires this positive incursion h_0 of 1 into 2 to be not *too* large. Indeed, $P_1 - P_2 = 2\mathcal{S}/r$ gives

$$\phi''(h) = \left(\frac{P_1 - P_2}{2\mathcal{S}} h - 1 \right) 2\pi\mathcal{S} = \left(\frac{h}{r} - 1 \right) 2\pi\mathcal{S}$$

So $h_0 < r$ is the condition $\phi''(h_0) < 0$ for stability: *Our sector must be shorter than a hemisphere.*⁷

Now, this conclusion can be reached less laboriously by asking: For what sectors will growth of the incursion of 1 into 2 *increase* the curvature of the surface, and so exert a restoring force? If 1 is a complete sphere, “incursion” is enlargement of that sphere, which decreases the curvature, so a drop or bubble of 1 in 2 is *not* stable, which forces us to look to the sector instead. It is visually obvious that it is for precisely sectors smaller than a hemisphere that the effect of incursion on curvature is reversed. But to be secure that the conclusion rests entirely on maximizing entropy in the model, excluding the notion of force, I deem the pottering above useful.

In further grubby detail, r is set thermodynamically through T and μ by $P_1 - P_2 = 2\mathcal{S}/r$. I imagine that the experimenter provides a ring of radius ρ *smaller* than r , to which the surface must somehow adhere. If we start out with a flat meniscus, this will bend until curvature $1/r$ is attained at the local h_0 maximum of $\phi(h)$, and as it fluctuates a little, it gets restored. But for large h , our cubic $\phi(h)$ gets arbitrarily large; a *large* incursion of 1 into 2 will grow indefinitely. So the phase 2 at lesser pressure is *metastable*, phase 1 is (relatively) stable. The greater stability of 1 as compared to 2 shows itself by the *positive* incursion $h_0 > 0$ of 1 into 2, yet metastability holds at h_0 , the entire collapse of phase 2 requiring either a large fluctuation or quantum tunneling to such $h > h_0$ where $\phi(h)$ begins its eventual rising at larger h ; this is fluctuation or tunneling to just past a full hemispherical incursion.

Our “ r ” is also the critical radius below which *whole* drops of 1 within 2 will shrink and above which they will grow. Testing for r by seeking this empirical borderline between shrinking and growing whole drops or bubbles of the stable phase within the metastable seems a hard way to go, experimentally, compared with observing the actual radius r of a locally *stable* meniscus—that is, provided the magic ring to which the surface adheres is available! Of course, another way metastable phase 2 can collapse is *imperfection* of this ring’s magic: a breaking away of the surface from the ring.

⁷Gibbs (1948, pp. 244, 245) similarly finds the hemisphere at the limit of stability.

4. DISTINGUISHING THE CONSTRAINT TO THE CLAPEYRON SUBSHEET FROM PE

If bulks 1 and 2 are to be equally stable, incursion of more than a hemisphere of the bulk at higher pressure into the other must not be possible, and this is accomplished by having $r = \infty$, $P_1 = P_2$. This is a Clapeyron relation between T and μ : Each bulk has a Gibbs relation

$$S = \frac{1}{T} U + \frac{P}{T} V - \frac{\mu}{T} N, \quad \text{or} \quad \frac{S}{V} = \frac{1}{T} \left(\frac{U}{V} + P - \mu \frac{N}{V} \right)$$

between its thermal parameters

$$\left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} = \frac{1}{T}, \quad \left(\frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} = \frac{P_1}{T}, \quad \left(\frac{\partial S_1}{\partial N_1} \right)_{U_1, V_1} = -\frac{\mu}{T}$$

and similarly for 2: The intensives S/V , U/V , and N/V are to be considered functions of T , P , and μ to read these as relations between T , P , and μ . Usually μ is thus considered a function of T and P , the per- N Gibbs function, but equivalently, each Gibbs relation may be taken as solved for its P , so bulk phase 1 goes with Gibbs pressure function $P_1(T, \mu)$, bulk phase 2 with $P_2(T, \mu)$, and these are regarded as known from bulk measurements; then

$$P_1(T, \mu) = P_2(T, \mu) \quad (\text{Clapeyron}) \quad (25)$$

is a relation between T and μ . This is a known relation, dependent upon bulk measurements, prior to any consideration of surfaces: my convention is that all bulk things are “known,” even if I do not have the necessary tables myself! Thus, all our intensives can, in the case of one chemical, be regarded as dependent on T alone, on the Clapeyron subsheet.

“Only temperature” sounds like “pure energy,” but to take confinement of one’s studies to Clapeyron as a justification of PE is wrong! To make sure that this is understood, I first rewrite (20) as

$$\frac{d(\mathcal{S}/T)}{d(1/T)} = u + n \frac{d(-\mu/T)}{d(1/T)}$$

where the d ’s refer to an arbitrary infinitesimal step (contravariant vector) in our $(1/T, -\mu/T)$ manifold; but this may be specialized to a step in the Clapeyron direction, where μ and T are related through (25) thus,

$$\left(\frac{d(\mathcal{S}/T)}{d(1/T)} \right)_{\text{Clapeyron}} = u + n \left(\frac{d(-\mu/T)}{d(1/T)} \right)_{\text{Clapeyron}} \quad (26)$$

For (26) to agree with PE’s equation (22), we need either nullity of self-adsorption n or to have $\mu_{\text{Clapeyron}}(T) = \mu_0 T$, μ_0 a constant, so that the derivative on the right of (26) is zero, which is all too simple to match the

correct behavior of any usual bulk function $\mu_{\text{Clapeyron}}(T)$. So having T the only independent variable through Clapeyron does *not* give PE.

5. FAILURE OF CONVEXITY IN PE, FOR HOT WATER

To prove convexity of the body $x^0 \leq S(x^1, \dots, x^v)$ for bulk systems, I split the list of additive quantities x^i arbitrarily into $(x^i + \epsilon^i)/2$ and $(x^i - \epsilon^i)/2$, so the vector ϵ^i points in an arbitrary direction, and consider the process of physically uniting or fusing two corresponding separated physical equilibria. The second law gives us

$$S(x^*) \geq S\left(\frac{x^* + \epsilon^*}{2}\right) + S\left(\frac{x^* - \epsilon^*}{2}\right)$$

that is, the entropy of the equilibrium after fusion exceeds the entropy before. Then the proportionality of entropy to the scale of a system allows factoring the $\frac{1}{2}$'s, to give the desired relation

$$S(x^*) \geq \frac{1}{2}S(x^* + \epsilon^*) + \frac{1}{2}S(x^* - \epsilon^*)$$

of convexity: geometrically, the entropy at x^* lies *over* the midpoint of the segment connecting the plot of entropy at $x^* + \epsilon^*$ with that at $x^* - \epsilon^*$. That fusing the separate equilibria at $(x^* \pm \epsilon^*)/2$ yields a new equilibrium that is indeed at the sum value x^* makes use of the presumed additivity of the arguments, when physical bulks are assembled together into larger bulks. In particular, volumes add—outside of general relativity!

But if I try to imagine fusing two separate preparations of *surface* equilibria, each at its own proper radius of curvature, I do *not* get any straightforward additivity of areas. Also, although the U_{tot} 's and N_{tot} 's do add, the energies and matter U and N *specific to the two surfaces* need not add up to the amount *specific to the final surface*, any discrepancy in the sum being compensated by a reverse discrepancy in the energies and matter assigned to the bulks: here I refuse to take seriously my early picture of surfaces truly isolated from bulks by “waists.” Hence, it is probably wrong to translate inequalities of convexity for bulks into analogous inequalities for surfaces by merely changing “volume” to “area.” What I show in this section is that one such inequality is surely wrong *taken together with the also doubtful model PE*, in the case of hot water.

The relation of convexity I treat is the analogue of the bulk $C_V \geq 0$, namely,

$$C_A \stackrel{?}{\geq} 0 \tag{27}$$

in PE. This reads

$$\frac{du}{dT} \stackrel{?}{\geq} 0 \tag{28}$$

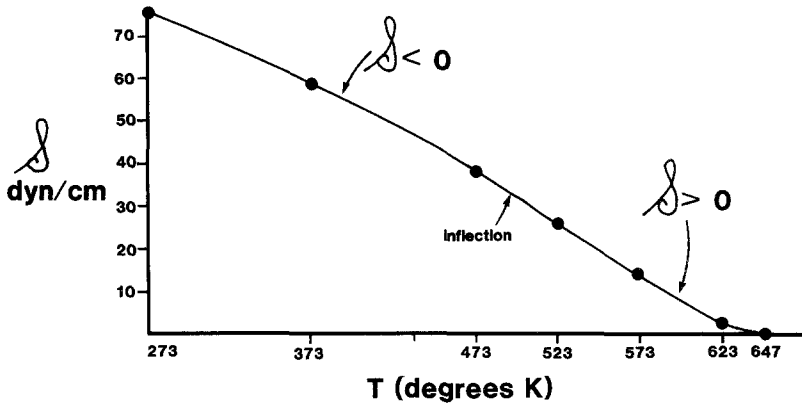


Fig. 5. Inflection in $\mathcal{S}(T)$ for hot water.

The question marks are intended to remind us that the relationships are in doubt. Then equation (22) gives us

$$-T \frac{d^2 \mathcal{S}}{dT^2} \stackrel{?}{\geq} 0 \tag{29}$$

The graph $T \rightarrow \mathcal{S}(T)$ is to be (?) convex upward. Instead, a plot (Fig. 5) is *concave* upward at the hot end, that is, from inflection at about 500 K, up to the critical point near 647 K (Zemansky and Dittman, 1981, p. 425). A fit near the critical point T_c with $\mathcal{S} = \mathcal{S}_0(1 - T/T_c)^\eta$ is said to have $\eta = 1.2$, whereas $\mathcal{S}'' < 0$ would require $\eta < 1$, in PE; indeed, this critical exponent η is said to *usually* lie between 1 and 2; hence, concavity of $\mathcal{S}(T)$ near the critical point is not peculiar to water, but is “usual.” I have copied positive “ u ” values, without knowing whether these are reliable (Table I): they

Table I

T, K	$\mathcal{S}, \text{dyne/cm}$	“ u ”, ergs/cm ²
273	75.50	143
373	58.91	138
473	37.77	129
523	26.13	122
573	14.29	111
623	3.64	80
647	0	0

may have been “deduced” from $\mathcal{S}(T)$ by using PE’s equation (22). In any case, a negative u would seem to be unusual.

Is the joint failure of convexity and PE a failure of convexity, of PE, or of both? It may be that *near* criticality, the large fluctuations interact so with the meniscus as to effectively make the microscopic density near the surface differ from that of either bulk phase, over a *large* thickness, and thus make the self-adsorption n large, despite the fact that *at* criticality, the difference between the bulk densities vanishes. Hence PE is particularly suspect near criticality. At any rate, the joint failure is large, holding over a range of about 150 deg; either convexity is truly wrong, or else self-adsorption is big.

6. NEGATIVE ENERGY AND ENTROPY IN PE FOR IMMISCIBILITY BETWEEN UPPER AND LOWER CRITICAL POINTS

The examples of such systems of two fluids in Findlay (1951) all have two independent chemicals, $c=2$, so neglecting all μ ’s and n ’s to get PE is perhaps even less plausible than for an interface between liquid and vapor with $c=1$. I copy Findlay’s graph for nicotine and water (Fig. 6). Whether PE be roughly valid or grossly off for such systems, my point is that using PE, one necessarily gets examples of negative u and s . If either one of these must for some reason unknown to me be nevertheless positive, then PE is here indeed grossly off.

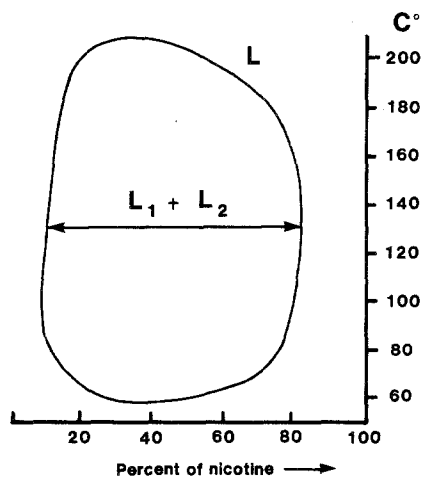


Fig. 6. Water and nicotine presumably at one pressure.

I introduce the abbreviations

$$\mathcal{F}/T = \sigma, \quad 1/T = \tau, \quad -\mu/T = \nu \tag{30}$$

so that (20) reads

$$d\sigma = u d\tau + n d\nu \tag{20a}$$

and our master function $(\mathcal{F}/T)(1/T, -\mu/T)$ is simply $\sigma(\tau, \nu)$, and (21) reads

$$s = \tau u + \nu n - \sigma \tag{21a}$$

Of course here, with $c = 2$, $n d\nu$ means $\sum_{i=1,2} n^i d\nu_i$, and νn means $\sum_{i=1,2} \nu_i n^i$; nevertheless, in setting forth "PE" here, these are omitted,

$$\text{PE:} \quad d\sigma = u d\tau \quad \text{and} \quad s = \tau u - \sigma = \tau d\sigma/d\tau - \sigma \tag{31}$$

or

$$\text{PE:} \quad u = d\sigma/d\tau \quad \text{and} \quad Ts = s/\tau = d\sigma/d\tau - \sigma/\tau$$

The smoothness of such loops as the one in Fig. 6 may suggest that there are really no special, intrinsically distinguished points along such a loop. However, a horizontal line across the loop is at constant τ and ν , i.e., constant ν_{water} and ν_{nicotine} , or ν_1 and ν_2 for brevity, with only the *proportion* of the two saturated solutions varying linearly in the abscissa. Hence, on a τ, ν_1 plot (Fig. 7), the loop (say, drawn at one value of ν_2 instead of at

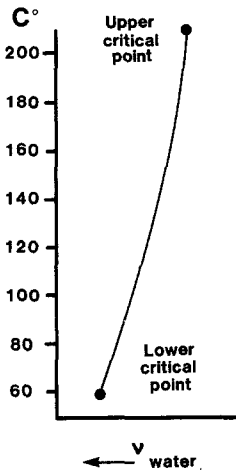


Fig. 7. Horizontal collapse of region $L_1 + L_2$, if a potential is made abscissa: a sketch.

one total pressure) collapses to a curve. The ends of this curve are the critical points, where the linear variation of Fig. 6 between the two compositions at the same τ and ν collapses to nothing.⁸

I am guessing that, as in the case of a critical point joining liquid and vapor, this vanishing immiscibility corresponds to a vanishing of \mathcal{S} , and hence of σ . Thus, the top and bottom points on the loop of Fig. 6 are special: \mathcal{S} and σ are 0 there, though positive elsewhere, and the redundancy of compositions at fixed τ and ν set forth by any horizontal line across the loop ceases at those points.

I draw a qualitative $\sigma(\tau)$ (Fig. 8); “upper” and “lower” refer directly to T , rather than to $\tau = 1/T$, which is why they may seem mislabeled. Here, I have σ go to zero slope at both critical points, in imitation of hot water’s critical exponent’s exceeding 1, but the conclusion that the slope u is zero at a maximum of σ , and that u is negative between such a maximum and the lower critical point, do not depend on this detail.⁹

Positive and negative s or $Ts = s/\tau = d\sigma/d\tau - \sigma/\tau$ meet where $d\sigma/d\tau = \sigma/\tau$, which is where a radial line through the graph’s origin touches the curve; thus, s is negative from such a point to the lower critical point.

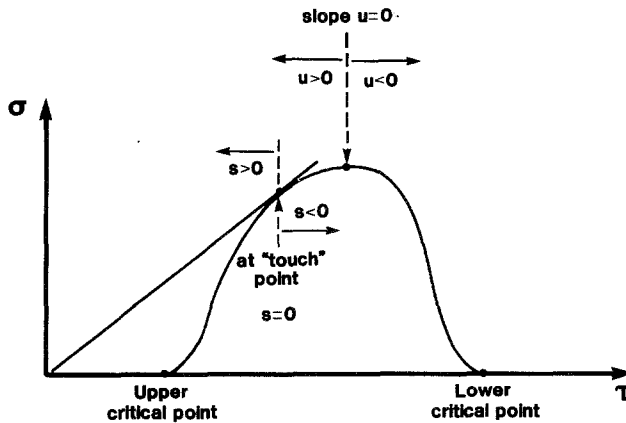


Fig. 8. Negative s and u near a lower critical point.

⁸A series of such planar plots (Fig. 7) at different ν_2 —analogous to redosings of Fig. 6 at various pressures—if assembled along a ν_2 axis, would unite upper critical points in a curve and lower critical points in another, with the μ, ν_1, ν_2 of transition a 2-sheet stretched between both curves; possibly the curves join in a critical loop. Such a loop should not be confused with the loop in Fig. 6, which is all at one pressure.

⁹My present task is to apply PE, hence my sketch of $\sigma(T)$ may be taken along with my Fig. 6 from Findlay, all at one P , and on Clapeyron, but a similar sketch could be taken as being at one value of ν_2 , with ν_1 then implicitly varying.

Of course a curve with several ripples in its horizontal structure will have several places where the sign of u changes; several ripples in the radial structure will respectively yield several places where the sign of s changes.

Note that the detail of σ going to zero slope at both critical points, that is, assuming critical exponents there greater than 1, makes $u = 0$ there. The condition of touch is then also met at such critical points, hence $s = 0$ there, too. Perhaps it is natural, as the distinguishability of a surface fades away, for the related energy levels and randomness associated thereto to vanish.

7. NEGATIVE ENTROPY FOR NICOTINE AND WATER, FREED FROM THE MODEL OF PE?

The full formulas (20a), (21a), free from PE, may lead to negative s by similar geometrical reasoning, but using a four-dimensional picture. I join the formulas to give

$$s = \tau \frac{\partial \sigma}{\partial \tau} + \nu_{\text{water}} \frac{\partial \sigma}{\partial \nu_{\text{water}}} + \nu_{\text{nicotine}} \frac{\partial \sigma}{\partial \nu_{\text{nicotine}}} - \sigma \quad (32)$$

where the partials are defined in the sense that τ , ν_{water} , ν_{nicotine} are our independent variables. Now imagine σ plotted vertically over a horizontal τ , ν_{water} , ν_{nicotine} three-space. Equation (32) signifies that where a radial line from the origin *touches* the graph, we again will have $s = 0$. The basal 3-flat at $\sigma = 0$ will also touch the σ graph at its critical edge, a loop of criticality in $(\tau, \nu_{\text{water}}, \nu_{\text{nicotine}})$ space, provided slopes go to criticality as in the case of water and steam, but our main interest is whether $s = 0$ elsewhere, separating positive from negative s zones; do touching lines exist, *other* than the basal ones? Yes, if there are 3-flats through the origin that touch at $\sigma > 0$; then the line between the origin and such a point of tangency is an example. Conversely, through a line that touches there is the 3-flat that touches.

Now, if the loop of criticality at the border of the σ plot lies well to one side of the origin, then we may pass a 3-flat through the origin that misses the whole σ graph by passing over it at too high σ values; then rotate this down upon the σ graph until it touches, to have our example.

But if not, if, for example, the loop of criticality tangles around the origin $\tau = 0$, $\nu_{\text{water}} = 0$, $\nu_{\text{nicotine}} = 0$, existence is no longer clear. However, our whole story is at $\tau = 1/T > 0$, and indeed lies between the positive hottest upper critical τ_{min} and the coldest lower critical τ_{max} , so that the origin is well to one side of the graph, which would seem to support the construction.

Yet most of $(\tau, \nu_{\text{water}}, \nu_{\text{nicotine}})$ space will be forbidden by gross instability, as contrasted with metastability near Clapeyron. Our $s = 0, \sigma > 0$ locus may be confined to such forbidden territory!

Indeed, the experimentalist will probably have data mainly on the Clapeyron 2-sheet

$$P_1(\tau, \nu_{\text{water}}, \nu_{\text{nicotine}}) = P_2(\tau, \nu_{\text{water}}, \nu_{\text{nicotine}})$$

with only some indications of behavior off this sheet, because a large step $P_1 - P_2$ in pressure will force $r = 2\mathcal{G}/(P_1 - P_2)$ to be small, and hence will force the radius $\rho < r$ of the ring to be small, which is awkward, and which eventually will mask the two-dimensional effects sought, by one-dimensional phenomena of adhesion to the ring: If the 2-sheet $s = 0$ fails to intersect Clapeyron, it probably will also miss the experimentally accessible small neighborhood around Clapeyron.

So it seems to me that the best chance for predicting $s < 0$ would be to show that the change in s due to other terms of the full theory, for some large negative value deduced naively from PE, may be estimated as too small to reverse the negativity, and not after all from the four-dimensional picture of this section.

8. SUMMARY OF THE FULL THEORY, FOR $c = 1$

This is for one chemical, so hot water is covered, whereas the similar but longer expressions for nicotine and water are not. In (30) I introduced the variables

$$\tau = 1/T, \quad \sigma = \mathcal{G}/T, \quad \nu = -\mu/T$$

so that

$$dS = \frac{1}{T} dU - \frac{\mathcal{G}}{T} dA - \frac{\mu}{T} dN$$

becomes

$$dS = \tau dU - \sigma dA + \nu dN$$

which scales to

$$S = \tau U - \sigma A + \nu N$$

Division by A gives

$$s = \tau u - \sigma + \nu n$$

Or, more symmetrically,

$$s + \sigma = \tau u + \nu n \tag{33}$$

Functions $s(u, n)$ and $\sigma(\tau, \nu)$ are literally mutual Legendre transforms:

$$ds = \tau du + \nu dn \quad \text{whereas} \quad d\sigma = u d\tau + n d\nu \quad (34)$$

8.1. Theoretically Easy Variables σ, τ, ν

I will first consider τ, ν to be my dominant list of independent variables, with $(\partial/\partial\tau)_\nu$ abbreviated as subscript τ , and no reminder that “ ν be fixed.” The experimenter is to tabulate (σ, τ, ν) triples, hence to provide a data base reasonably equivalent to function $\sigma(\tau, \nu)$; then the otherwise hard to measure quantities u, n , and s are simply

$$u = \sigma_\tau, \quad n = \sigma_\nu, \quad s = \tau\sigma_\tau + \nu\sigma_\nu - \sigma \quad (35)$$

Because $s(u, n)$ and $\sigma(\tau, \nu)$ are mutual Legendre transforms (33)–(35), the question of whether $s(u, n)$ is convex upward is equivalent to the question of whether $\sigma(\tau, \nu)$ is convex upward: For $s(u, n)$, the convexity is negativity of the symmetrix matrix

$$\begin{pmatrix} s_{uu} & s_{un} \\ s_{nu} & s_{nn} \end{pmatrix}$$

where of course sub u and sub n mean $(\partial/\partial u)_n$ and $(\partial/\partial n)_u$, respectively, whereas for $\sigma(\tau, \nu)$, the convexity is negativity of the symmetric matrix

$$\begin{pmatrix} \sigma_{\tau\tau} & \sigma_{\tau\nu} \\ \sigma_{\nu\tau} & \sigma_{\nu\nu} \end{pmatrix} \quad (36)$$

and the situation concerning the Legendre transform has these matrices as each the inverse of the other. So instead of directly writing out “ c_A ”, the strong possibility that *violation* of convexity in PE for hot water persists in the full theory, hence is a fact, is most simply expressed as whether negativity of the matrix (36) indeed *fails*. That is, $\zeta s(u, n)$ convex upward?

$$\Leftrightarrow \zeta \sigma(\nu, \tau) \text{ convex upward?} \Leftrightarrow \begin{pmatrix} -\sigma_{\tau\tau} & -\sigma_{\tau\nu} \\ -\sigma_{\nu\tau} & -\sigma_{\nu\nu} \end{pmatrix} \stackrel{?}{\geq} 0$$

“Positivity of matrix $-\sigma$ ” means positivity of its quadratic form, which is computationally most simply given as

$$-\sigma_{\tau\tau} \stackrel{?}{\geq} 0 \quad (37a)$$

$$-\sigma_{\nu\nu} \stackrel{?}{\geq} 0 \quad (37b)$$

$$\sigma_{\tau\tau}\sigma_{\nu\nu} - \sigma_{\tau\nu}^2 \stackrel{?}{\geq} 0 \quad (37c)$$

Furthermore, the strong form of (37c) implies that (37a) is equivalent to (37b). Again, (37a)–(37c) express the naive convexity; it is their *violation* for hot water that would correspond to the tentative conclusion based on PE.

8.2. Experimentally Easy Variables σ , t , p

The variable $\nu = -\mu/T$ is less accessible to the experimenter than the others, unless we pretend that all bulk quantities are perfectly known, which has been my convention till now.¹⁰ Of course, the problem is that the chemical potential μ , though the bulk Gibbs function per unit of N , hence bulk-determinate, is not going to be read off a meter!

Perhaps a more significant reason for writing this section is that it is desired, apart from awkwardness of μ and hence of ν , to have a notation that makes it obvious just what things may be taken to refer to Clapeyron, what things have to do with first-order deviation from Clapeyron, and what with second-order. For the case of one chemical, both purposes are fulfilled by replacing ν as independent variable by p , defined as

$$p = (P_1 - P_2)/T \quad (38)$$

Because Clapeyron is $P_1 = P_2$, it is here simply $p = 0$; various orders of deviation from Clapeyron are expressed by corresponding orders of differentiation with respect to p . The dependent quantity of interest is still $\sigma = \mathcal{S}/T$, which I will not rename, but I will call my complete list of independent variables t , p , with

$$t = \tau = \frac{1}{T} \quad \text{and} \quad p = \frac{P_1(T, \nu) - P_2(\tau, \nu)}{T} \quad (39)$$

The reason for renaming the unchanged variable τ is that *subscript* τ implies that ν is held constant, whereas *subscript* t implies that p is held constant, and it would not do to confuse these!

8.3. What the Experimenter Takes as Data, for the Surface

The temperature T or coldness $t = 1/T$, the two bulk pressures P_1 and P_2 , hence $p = (P_1 - P_2)/T$, are known—and either the surface tension \mathcal{S} directly—hence also $\sigma = \mathcal{S}/T$, is known—or the radius of curvature r of the meniscus, perhaps optically, as then \mathcal{S} is accessible from $\mathcal{S} = \frac{1}{2}(P_1 - P_2)r$, or $\sigma = \frac{1}{2}pr$. Thus, the experimenter tabulates quintuples (σ, t, p, P_1, P_2) —to put it a bit redundantly. From these, of course the triples σ, t, p are a data base for the function $\sigma(t, p)$. The reason P_1 or P_2 is wanted separately from cooking up p is that the function $\nu(t, p)$ will also be needed. Either $T = 1/t$ and P_1 and the per- N Gibbs free energy μ from bulk tables for phase 1, or T and P_2 and the same for phase 2, gives us $\nu = -\mu/T$; on different sides of Clapeyron either bulk 1 or bulk 2 will be more likely available in

¹⁰This is indeed explicitly Gibbs' convention, too, in his treatment of surfaces or "capillarity" (Gibbs, 1948, footnote on p. 231).

tables. Of course, the ν so deduced, displayed in (ν, t, p) triples, gives us the desired data base for $\nu(t, p)$; thus, the raw σ, t, p, P_1, P_2 plus bulk tables give us the desired (σ, ν, t, p) , from which $\sigma(t, p)$ and $\nu(t, p)$ become regarded as known. Then a mess of calculus gets us to last section's significant derivatives of $\sigma(\tau, \nu)$ as follows; however, the next subsection bypasses the mess!

The general device needed is to relate first derivatives $f_i = \partial f / \partial x^i$ of a quantity dependent on v variables x^1, \dots, x^v , and second derivatives f_{ij} to derivatives $f'_i = \partial f / \partial x'^i$ and corresponding f'_{ij} of the same quantity f , referred to v other variables x'^1, \dots, x'^v . Then (Veblen, 1962) the chain rule

$$f'_i = \frac{\partial x^a}{\partial x'^i} f_a \tag{40}$$

transforms the first derivatives, and

$$f'_{ij} \left[= \frac{\partial}{\partial x'^j} \left(\frac{\partial x^a}{\partial x'^i} f_a \right) \right] = \frac{\partial^2 x^a}{\partial x'^j \partial x'^i} f_a + \frac{\partial x^a}{\partial x'^i} \frac{\partial x^b}{\partial x'^j} f_{ab} \tag{41}$$

uses both old first and second derivatives to give the new second derivatives.

Here, “ f ” is of course σ , v is 2, and $x^1 = t, x^2 = p$, whereas $x'^1 = \tau, x'^2 = \nu$, because we are going from the t, p -based data to the theoretically desired τ, ν basis. Equation (40) becomes

$$\sigma_\nu = \frac{1}{\nu_p} \sigma_p, \quad \sigma_\tau = \sigma_t - \frac{\nu_t}{\nu_p} \sigma_p \tag{42}$$

and (41) becomes

$$\begin{aligned} \sigma_{\tau\tau} &= \left(-\frac{1}{\nu_p} \nu_{tt} + 2 \frac{\nu_t}{\nu_p^2} \nu_{tp} - \frac{\nu_t^2}{\nu_p^3} \nu_{pp} \right) \sigma_p + \sigma_{tt} - 2 \frac{\nu_t}{\nu_p} \sigma_{tp} + \frac{\nu_t^2}{\nu_p^2} \sigma_{pp} \\ \sigma_{\nu\nu} &= -\frac{1}{\nu_p^3} \nu_{pp} \sigma_p + \frac{1}{\nu_p^2} \sigma_{pp} \\ \sigma_{\tau\nu} &= \left(\frac{\nu_t}{\nu_p^3} \nu_{pp} - \frac{1}{\nu_p^2} \nu_{tp} \right) \sigma_p - \frac{\nu_t}{\nu_p^2} \sigma_{pp} \end{aligned} \tag{43}$$

From these, not much cancels in getting the determinant; I get

$$\begin{aligned} \sigma_{\tau\tau} \sigma_{\nu\nu} - \sigma_{\tau\nu}^2 &= \left(\sigma_{tt} - 2 \frac{\nu_t}{\nu_p} \sigma_{tp} \right) \left(-\frac{1}{\nu_p^3} \nu_{pp} \sigma_p + \frac{1}{\nu_p^2} \sigma_{pp} \right) \\ &\quad + \left(-\frac{1}{\nu_p^3} \nu_{tt} + \frac{\nu_t}{\nu_p^4} \nu_{tp} \right) \sigma_p \sigma_{pp} + \frac{1}{\nu_p^4} (\nu_{tt} \nu_{pp} - \nu_{tp}^2) \sigma_p^2 \end{aligned} \tag{44}$$

Suppose we are only interested in u , n , s , and convexity of specific heats, that is, negativity of

$$\begin{pmatrix} \sigma_{\tau\tau} & \sigma_{\tau\nu} \\ \sigma_{\nu\tau} & \sigma_{\nu\nu} \end{pmatrix}$$

on Clapeyron. Then, whereas all quantities in (42)-(44) are to be evaluated at $p=0$, on the sheet, yet σ_p in (42) shows that first-order deviation from $\sigma_{\text{Clapeyron}}(t)$ or $\mathcal{S}_{\text{Clapeyron}}(T)$ must be known to reliably get u , n , and s , even on Clapeyron. Of course,

$$\sigma_t = \frac{d}{d(1/T)} \left(\frac{\mathcal{S}_{\text{Clapeyron}}(T)}{T} \right)$$

does not involve any deviation from Clapeyron, and neither does σ_{tt} . Similarly, σ_{tp} involves only first-order deviation, but the most severe test of an experiment is σ_{pp} , unfortunately present in each of the quantities (43), (44) relating to convexity, which brings in experimental assessment of deviation to the *second* order.

Degeneration to PE may be obtained by using $\sigma(t, 0)$ in place of $\sigma(t, p)$ on the right of (42)-(44), which puts all p -subscripted σ 's to zero, leaving only $\sigma_\tau \rightarrow \sigma_t$ and $\sigma_{\tau\tau} \rightarrow \sigma_{tt}$ as nonzero outputs in PE. Thus, the anticonvex curvature in PE for hot water would have $\sigma_{\tau\tau}$ positive, which makes *that* the most interesting element of the $\sigma_{..}$ matrix to get correctly.

It should be stressed that weak dependence on p , that is, smallness of p derivatives, should not be thought of as making experiments futile, because certification of such smallness would establish the otherwise unsupported conclusions of PE: experiments need not aim fine enough to bound the p derivatives away from zero.

8.4. Bypassing the Mess

Let us back up to where our experimenter has first used bulk tables, to get $(\sigma, \nu, t = \tau, p)$ quadruples. He or she foolishly extracted $\sigma(t, p)$ and $\nu(t, p)$ functions of triples, instead of (σ, τ, ν) triples, a direct data base for the desired function $\sigma(\tau, \nu)$!

The only virtue in having elaborated the messy route is to have clarified just how much is known from tension data *strictly* on Clapeyron, $\sigma(t, p=0)$; none of our quantities u , n , s , or $\sigma_{..}$ is completely free of data from curved menisci.

9. REMARKS ON THE FULL THEORY, FOR $c=2$

This is for nicotine and water, not because the story of convexity will go to a 3 by 3 matrix, which is dull, but because PE "predicts" that the easier quantities u , n , and s will show negative u and s near a lower critical

point, which is exciting, and Findlay (1951) gives no example of a lower critical point for a single chemical. The theoretical desideratum is the function $\sigma(\tau, \nu_1, \nu_2)$, where $\nu_i = -\mu_i/T$ and $i = 1$ for water, $i = 2$ for nicotine; we have two awkward chemical potentials. The raw, once-redundant quintuples of the last section must become similarly once-redundant sextuples $(\sigma, t, p, P_1, P_2, N^1:N^2)$, where the ratio $N^1:N^2$ of amounts of water to nicotine is new. P_1 and P_2 are total pressures of *phases* 1 and 2, not “partial pressures”! If there are bulk tables for such a mixture, then t , P_1 , and $N^1:N^2$ into the table for phase 1, or t , P_2 and $N^1:N^2$ into table 2, should come up with both ν_1 and ν_2 . Then the bypass directly to $(\sigma, t, \nu_1, \nu_2)$ would seem preferable to any intermediate stage that featured p as a variable, for the sake of separating deviations from Clapeyron.

The likely absence of bulk tables for nicotine–water would set a premium on *directly* measuring the chemical potentials. Semipermeable membranes to pods of pure water and pure nicotine, plus measurement of each pod’s pressure, would of course lead to the separate chemical potentials from separate tables for pure water and pure nicotine. The smallness of the molecule H_2O should make a membrane selectively permeable to water feasible; a passive, wide-open hydrophobic channel for nicotine is harder to imagine. Whether some chemists’ parametrization of thermodynamics for $c = 2$, oriented to yields in reactions, is fine enough to use for one or both ν ’s in my chosen task of fixing signs for the surface’s densities of energy and entropy is a topic I do not enter upon now.

10. FROM AMBIGUITY TO OVERDETERMINATION

What ambiguity arises from the arbitrariness that would be involved in drawing some particular mathematical surface to part V_{tot} into V_1 and V_2 ? For each extensive property except volume, we have an equation of form $X_{\text{tot}} = X_1 + X + X_2$, and if we generally use small letters for densities, $X_{\text{tot}} = x_1 V_1 + xA + x_2 V_2$. A shift δ of a planar dividing surface A perpendicular to itself would make $V_1 \rightarrow V_1 + A\delta$, $V_2 \rightarrow V_2 - A\delta$, hence would increase the bulk X by $(x_1 - x_2)A\delta$, so that to keep X_{tot} fixed, we would have to change the density per unit area x to $x - (x_1 - x_2)\delta$. But our model computes these densities *unambiguously* from the master function (Gibbs’ term is “fundamental equations”) $\mathcal{S}(T, \mu)$ or $\sigma(\tau, \nu)$. Indeed, the arguments are intensives, which also apply to either bulk, and if one sought to defend the ambiguity of densities to shifts in the choice of mathematical surface, one would have to seek ambiguity in the tension \mathcal{S} . Either I go to Newtonian force to dispel this, and monitor *dynamically* by measuring the force exerted upon the ring of attachment, or else I appeal to $\mathcal{S} = \frac{1}{2}r(P_1 - P_2)$ and measurement of the radius of curvature of a spherical surface. Now here it may be

thought one has the originally posed sort of ambiguity, since for a curved surface a shift may be imagined that would alter the radius, but by using small $P_1 - P_2$, large r will be involved, hence any few-Angstrom ambiguity in r will be of no import to \mathcal{S} ; and r measured by scattering—say light—is associated with the physical surface rather than with any mathematical surface subject to arbitrary conceptual shifts.

Hence all densities, \mathcal{S} , r , and even area A are empirically determinate, given our spherical sector of basal radius ρ and radius r . The experimentalist will be much less willing to set up to monitor S_{tot} , U_{tot} , N_{tot} , V_{tot} , but we must in principle take these as determinate, too; these are $c+3$ determinate extensives. But the indeterminates left in our model are then only two, V_1 and V_2 , whence my conclusion, *that the model is in principle $(c+1)$ -fold overdeterminate!* In the case $c=1$, failure to monitor two totals, e.g., S_{tot} and U_{tot} , would obscure this point.

Further, monitoring of totals must be excruciatingly sharp, to catch the model with its pants down: We are trying to see the heat lost from bulk in making more interface, by monitoring the channel of heat between the bath and the bulk. Any other surfaces will add comparable shifts, however, unless we can find boundary-free compact gobs of space for containers. If we accept unknown shifts as inevitable, we thereby give up any possible empirical criticism of the model on this score of overdeterminancy.

To sum up, then: the master function $\mathcal{S}(T, \mu)$ or $\sigma(\tau, \nu)$ so sharply delimits everything that, if the totals be taken as fixed, the apportionment of V_{tot} into V_1 and V_2 is fixed; surprisingly, there is *no* consistent invariance of the model to a shift of mathematical dividing surface.

It is my late reading in Gibbs, who has some pages on shifts, that causes me to include the above; otherwise, having concluded that none are possible, it seems perhaps well to omit it.

11. GIBBS GENERALIZED FORCES C_1 AND C_2

I have just seen that Gibbs (1948, p. 225) puts terms $C_1\delta c_1 + C_2\delta c_2$ into his differential of energy, where $c_1 = 1/r_1$ and $c_2 = 1/r_2$ are the principal curvatures. My first reaction was that my own treatment must be an inadequate truncation! Gibbs immediately rewrites this as

$$\frac{1}{2}(C_1 - C_2)(\delta c_1 - \delta c_2) + \frac{1}{2}(C_1 + C_2)(\delta c_1 + \delta c_2)$$

in terms then of what I will call *twist* $\frac{1}{2}(c_1 - c_2)$ and *mean curvature* $\frac{1}{2}(c_1 + c_2)$. So, for spheres, only the second term counts. Then he gives an account I find confusing, involving some nonlinear shifts of mathematical surface, to conclude that the generalized force $C_1 + C_2$ may be made to vanish, unless

one wished to use shifts to achieve alternative simplifications, so even on the basis of Gibbs' text, I am not really in bad shape.

I wish furthermore to give two arguments against so complicating the model.

First, for the purpose here of learning about small departures from Clapeyron, the terms should be too small to matter; here I think Gibbs agrees. A definite departure varies μ and $\mu_{\text{Clapeyron}}(T)$, hence leads to a definite mean curvature through

$$\frac{P_1(T, \mu) - P_2(T, \mu)}{\mathcal{S}(T, \mu)} = c_1 + c_2 \quad (4a)$$

but the near-neighbor effects upon which dynamical \mathcal{S} is based are expected to be a response to the immediately local effect of the change in μ , and not a response to the distant geometric bending expressed by curvature.¹¹

Second, T , μ , and the system's response already control the *mean* curvature, so there is no call to introducing that as a new coordinate. This would eliminate $C_1 + C_2$ identically, without any shifts of mathematical surface. Combined with my strategy of dealing with only spherical surfaces, no twist, both C_1 and C_2 happily disappear from the discussion.

12. HELIUM

This writeup of notions a few years old is provoked by a lecture of Akira Ikushima's describing ongoing careful experimental studies of the tension of the interface between liquid and vapor for ^3He , ^4He , and mixtures of both, but as my notions have no specific roots in helium, I have chosen to mention this only here at the end, as a sort of acknowledgment. Of course I am saying that a thorough study must deal with curved surfaces, and here my picture of spontaneous tethering of a curved meniscus to a ring of radius ρ may be unproducible, partly because of creeps associated with superfluidity, partly because helium may be expected not to stick to anything. If it is this bad, then one can yet study unstable whole spheres—one advantage of which is the exclusion of phenomena associated with contact against a material ring extraneous to the theory.

But perhaps rings made of the most reactive agents known might show some stickiness, perhaps rings of free radicals, deposited themselves in the cold.

¹¹This microscopic hand-waving would assess the whole effect of twist to be negligible, even for aspherical shapes—but note that (4a) then specifies that *these shapes be of constant mean curvature*, that is, we have this constancy for the relevant generalized problem of Plateau if possible dependence at fixed T and μ of tension \mathcal{S} on twist be neglected.

I have also excluded deformations due to gravity; one can imagine dealing with small surfaces to avoid this, but then the one-dimensional edge along the ring would become important; or one can wait for a laboratory in free fall!

Ikushima uses vibrations in his measurements, and these involve a range, probably slight, in curvature of the surface. *Large* vibrations could be another avenue to study effects integrated over a range of curvatures with a variable spread. Heating from dissipation of large vibrations may veto such an approach; failure to reach equilibrium quickly could pose a second veto.

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