May 30, 1980

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The eternal mystery of the thermo-relations. Consider an isolated system. This means you fix the volume V and the internal energy E. You then want to understand equilibrium which is a state, i.e. a way of assigning probabilities to the different energies, of maximum randomness. This defines S as a function of E and V, or E as a function of S, V. Equilibrium means max S for fixed E, V or minimum E for fixed S, V.

Then temperature and pressure are given by

$$dE = TdS - pdV$$

or

$$dS = \frac{1}{T}dE + \frac{p}{T}dV$$

The latter relation says

$$dS = \frac{dE + pdV}{T} = \frac{\text{heat added}}{T}$$

What's important perhaps is that $S = S(E,V)$ and $E = E(S,V)$ are defined by variational principles. Now for chemistry one controls p, T — most reactions take place at constant temperature & pressure. Therefore we want quantities such that equilibrium is easily seen for constant p, T. So let's make the Legendre transformation of $-E$ with respect to S, V:

$$F = S \frac{\partial(-E)}{\partial S} + V \frac{\partial(-E)}{\partial V} - (-E)$$

$$= E - TS + pV$$

This is the Gibbs free energy. One should think of it as a function of the variables p, T.

$$dF = -SdT + Vdp$$

Thus $dF = 0$ when $dT = dp = 0$

similarly one has the Helmholtz free energy

$$A \equiv S \frac{\partial(-E)}{\partial S} - (-E) \equiv E - TS$$

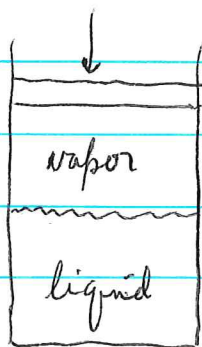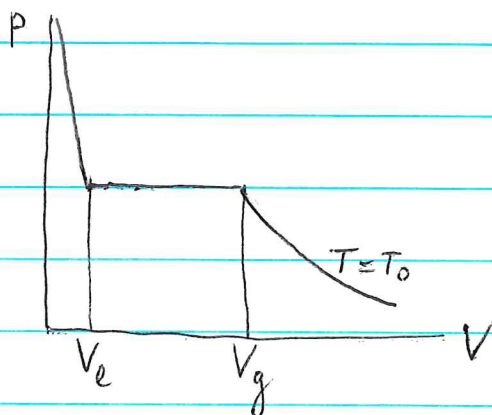which one thinks of as a function of T, V. Then

$$dA = -S\,dT - p\,dV.$$

Also one has the enthalpy

$$H \equiv \;\;\rule{3cm}{0.8cm}\;\; = V\frac{\partial(-E)}{\partial V} - (-E) = E + pV$$

which is a function of S, p and satisfies

$$dH = T\,dS + V\,dp.$$

Clausius-Clapeyron equation. Consider a liquid-vapor mixture inside a cylinder. If the pressure is held constant, then as heat is added, the heat goes into evaporating the liquid into gas, and so the temperature remains constant as the volume increases. Isothermals look as follows:
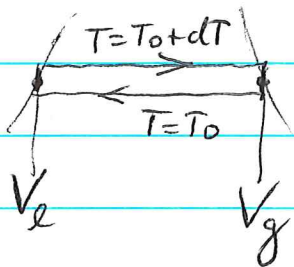

In the liquid-vapor equilibrium region, the pressure is a function of the temperature. Incidentally, the pressure is the vapor pressure of the liquid at that temperature. The Clausius-Clapeyron equation tells how p_{vap} varies with respect to T, or equivalently, how the boiling point varies wrt p.

The data are: The volume V_ℓ of the liquid and of the gas at the temperature of interest T_0.

More precisely V_ℓ = volume when the mixture is completely liquified, and V_g = volume when completely vaporized. Also we are given λ = the heat required to vaporize the liquid. Usually these quantities are given per mole.

Now let us resum a cycle and compute the work in two ways:

$$\oint p\,dV = \blacksquare \ (V_g - V_\ell)\,dp$$

Because $dE = TdS - pdV$, ▨ we have

$$\oint p\,dV = \oint T\,dS = (T_0 + dT)\int_{V_\ell}^{V_g} dS - T_0 \int_{V_\ell}^{V_g} dS$$

$$= [S]_{V_\ell}^{V_g} \cdot dT$$

But $dS = \dfrac{\text{heat added}}{T}$ in general, so that

$$[S]_{V_\ell}^{V_g} = \frac{\lambda}{T_0}$$

Thus

$$(V_g - V_\ell)\,dp = \frac{\lambda}{T_0}\,dT$$

or

$$\boxed{\frac{dp}{dT} = \frac{\lambda}{(V_g - V_\ell)\,T_0}} \qquad \blacksquare \text{ Clausius-Clapeyron}$$

Another derivation which essentially uses only a small Carnot cycle goes as follows. Let m denote the fraction of gas. Then

$$V = (1-m)V_\ell + mV_g$$

so

$$dV = dm(V_g - V_\ell).$$ On the other hand to

evaporate dm of liquid requires $dQ = \lambda dm$, hence

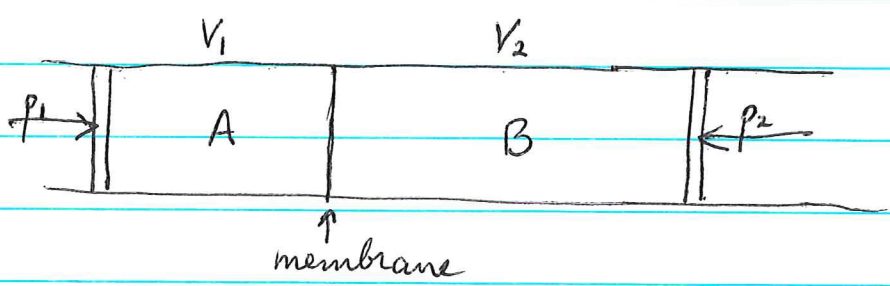$$dS = \frac{\lambda dm}{T_0} = \frac{\lambda}{T_0 (V_g - V_\ell)} dV$$

Now from

$$dE = TdS - pdV \qquad \text{one gets}$$

$$0 = d^2 E = dT \wedge dS - dp \wedge dV$$

$$= dT \, dV \left(\frac{\lambda}{T_0 (V_g - V_\ell)} - \frac{dp}{dT} \right)$$

yielding the same relation.

May 31, 1980

Entropy of mixing two ideal gases at the same temperature. Start with

membrane

Initially the holes in the membrane are blocked and one has n_A moles on the left, and n_B moles on the right. The membrane allows B-molecules to pass thru but not A-molecules.

Removing the membrane and allowing A, B molecules to mix seems to be an irreversible process, hence unsuitable for entropy calculations. However let us first slowly draw out the piston on the right so the B molecules have large volume V_3. The work done on the system is

$$-\int_{V_2}^{V_3} p_2 \, dV_2 = -\int_{V_2}^{V_3} \frac{n_B RT}{V_2} dV_2 = -n_B RT \log\left(\frac{V_3}{V_2} \right)$$

For an ideal gas $E = \frac{3}{2} n_B RT$ (monatomic gives $\frac{3}{2}$; in

general it's a constant), hence there's no internal energy change, so that this work done comes from heat absorbed. The entropy change is therefore

$$\Delta S_1 = \frac{\Delta Q}{T} = + n_B R \log\left(\frac{V_3}{V_2}\right)$$

At this point, let us open the holes in the membrane. Since V_3 is very large, nothing serious changes as B molecules diffuse into the A region. Now push the right piston all the way in. The work done is

$$\int_0^{V_3} p_2 \, dV_2 = \int_0^{V_3} \frac{n_B RT}{V_1 + V_2} \, dV_2 = n_B RT \log\left(\frac{V_1 + V_3}{V_1}\right)$$

and the entropy change is

$$\Delta S_2 = - n_B R \log\left(\frac{V_1 + V_3}{V_1}\right)$$

Finally let the left side expand until the volume is $V_1 + V_2$. The work done is

$$-\int_{V_1}^{V_1 + V_2} \underbrace{P_1}_{P_A + P_B} dV_1 = -\int_{V_1}^{V_1 + V_2} \frac{(n_A + n_B) RT}{V_1} \, dV_1 = -(n_A + n_B) RT \log\left(\frac{V_1 + V_2}{V_1}\right)$$

and so

$$\Delta S_3 = + (n_A + n_B) R \log\left(\frac{V_1 + V_2}{V_1}\right)$$

Thus the total entropy change is

$$\Delta S_1 + \Delta S_2 + \Delta S_3 = -\left(+ n_B R \left[-\log\left(\frac{V_3}{V_2}\right) + \log\left(\frac{V_1 + V_3}{V_1}\right) - \log\left(\frac{V_1 + V_2}{V_1}\right) \right] + n_A R \log\left(\frac{V_1}{V_1 + V_2}\right) \right)$$

In the limit $V_3 \rightarrow \infty$, this is

$$\Delta S = -\left(n_A R \log\left(\frac{V_1}{V_1 + V_2}\right) + n_B R \log\left(\frac{V_2}{V_1 + V_2}\right) \right)$$

or

$$\Delta S = n_A R \log\left(\frac{V_1 + V_2}{V_1}\right) + n_B R \log\left(\frac{V_1 + V_2}{V_2}\right)$$
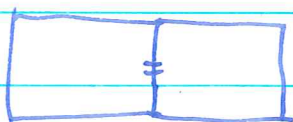
Thus the entropy increases and gives the same as allowing A to expand to new volume, and B to the new volume and then adding.

Actually the easiest way to see that mixing is reversible is to use two membranes, one permeable to A but not B, and the other the reverse. Then you move them in from the sides. to separate the gases.

Mixing by diffusion is irreversible, because you don't get the work which you could get if you did the mixing by moving semi-permeable membranes.

Simpler example: Joule expansion of an ideal gas
Open valve. Temperature stays same, but you don't get out the work you could if you allowed expansion against a piston.

June 1, 1980

Let's consider an Ising model with energy

$$E(s) = -\mathcal{H} \sum s_i - \frac{1}{2} \sum K_{ij} s_i s_j .$$

Here $\mathcal{H}$ is the external field. I am going to think of $\mathcal{H}$ as being like the volume for a gas.

Now we want to find the equilibrium state for a given total energy E and external field $\mathcal{H}$. This means we want a probability distribution $\rho = \{\rho_s\}$ on the set of pure states such that the energy is E:

$$\sum \rho_s = 1 \qquad\qquad \sum_s \rho_s E(s) = E$$

which maximizes the entropy $S = -\sum \rho_s \log \rho_s$. Use Lagrange multipliers and you get Maxwell-Boltzman:

$$\rho_s = \frac{e^{-\beta E(s)}}{Z} \qquad\qquad Z = \sum e^{-\beta E(s)}$$

where β is chosen so that $\sum \rho_s E(s) = E$. Then it follows that

$$S = \beta E + \log Z \qquad\qquad E = -\frac{\partial}{\partial \beta} \log Z$$

so that S is the Legendre transform of $-\log Z$ wrt β.

If you write out the Lagrange multiplier equation you get

$$\delta \left(\sum \rho_s \log \rho_s + \alpha \left(\sum \rho_s - 1 \right) + \beta \left(\sum \rho_s E(s) - E \right) \right) = 0$$

or $$\log \rho_s + 1 + \alpha + \beta E(s) = 0$$

Notice that similar equations result if we try to ~~maximize~~

minimize the energy $\sum_i \rho_s E(s)$, holding $-\sum \rho_s \log \rho_s$ fixed as well as $\sum_i \rho_s = 1$.

So far we have held $\mathcal{H}$ fixed. But suppose this were inconvenient for calculations. The standard way to avoid fixing $\mathcal{H}$ is to add a term $B\mathcal{H}$? to the energy, then solve the same problem with all possible $\mathcal{H}$, and then adjust B so as to get the average value of $\mathcal{H}$ equal to the desired value. It doesn't seem to be necessary to change the energy. What you look for is $\rho(s, \mathcal{H})$ such that

$$\int \rho(s, \mathcal{H}) = 1$$

$$\int \rho(s, \mathcal{H}) E_s = E$$

$$\int \rho(s, \mathcal{H}) \mathcal{H} = H$$

and again you want the entropy $-\int \rho_s \log \rho_s$ to be maximum. This leads to

$$\rho(s, \mathcal{H}) = \frac{1}{Z} e^{-\beta E_s - \gamma \mathcal{H}}$$

where $Z = \int e^{-\beta E_s - \gamma \mathcal{H}}$

There's a problem in that this integral doesn't exist. However recall that $E_s = -\mathcal{H} \int s - K(s)$

?

June 3, 1980

Derivation of MB law from Feynman's book. Suppose we have a system with energy levels E_n connected weakly to a large system with nearly continuous energy levels called the heat reservoir. Let us suppose the combined system has a large energy E and try to find the probability that the small system is in the state $|n\rangle$ with energy E_n. We suppose that states of equal energy are equally likely. Feynman argues this is so, because for states of different energy the high state decays into the lower state with a certain probability, hence these states have different probabilities. (But this doesn't imply equal energy states have the same probability, however maybe one can always perturb degeneracies. In effect, given two equal energy states, perturb so as to make the first higher than the second. Then the first is less likely than the second. Now remove the perturbation and argue by continuity.)

Take two states ▨ $|m\rangle$, $|n\rangle$ of the small system. The number of states in the combined system in which $|m\rangle$ occurs is the number $\upsilon(E-E_m)$ of states of the reservoir of energy $E-E_m$. Thus the probability P_m of $|m\rangle$ occurring is

$$(\ast) \qquad P_m = \frac{\upsilon(E-E_m)}{\sum_n \upsilon(E-E_n)}$$

Wait: This went too fast. P_m is the number of states of

the combined system of energy E in which $|m\rangle$ occurs (this number is $v(E-E_m)$) divided by the total number of states of the combined system of energy E (which is a number independent of $|m\rangle$). Thus

$$\frac{p_m}{p_n} = \frac{v(E-E_m)}{v(E-E_n)}$$

from which ⊛ follows, since $\sum_i p_n = 1$.

Now to get MB law, we need to show that

$$\frac{v(E-E_m)}{v(E)} = c^{-\beta E_m}$$

for some β. We can try to understand this when the reservoir consists of a large number N of identical systems (classical). Then $v(E)$ is

$$v(E) = \int \partial(E - H_N) \, d\mu_N$$

where $d\mu_N$ is the product measure. Take Laplace transform.

$$\int e^{-sE} v(E) \, dE = \int \left(\int e^{-sE} \partial(E-H_N) \, dE \right) d\mu_N$$

$$= \int e^{-s H_N} d\mu_N = \left(\int e^{-sH} d\mu \right)^N = Z(s)^N$$

so that by Laplace inversion

$$v(E) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} Z(s)^N e^{sE} \, ds$$

Take $E = N\varepsilon$ where ε = average energy per system.
Then steepest descent says the integral has main contribution
coming from the point β where $\log Z(s) + s\varepsilon$ is stationary.
Therefore

$$\frac{v(E + \Delta E)}{v(E)} = \frac{\frac{1}{2\pi i}\int Z(s)^N e^{sE + s\Delta E}\, ds}{\frac{1}{2\pi i}\int Z(s)^N e^{sE}\, ds} \doteq e^{\beta \Delta E}$$

Consider a single system for the reservoir, supposed
to be classical. Then

$$\int e^{-sE} v(E)\, dE = Z(s)$$

so by Laplace transform

$$v(E) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} Z(s) e^{sE}\, ds.$$

Supposing that steepest descent can be applied to this
integral, we get

$$\frac{v(E + \Delta E)}{v(E)} \doteq e^{\beta \Delta E}$$

where $s = \beta$ is the ▮▮▮ minimum point for ▮▮▮▮

$$\log Z(s) + sE.$$

Maybe this is too complicated. If you want

$$\frac{v(E + \Delta E)}{v(E)} = e^{\beta \Delta E}$$

then clearly $\qquad \log v(E) = \beta E + \text{const.}$

In any case we always have

$$\frac{v(E+\Delta E)}{v(E)} = e^{\beta \Delta E} \left(1 + O((\Delta E)^2)\right)$$

$$\text{if} \qquad \beta = \frac{d}{dE} \log v(E)$$

So we see that more or less any classical system for which $v(E)$ is increasing will function as a reservoir provided the energy changes in the system are small ^small.

Example: harmonic oscillator in n-dimensions

$$v(E) = \int \delta\left(\frac{r^2}{2} - E\right) \frac{vol(S^{2n-1})}{(2\pi)^n} \underbrace{r^{2n-1} dr}_{(r^2)^{n-1} r dr}$$

$$= 2^{n-1} \frac{vol(S^{2n-1})}{(2\pi)^n} \int \delta\left(\frac{r^2}{2} - E\right) \left(\frac{r^2}{2}\right)^{n-1} d\left(\frac{r^2}{2}\right)$$

$$= 2^{n-1} \frac{vol(S^{2n-1})}{(2\pi)^n} E^{n-1}$$

$$\int e^{-sE} v(E) dE = Z(s)^n \qquad Z(s) = \int e^{-s\frac{p^2+q^2}{2}} \frac{dp\,dq}{2\pi} = \frac{1}{s}$$

$$\int_0^\infty e^{-sE} E^{n-1} dE = \frac{\Gamma(n)}{s^n} \qquad \therefore \quad vol(S^{2n-1}) = \frac{2\pi^n}{(n-1)!}$$

which agrees with

$$vol(D^{2n}) = \int_0^1 \frac{2\pi^n}{(n-1)!} r^{2n-1} dr = \frac{\pi^n}{n!}$$

June 4, 1980

Yesterday I was trying to understand the idea of a heat reservoir. The idea is that it is a system at a fixed energy E whose behavior is essentially the same as its thermal behavior at that energy. For example suppose the system is a classical one described by a Hamiltonian function on phase space. The partition function is

$$Z(\beta) = \int e^{-\beta E} \, v(E) \, dE$$

$$v(E) = \int \delta(H - E) \, d\mu$$

Let me assume the system has the energy E_0, and let β_0 be the inverse temperature giving this energy

$$-\frac{Z'(\beta)}{Z(\beta)} = \frac{\int E e^{-\beta E} v(E) \, dE}{\int e^{-\beta E} v(E) \, dE} = E_0 \quad \text{when } \beta = \beta_0.$$

To say that the system at energy E_0 has the same behavior as its thermal behavior means that the measure (Boltzmann)

$$\frac{e^{-\beta_0 H}}{Z(\beta_0)} \, d\mu$$

effectively coincides with the micro-canonical measure

$$\frac{\delta(H - E_0) \, d\mu}{v(E_0)}$$

This means that in the partition function

$$Z(\beta) = \int e^{-\beta_0 E} v(E) \, dE$$

the integrand peaks at $E = E_0$. Hence we have

$$\frac{d}{dE}\left(-\beta_0 E + \log \upsilon(E)\right) = 0 \qquad \text{at} \quad E = E_0 \qquad \text{or}$$

$$\beta_0 = \frac{\upsilon'(E_0)}{\upsilon(E_0)}$$

Also we have

$$Z(\beta_0) \doteq e^{-\beta_0 E_0 + \log \upsilon(E_0)} \int e^{+\frac{1}{2}(E-E_0)^2 \frac{d^2}{dE^2} \log \upsilon(E)\Big|_{E=E_0}} dE$$

$$\doteq e^{-\beta_0 E_0 + \log \upsilon(E_0)} \left(2\pi \left(-\frac{\upsilon'}{\upsilon}\right)'(E_0)\right)^{-1/2}$$

Let's ignore the second factor. Then

$$\log Z(\beta_0) \doteq -\beta_0 E_0 + \log \upsilon(E_0)$$

which expresses the relation that the entropy is $\log \upsilon(E_0)$.

~~[crossed out]~~

 The above use of steepest descent is a bit ~~[crossed out]~~ crude. It seems better to argue that because $e^{-\beta_0 E} \upsilon(E) dE$ peaks at $E = E_0$ we can approximate this measure by a Gaussian in computing the partition function $Z(\beta)$ for β near β_0. Then we get good formula for changes in $\log Z(\beta)$, or in entropy. Precisely

$$e^{-\beta_0 E} \upsilon(E) \doteq e^{-\beta_0 E_0} \upsilon(E_0) \, e^{-\frac{1}{2}a(E-E_0)^2}$$

where

$$a = -\frac{d^2}{dE^2} \log \upsilon(E) \Big|_{E=E_0}$$

Then

$$Z(\beta) = \int e^{-(\Delta\beta + \beta_0)E} \upsilon(E) dE \qquad \text{~~[crossed out]~~}$$

$$= \int e^{-(\Delta\beta)E} e^{-\beta_0 E} \upsilon(E) dE = e^{-(\Delta\beta)E_0} e^{-\beta_0 E_0} \upsilon(E_0) \int e^{-(\Delta\beta)(\Delta E) - \frac{1}{2}a(\Delta E)^2} dE$$

$$= e^{-(\Delta\beta)E_0} \; e^{-\beta_0 E_0} \nu(E_0) \; e^{\frac{1}{2a}(\Delta\beta)^2} \frac{1}{\sqrt{2\pi a}}$$

Therefore

$$\frac{Z(\beta)}{Z(\beta_0)} \doteq e^{-(\Delta\beta)E_0 + \frac{1}{2a}(\Delta\beta)^2}$$

is a good approximation, or at least should be for $\Delta\beta$ small. Similarly

$$\frac{\nu(E)}{\nu(E_0)} \doteq e^{\beta_0 \Delta E - \frac{1}{2}a(\Delta E)^2}$$

The point is that $\log \nu(E)$, $\log Z(\beta)$ are quadratic functions of E and β resp. near $E = E_0$, $\beta = \beta_0$, and within this approximation:

$$\log Z(\beta) = -\beta E + \log \nu(E) + \text{const}$$

$$\text{where} \quad E = -\frac{d}{d\beta} \log Z(\beta)$$

June 8, 1980

Review first order PDE's :

$$F\left(x, u, \frac{\partial u}{\partial x}\right) = 0 \qquad\qquad x = (x_1, \cdots, x_n)$$

where u is a scalar function. A solution is a submanifold of (x, u, p) space projecting non-singularly on x-space such the function $F(x, u, p)$ and the form $\eta = p\,dx - du$ vanish on this submanifold. Fix a point (x, u, p) where $F = 0$ and look at the tangent space which has dim. $2n+1$. The condition $\eta = 0$ gives a hyperplane on which $d\eta = dp\,dx$ is a non-singular 2-form. Hence there is a unique tangent vector X such that

$$i(X)\, d\eta = -dF \qquad \text{on the hyperplane } \eta = 0.$$

Let $\quad X = a\frac{\partial}{\partial x} + b\frac{\partial}{\partial u} + c\frac{\partial}{\partial p} \quad$ and write things in terms of the independent linear functionals dx, dp :

~~$i(X)(dp\,dx) = -a\,dp + c\,dx$~~ $\qquad i(X)\eta = ap - b = 0$

$$i(X)(dp\,dx) = -a\,dp + c\,dx$$

$$+dF = \frac{\partial F}{\partial x}dx + \frac{\partial F}{\partial u}du + \frac{\partial F}{\partial p}dp$$

$$= \left(\frac{\partial F}{\partial x} + p\frac{\partial F}{\partial u}\right)dx + \left(\frac{\partial F}{\partial p}\right)dp$$

So the vector field is

$$X = \frac{\partial F}{\partial p}\frac{\partial}{\partial x} + p\frac{\partial F}{\partial p}\frac{\partial}{\partial u} + \left(-\frac{\partial F}{\partial x} - p\frac{\partial F}{\partial u}\right)\frac{\partial}{\partial p}$$

which gives the bicharacteristic equations:

$$
\begin{cases}
\dot{x} = \dfrac{\partial F}{\partial p} \\[2mm]
\dot{u} = p\dfrac{\partial F}{\partial p} \\[2mm]
\dot{p} = -\dfrac{\partial F}{\partial x} - p\dfrac{\partial F}{\partial u}
\end{cases}
$$

This is a vector field in (x, u, p) space depending on F. Since

$$
-i(X)\, d\eta = \frac{\partial F}{\partial p}\, dp + \left(\frac{\partial F}{\partial x} + p\frac{\partial F}{\partial u}\right) dx
$$

$$
= dF + \frac{\partial F}{\partial u}\underbrace{(p\, dx - du)}_{\eta}
$$

and $i(X)\eta = 0$ we have

$$
i(X)\, dF = -i(X)^2\, d\eta = 0
$$

and hence F is constant along the trajectories.

$$
\theta(X)\eta = d\,i(X)\eta + i(X)\, d\eta
$$

$$
= -dF - \frac{\partial F}{\partial u}\eta
$$

From this it follows that if we have a submanifold stable under the bicharacteristic flow such that each trajectory has a point where dF, η are zero, then $\theta(X)\eta \equiv 0$ and so $\eta \equiv 0$. We construct such a submanifold as follows. Start with giving u as a function of x on a hypersurface in x-space. Then ∇u is known in directions

tangent to the hypersurface and we assume it is possible
to solve $F(x, u, p) = 0$ for the normal derivative of u by
the implicit function thm. This means that if $p = (p_n, p_t)$
then $\frac{\partial F}{\partial p_n} \neq 0$ and so $\dot{x}_n = \frac{\partial F}{\partial p_n} \neq 0$ so the bicharacteristic
flows moves transversally to the submanifold of (x, u, p)
space given by u on the hypersurface & our nice choice for p_n.
Thus we sweep out this $(n-1)$ diml. submanifold to get an
n-diml one. Then we have seen that $F = 0$, $\gamma = 0$ on this
submanifold of dim. n, so we get a solution of $F(x, u, \nabla u) = 0$.

See June 4, 1979   p. 935   for the good way
to reduce $F(x, u, \nabla u) = 0$ to $H\left(q, \frac{\partial S}{\partial q}\right) = 0$ with
H homogeneous in p of degree 1 and $q = (x, u)$.

June 13, 1980

Consider the flow on (t, q, p) space described by Hamilton's equations

$$\frac{dq}{dt} = \frac{\partial H}{\partial p} \qquad \text{and} \qquad \frac{dp}{dt} = -\frac{\partial H}{\partial q}$$

where $H(t, q, p)$ is given. The trajectories $q(t), p(t)$ are the stationary curves for the action integral

$$\int_{t'}^{t} (p\,dq - H\,dt)$$

Let's consider the set of trajectories. It is a manifold on which the functions q_t, p_t, giving the position and momentum at time t, are coordinates. If we have a trajectory $q(t), p(t)$ and a variation of it $\delta q(t), \delta p(t)$, then

$$\delta \int_{t'}^{t} (p\,dq - H\,dt) = \int_{t'}^{t} \delta p(t)\, dq(t) + p(t)\,\delta dq(t)$$
$$- \left(\frac{\partial H}{\partial q}\,\delta q + \frac{\partial H}{\partial p}\,\delta p \right) dt$$
$$= \int_{t'}^{t} \left(p\,\delta \dot{q} + \dot{p}\,\delta q \right) dt = p\,\delta q \Big|_{t'}^{t}$$

Therefore if $S_{t, t'}$ is the function on the manifold of trajectories giving the action from t' to t we have

$$\delta S_{t, t'} = p_t\,\delta q_t - p_{t'}\,\delta q_{t'}$$

for an arbitrary variation. In terms of differentials

$$dS_{t, t'} = p_t\,dq_t - p_{t'}\,dq_{t'}$$

Let's change notation — let q, p denotes $q_{t'}, p_{t'}$

and Q, P denote q_t, p_t and $S = S_{t,t'}$ so that

$$dS = PdQ - pdq$$

The situation is like thermo — we have a manifold on which any two of the coordinates q, p, Q, P can be used to describe the manifold. The above relation suggests that S is naturally a function of the variables q, Q which give the endpoints of the trajectory. One has

$$\left(\frac{\partial S}{\partial Q}\right)_q = P \qquad\qquad \left(\frac{\partial S}{\partial q}\right)_Q = -P$$

Legendre transforms can be used to change Q to P or q to p if desired, but there doesn't seem to be an easy way to make q, p independent variables.

If $S(Q, q)$ is the action just described, then we can find the final position Q of the trajectory starting at (q, p) by solving the equations

$$\frac{\partial S}{\partial q}(Q, q) = -p$$

So if $S(t, q, t', q')$ is the action of the trajectory going from (t', q') to (t, q), we get the trajectory starting at (t', q', p') by solving

$$\frac{\partial S}{\partial q'}(t, q, t', q') = -p'$$

for q as a function of t.

Once we know $S(t, q; t', q')$ we can solve the Cauchy problem for the Hamilton-Jacobi PDE

$$\frac{\partial S}{\partial t} + H\left(t, q, \frac{\partial S}{\partial q}\right) = 0 \qquad S = S(t, q)$$

as follows. Assuming $S(t', q')$ given for all q' define

$$S(t, q) = S(t, q; t', q') + S(t', q')$$

where q' is chosen so that the trajectory from $t'q'$ to tq has the momentum $\frac{\partial S}{\partial q'}(t', q')$ at t':

$$\frac{\partial S}{\partial q'}(t, q; t', q') + \frac{\partial S}{\partial q'}(t', q') = 0$$

It then follows that $p = \frac{\partial S}{\partial q}(t, q)$ is the final momentum of the trajectory in the family described by $p' = \frac{\partial S}{\partial q'}(t', q')$. Moreover

$$p\dot{q} - H = L \underset{\text{gp}}{=} \frac{d}{dt} S(t, q) = \frac{\partial S}{\partial t} + \frac{\partial S}{\partial q}\dot{q} \quad \Rightarrow \quad \frac{\partial S}{\partial t} = -H$$
$$= -H\left(t, q, \frac{\partial S}{\partial q}\right)$$

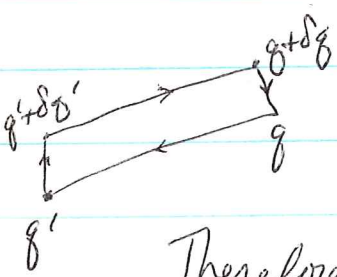because this is true for $S(t, q; t', q')$ so S satisfies HJ.

Next suppose $H = H(q, p)$ is time-independent. Then we can look at the Hamiltonian flow on (q, p) space, and we know that $\frac{dH}{dt} = 0$ so that the trajectories are contained in $H(q, p) = E$ where E is constant. The Maupertuis principle says that the trajectories as curves in $H(q, p) = E$ are stationary curves for the action integral $\int p \, dq$. (Recall the proof: The form $dp \, dq$ restricted to $H = E$ has a 1-diml kernel generated by X_H where $i(X_H) \, dp \, dq = dH$. A curve is stationary for $\int p \, dq$ where $i(X) \, d(p \, dq) = 0$ where X is the

tangent vector ▩ to the curve. Thus stationary curves for $\int p\,dq$
in $H=E$ are integral curves for the Hamilton flow.)

Let $W(q,q') = \int p\,dq$ be the action for the trajectory
of energy E joining q' to q. Thus we consider all p'
with ▩ $H(q',p') = E$ and look for the corresponding
trajectory to go thru q. If we have a variation $\delta q'; \delta q$
then

$$\delta W = \int_{q+\delta q'}^{q+\delta q} p\,dq - \int_{q'}^{q} p\,dq = p\,\delta q - p'\,\delta q' + \iint dp\,dq$$

O because
integral curves
are stationary

Therefore

$$\boxed{dW = p\,dq - p'\,dq'}$$

so

$$\left(\frac{\partial W}{\partial q}\right)_{q'} = P$$

and therefore $W(q,q')$ for fixed q' is a solution of

$$H\left(q, \frac{\partial W}{\partial q}\right) = E$$

To solve the Cauchy problem for this first order PDE
suppose $W(q')$ given with q' on a nice hypersurface
which means we have no trouble solving for the derivative of W
in the normal direction to the hypersurface. Thus ▩ from W
on the hypersurface we can find q',p' and construct trajec-
tories of energy E. Then we put

$$W(q) = W(q,q') + W(q')$$

where q' is ▩ chosen so the trajectory thru q' passes thru q,
hence

$$\frac{\partial W}{\partial q'}(q,q') + \frac{\partial W}{\partial q'}(q') = 0.$$

It follows that

$$\frac{\partial W}{\partial q}(q) = p = \text{momentum of the trajectory thru } q.$$

and hence that $W(q)$ satisfies $H\left(q, \frac{\partial W}{\partial q}\right) = 0.$

June 15, 1980

The usual Maupertuis least action principle refers not to curves in the hypersurface $H(q,p) = E$ but to curves in q-space. Suppose

$$H(q,p) = \frac{p^2}{2m} + V(q)$$

so that along a trajectory we have

(1)
$$\frac{dq}{dt} = \frac{\partial H}{\partial p} = \frac{p}{m}.$$

Since the total energy is E, we have

$$\frac{m}{2}\left(\frac{dq}{dt}\right)^2 + V = E$$

or
$$|dq| = \sqrt{\frac{2(E-V)}{m}}\, dt$$

(2)
or
$$dt = \frac{1}{\sqrt{\frac{2(E-V)}{m}}}\,|dq|$$

Consequently the action along a trajectory is the integral of

$$\int p\,dq = m\frac{dq}{dt}\cdot dq = m\left(\frac{dq}{dt}\right)^2 dt$$

$$= m\,\frac{2(E-V)}{m}\,\frac{1}{\sqrt{\frac{2(E-V)}{m}}}\,|dq| = \sqrt{2m(E-V)}\,|dq|$$

Now instead of looking at stationary curves

in $H(q,p) = E$ for the action, we can look at stationary curves in q-space for the integral

$$\int \sqrt{2m(E-V)} \, ds \qquad\qquad ds = |dq| \quad .$$

The point is that to a curve in q-space we have associated one in $H = E$, by the formulas (1) and (2), and that we ~~obtain~~ all stationary curves in $H = E$ from curves in q-space.

Consider a time-dependent Hamiltonian $H(q, p)$, say for example $\frac{p^2}{2m} + V(q)$. Because H is time-independent, it is possible for

$$\frac{\partial S}{\partial t} + H\left(q, \frac{\partial S}{\partial q}\right) = 0$$

to additively separate variables, i.e. find solutions of the form

$$S(t, q) = W(q) - Et$$

(strictly speaking, one looks for solutions $S = W(q) + F(t)$ and then finds $F'(t) = \text{constant}$), where W is to satisfy

$$H\left(q, \frac{\partial W}{\partial q}\right) = E.$$

Question. Is it possible to express $S(t, q; t', q')$ in terms of the action functions $W_E(q, q')$ at constant energy?

Look at the quantum situation.

$$U(t, q; t', q') = \langle q | e^{-\frac{i}{\hbar}(t - t')H} | q' \rangle$$

If I want the forward fundamental solution, then using the fact that H is bounded below we have
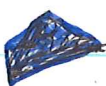
$$e^{-\frac{i}{\hbar}(t-t')H} = \frac{1}{2\pi i} \int e^{-\frac{i}{\hbar}(t-t')E} \frac{dE}{E - H}$$

For $t - t' > 0$, the fn. $e^{-\frac{i}{\hbar}(t-t')E}$ decays in the LHP, hence

$$-\frac{1}{2\pi i}\int \frac{dE\ c^{-\frac{i}{\hbar}(t-t')E}}{E-H} = \begin{cases} e^{-\frac{i}{\hbar}(t-t')H} & t>t' \\ 0 & t<t' \end{cases}$$

so finally we obtain

$$U(t,q,t',q') = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\ e^{-\frac{i}{\hbar}(t-t')E}\langle q|\frac{1}{E+i0^+-H}|q'\rangle$$

On the other hand we have the path integral formula

$$U(t,q,t',q') = \int_{\substack{\text{from } (t',q') \\ \text{to } (t,q)}} \mathcal{D}q\,\mathcal{D}p\ e^{\frac{i}{\hbar}\int p\,dq - H\,dt}$$

$$= \int_{\text{from } t'q' \text{ to } tq} \mathcal{D}q\ e^{\frac{i}{\hbar}\int L\,dt}$$

Question: Is there a path integral formula for the kernel $\langle q|\frac{1}{E-H}|q'\rangle$?