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Harold Hilton

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LVI. *A Note on van der Waals' Equation.*

By HAROLD HILTON*.

BEARING in mind the great importance of van der Waals' equation, it seems worth while to collect the various mathematical properties of the family of curves which is the graphical representation of the equation, together with some accurate tracings of several members of the family.

The form of van der Waals' equation we shall consider is

$$y = \frac{8\theta}{3x-1} - \frac{3}{x^2}, \quad \dots \quad (\alpha)$$

or, as it may be written,

$$3yx^3 - (y+8\theta)x^2 + 9x - 3 = 0,$$

where x , y , and θ are respectively the "reduced" volume, pressure, and temperature; *i. e.*, the volume, pressure, and temperature expressed with the *critical* volume, pressure, and temperature respectively as units.

The equation (α) may be considered as representing a family of curves of the fourth degree, of which θ is the parameter.

The curve (α) cuts the axis of x in finite points, where $8\theta x^2 - 9x + 3 = 0$; the roots of this equation are unreal if $\theta > \frac{27}{32}$; both equal to $\frac{2}{3}$ if $\theta = \frac{27}{32}$; both positive and $> \frac{1}{3}$, if θ lies between $\frac{27}{32}$ and 0; one root is infinite if $\theta = 0$; both roots are real, one lying between $-\infty$ and 0, and the other between 0 and $\frac{1}{3}$, if θ is negative. The curve cuts the axis of y in no finite point. The curve has the axis of x as an ordinary asymptote, and a triple point at infinity in the direction of the axis of y , at which $x = \frac{1}{3}$ is the tangent to one branch, and the tangents to the other two branches coincide in $x = 0$.

Hence to every value of x there can be at most one finite value of y ; and to every value of y there can be at most three finite values of x of which two may be imaginary.

If θ is positive, the curve has a branch between $x = \infty$ and $x = \frac{1}{3}$, touching $y = 0$ and $x = \frac{1}{3}$ at infinity; so that y is in each case positive; a branch lying between $x = \frac{1}{3}$ and $x = 0$, and touching these lines at infinity, so that y is in each case negative (in fact for most positive values of θ this branch lies altogether so far on the negative side of $y = 0$ that it cannot well be drawn on any diagram, and hence does not appear in fig. 1); and a branch on the negative side of $x = 0$ touching

* Communicated by the Author.

$x=0$ and $y=0$ at infinity, so that x and y for the branch are always negative.

If $\theta=0$, the curve breaks up into the straight line $x=\frac{1}{3}$ and the curve $yx^2+3=0$; these two branches meet at the point $(\frac{1}{3}, -27)$.

If θ is negative, there is a branch between $x=\infty$ and $x=\frac{1}{3}$ touching $y=0$ and $x=\frac{1}{3}$ at infinity, y for this branch being always negative; a branch between $x=\frac{1}{3}$ and $x=0$ touching these lines at infinity, so that near $x=\frac{1}{3}$ the ordinate of the curve is positive and near $x=0$ negative (the branch crosses the axis of x and has an inflexion, but cannot in a diagram be well distinguished from a straight line); and a branch on the negative side of $x=0$ for which y is negative near $x=0$ and positive near $x=-\infty$ (the branch crosses the axis of x , has a tangent parallel to this axis, and an inflexion).

Any member of the family can be readily traced by taking a series of values for x and calculating the corresponding values of y . Fig. 1 shows as much of the curves $\theta=\frac{1}{2}$ and $\theta=-1$ as can be conveniently put on a diagram. Fig. 2 shows the part of the curves lying between $x=\frac{1}{3}$ and $x=5$ (which is the part interesting from a physical point of view) for 19 positive values of θ .

The tables given below show the values of y calculated to three places of decimals from which the figures were drawn.

Any member of the family is of degree 4, of class 5, and of deficiency zero; it has two double points and one cusp (coinciding in the multiple point at infinity); two bitangents; and four inflexions (of which two are always imaginary, and the other two are also imaginary if $\theta > \frac{2187}{2048}$).

The area included between any curve of the family and the lines $y=0$, $x_1=0$, $x_2=0$, is

$$\frac{8\theta}{3} \log \frac{3x_2-1}{3x_1-1} + \frac{3}{x_2} - \frac{3}{x_1}.$$

The orthogonal trajectory of the system is

$$x^3(3x-1) = \frac{dy}{dx}(3x^3y-9x+6).$$

The radius of curvature at any point is

$$\frac{\{x^6(3x-1)^2 + (24\theta x^3 - 6(3x-1)^2)\}^{\frac{3}{2}}}{18x^6(3x-1)^2[8\theta x^4 - (3x-1)^3]};$$

if the tangent at the point is parallel to $y=0$, this simplifies into

$$\frac{x^4(3x-1)}{18(1-x)}.$$

FIG. I.

TABLE I.

x.	3x-1.	$\frac{3}{x^2}$.	Values of y for Different Values of 8θ.																			
			8θ=4.	5.	6.	6.75	7.	7.5	8.	9.	12.	16.	24.	32.	40.	48.	56.	64.	72.	80.	—8.	
4	2	18.750	1.250	6.250	11.250	15.000	16.250	18.750														—58.750
4.5	3.5	14.815	—3.386	—5.329	2.328	4.671	5.185	6.614	4.000	6.000	12.000											—28.000
5	5	12.000	—4.000	—2.000	0.000	1.500	2.000	3.000	3.000	3.920	8.545											—18.333
5.5	6.5	9.917	—3.763	—2.225	—6.861	.467	.852	1.621	1.670	2.917	6.667											—18.333
6	8	8.333	—3.333	—2.083	—8.833	.104	.417	.942	1.320	2.373	5.531											—18.333
6.5	9.5	7.101	—2.890	—1.838	—7.85	.004	.267	.794	1.150	2.060	4.787											—18.333
7	11	6.122	—2.486	—1.577	—6.67	.014	.242	.706	1.067	1.867	4.267											—18.333
7.5	12.5	5.333	—2.133	—1.333	—5.33	.067	.267	.667	1.026	1.741	3.883											—18.333
8	14	4.688	—1.831	—1.117	—4.02	.133	.312	.669	1.026	1.741	3.883											—18.333
9	17	3.704	—1.351	—7.63	—1.75	.267	.414	.708	1.002	1.590	3.355	5.708										—10.402
10	20	3.000	—1.000	—5.00	.000	.375	.500	.750	1.000	1.500	3.000	5.000										—7.000
11	23	2.479	—7.740	—3.05	.130	.456	.567	.782	.999	1.434	2.738	4.478										—7.000
12	26	2.083	—5.545	—1.60	.225	.513	.609	.802	.995	1.379	2.553	4.071										—7.000
13	29	1.775	—3.806	—1.044	.294	.552	.639	.811	.983	1.328	2.363	3.742										—7.000
14	32	1.531	—3.44	.031	.344	.578	.636	.813	.969	1.281	2.219	3.469	5.969									—4.523
15	35	1.333	—3.190	.086	.381	.596	.667	.810	.963	1.238	2.096	3.238	5.524									—4.523
16	38	1.172	—1.119	.144	.407	.605	.670	.802	.933	1.196	1.986	3.039	5.144									—3.619
17	41	1.038	—1.062	.182	.425	.608	.669	.791	.913	1.157	1.889	2.864	4.816									—3.619
18	44	.926	—1.017	.210	.438	.608	.665	.779	.892	1.119	1.801	2.710	4.529									—3.619
19	47	.831	.021	.233	.446	.605	.658	.765	.871	1.084	1.722	2.573	4.275	5.978								—3.619
20	50	.750	.050	.250	.450	.600	.650	.750	.850	1.050	1.650	2.450	4.050	5.650								—3.619
20.5	6.5	.750	.186	.289	.443	.558	.597	.674	.751	.904	1.366	1.982	3.212	4.443	5.682							—3.619
21	8.0	.633	.167	.292	.427	.511	.542	.604	.667	.792	1.167	1.667	2.667	3.667	4.667	5.667	6.667					—1.083
21.5	9.5	.541	.180	.285	.391	.470	.496	.548	.601	.706	1.022	1.443	2.285	3.127	3.970	4.812	5.654					—1.083
22	11.0	.487	.176	.267	.358	.426	.449	.495	.540	.631	.903	1.268	1.994	2.722	3.449	4.156	4.913	5.631				—914
22.5	12.5	.448	.172	.252	.332	.392	.412	.452	.492	.572	.812	1.132	1.772	2.412	3.052	3.692	4.332	4.972	5.612			—788
23	14.0	.420	.166	.237	.309	.362	.380	.416	.451	.523	.737	1.023	1.594	2.166	2.737	3.309	3.880	4.451	5.023	5.594		—701

TABLE II.

x .	$3x-1$.	$\frac{3}{x^2}$.	Values of y for Different Values of θ .	
			$8\theta=4$.	$8\theta=-8$.
·3	—1	33·333	— 73·333	46·667
·25	—·25	48·000	— 64·000	— 16·000
·2	—·4	75·000	— 85·000	— 55·000
·15	—·55	133·333	—140·606	—118·788
·1	—·7	300·000	—305·814	—288·571
—·5	—2·5	12·000	— 13·600	—8·800
—1·0	—4·0	3·000	—4·000	—1·000
—1·5	—5·5	1·333	—2·060	·121
—2·0	—7·0	·750	—1·321	·393
—2·5	—8·5	·480	—·951	·461
—3·0	—10·0	·333	—·733	·467
—3·5	—11·5	·241	—·589	·455
—4·0	—13·0	·187	—·495	·428
—4·5	—14·5	·148	—·424	·404
—5·0	—16·0	·120	—·370	·380

Differentiating (α) we have

$$\frac{dy}{dx} = \frac{-24\theta}{(3x-1)^2} + \frac{6}{x^3}.$$

$\therefore$ The tangent is parallel to $y=0$ when $(3x-1)^2=4x^3\theta$.
Eliminating θ between this equation and (a), we have

$$(3x-2)=yx^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

as the curve through the points where y has a maximum or minimum value.

Differentiating (β) we have

$$\frac{dy}{dx} = \frac{6(1-x)}{x^4} \quad \text{and} \quad \frac{d^2y}{dx^2} = \frac{6(3x-4)}{x^5};$$

$\therefore$ (S) has a tangent parallel to the axis of x at point $(1, 1)$ and an inflexion at the point $(\frac{4}{3}, \frac{27}{32})$. This curve cuts $y=0$ where $x=\frac{2}{3}$, has a triple point at infinity at which tangents coincide with $x=0$, and has an inflexion at infinity at which the tangent is $y=0$. It is of degree 4, class 4, and deficiency zero; has 1 double point and 2 cusps (coinciding in the multiple point at infinity), 1 double tangent and 2 inflexions (one at infinity).

It passes through the points $(-6; \cdot 093)$ $(-5; \cdot 136)$
 $(-4; \cdot 169)$ $(-3; \cdot 407)$ $(-2; 1)$ $(-1\cdot 5; 1\cdot 926)$ $(-1; 5)$
 $(-0\cdot 5; 28)$ $(1; -1700)$ $(2; -175)$ $(3; -40\cdot 741)$

The curves (β) and (γ) only meet in 2 finite points, namely $(1; 1)$ $(\frac{1}{3}; -27)$.

Their radii of curvature at the point whose abscissa is x are respectively

$$\frac{\{x^8 + 36(1-x)^2\}^{\frac{3}{2}}}{6x^7(3x-4)} \quad \text{and} \quad \frac{\{x^{10} + 4(6x^2 - 9x + 2)^2\}^{\frac{3}{2}}}{4x^9(3x-5)(3x-1)}.$$

If ACE is a straight line parallel to $y=0$, such that for a certain value of θ the areas ABC, EDC are equal (see fig. 3); then the ordinate of A (or E) represents the pressure

Fig. 3.

at which the substance boils for that particular value of θ . The curve through all such points as A and E we will call the "border" curve. (Cf. Memoirs of Phys. Soc. London, vol. i. part 3, p. 453.) Let x_1, x_2, x_3 be the abscissæ of A, E, and C respectively, and y their ordinate. Then

$$\left(y + \frac{3}{x_2 x_1}\right)(x_2 - x_1) = \frac{8\theta}{3} \log \left(\frac{3x_2 - 1}{3x_1 - 1}\right). \quad \text{. . . (i.)}$$

[See Nernst's 'Theoretical Chemistry.']

Now x_1, x_2, x_3 are the roots of $3yx^3 - (y + 8\theta)x^2 + 9x - 3 = 0$,

$$\text{and therefore} \quad x_1 x_2 + x_2 x_3 + x_3 x_1 = \frac{3}{y}; \quad x_1 x_2 x_3 = \frac{1}{y}.$$

$\therefore$ eliminating x_3 , $yx_1^2 x_2^2 + x_1 + x_2 - 3x_1 x_2 = 0$, and therefore

$$x_2 = \frac{3x_1 - 1 + \sqrt{(3x_1 - 1)^2 - 4yx_1^3}}{2yx_1^2},$$

the positive sign being taken, for y is positive in the region considered, and $x_2 > x_3$.

Substituting this value for x_2 and $\frac{(yx_1^2 + 3)(3x_1 - 1)}{x_1^2}$

8θ in (i.) we have (writing x for x_1)

$$\begin{aligned} & 3(2x^2y + 9x - 3 - 3\sqrt{1-6x+9x^2-4yx^3})(\sqrt{1-6x+9x^2-4yx^3}-1+3x-2yx^3) \\ &= 4yx^2(yx^2+3)(3x-1) \times \log \left(\frac{3\sqrt{1-6x+9x^2-4yx^3}-3+9x-2yx^2}{2yx^2(3x-1)} \right) \end{aligned} \quad (\delta)$$

as the equation of the border curve between $x=\frac{1}{3}$ and $x=1$.

Similar reasoning shows that the equation of the border curve between $x=1$ and $x=\infty$ is found by changing the sign of the radical in (δ).

To trace the curve (δ) directly is not easy, but we can readily determine a number of points on it with fair accuracy when once a number of curves of the family (α) are carefully drawn. We have in fact to choose the points A, E (fig. 3) so that the areas ABC, EDC are equal, and this may be done by help of a planimeter; or, more simply, by ensuring the equality of the number of millimetre squares in these two areas when the curves (α) are plotted out on paper ruled in square millimetres.

The curve (δ) evidently passes through the points (1; 1) and ($\frac{1}{3}$; 0) [as may be verified also from its equation]. The tangent at each point is parallel to the axis of x : this is evident in the case of the former point, we may prove it in the case of the latter, thus:—A tangent to (α) parallel to the axis of x is $y = \frac{8\theta}{3x-1} - \frac{3}{x^2}$, where $(3x-1)=4\theta x^3$; if θ is small, x must be large [supposing $3x-1 \neq 0$], and we have approximately $4\theta x=9$. Then the tangent becomes (substituting $\frac{9}{4\theta}$ for x , and neglecting higher powers of θ than the second) $y = \frac{16}{27}\theta^2$. Hence the ordinate of the point on the border curve corresponding to this value of θ is $< \frac{16}{27}\theta^2$.

Now the curve (α) cuts $y=0$,

$$\text{where} \quad x = \frac{9-9\sqrt{1-\frac{32}{27}\theta}}{16\theta} = \frac{1}{3} + \left(\frac{4}{27}\right)^{\frac{1}{2}}\theta,$$

(if θ is small), and makes an angle

$$\tan^{-1} \left\{ \frac{-24\theta}{(3x-1)^2} + \frac{6}{x^3} \right\} \text{ or } \tan^{-1} \left\{ \frac{-3^{11}}{2^5\theta} + \frac{6}{x^3} \right\}$$

or $\frac{\pi}{2}$ when θ is small, with the axis of x ; hence the abscissa

of the point on (δ) corresponding to this value of θ is

$$\frac{1}{3} + \left(\frac{4}{27}\right)^2 \theta;$$

hence the tangent to (δ) at point $(\frac{1}{3}; 0)$ makes an angle

$$< \tan^{-1} \left[\frac{\frac{16}{27} \theta^2}{\left(\frac{4}{27}\right)^2 \theta} \right]_{\theta=0}$$

with the axis of x ; *i. e.*, it touches the axis of x at this point.

The curve (δ) is shown in fig. 1.

The relation between the reduced temperature and volume at the boiling-point is found by eliminating y between (α) and (δ); it is:—

$$\begin{aligned} & 3 \left\{ (16\theta + 27)x^2 - 36x + 9 \right. \\ & - 3(3x-1) \sqrt{\frac{(27-32\theta)x^3 + 9x^2 - 3x - 1}{3x-1}} \left. \right\} \left\{ -16x^3\theta + 27x^2 - 12x + 1 \right. \\ & + (3x-1) \sqrt{\frac{(27-32\theta)x^3 + 9x^2 - 3x - 1}{3x-1}} \left. \right\} = 32x^2(3x-1)(8x^2\theta - 9x + 3)\theta \\ & \times \log \left\{ \frac{(27-16\theta)x^2 - 3 + 3(3x-1) \sqrt{\frac{(27-32\theta)x^3 + 9x^2 - 3x - 1}{3x-1}}}{(3x-1)(16\theta x^2 - 18x + 6)} \right\} \end{aligned}$$

between $x=\frac{1}{3}$ and $x=1$; and the same with the sign of the radical changed between $x=1$ and $x=\infty$.

When y is so large that the equation

$$3yx^3 - (y+8\theta)x^2 + 9x - 3 = 0$$

has only one real root, this root is (*cf.* Works on Theory of Equations)

$$\begin{aligned} & \frac{1}{3y} \left[\frac{y+8\theta}{3} + \sqrt[3]{\frac{1}{2} \left\{ 18y(y-4\theta) + \frac{2}{27}(y+8\theta)^3 \right. \right.} \\ & \left. \left. + 2y \sqrt{729y + 54(y^2 - 20y\theta - 8\theta^2)} + (y+8\theta)^3 \right\} + \sqrt[3]{\frac{1}{2} \left\{ 18y(y-4\theta) \right. \right.} \\ & \left. \left. + \frac{2}{27}(y+8\theta)^3 - 2y \sqrt{729y + 54(y^2 - 20y\theta - 8\theta^2)} + (y+8\theta)^3 \right\} \right] \end{aligned}$$

If we assume that this expression, which is the real root of x when y is large, by the principle of continuity represents the smallest root of the equation when y becomes so small that the equation has three real roots, we obtain the relation be-

tween the reduced pressure and temperature by substituting this expression for x in the equation (δ).

It should be noted that we have confined ourselves to a strictly mathematical treatment without taking physical considerations into account. The equation (α) can hardly be considered to have any physical application when θ is negative, and ceases to represent *necessarily* the relation between the volume, pressure, and temperature of a substance when $x < \frac{2}{3}$, for then doubly central impacts between the molecules become impossible (*cf.* Memoirs of Phys. Soc. of London, vol. i. part 3, page 384).

References in the Figures.

Reference number...	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
.....	0	4	5	6	6.75	7	7.5	8	9	12	16	24	32	40	48	56	64	72	80	-8

All the curves in fig. 2 (except δ) should run up to the asymptote $x = \frac{1}{3}$; but, for the sake of clearness, they are discontinued before they approach each other so closely as to be mutually indistinguishable.

Figs. 1 and 2 are ruled into reference squares whose sides are half the unit of length.

Note. Since I wrote the above I have heard from Mr. R. E. Baynes, M.A., Christchurch, Oxford, that he obtained an identical result for the equation of the border-curve many years ago.

LVII. *On the Propagation of Cusped Waves and their Relation to the Primary and Secondary Focal Lines.* By Prof. R. W. WOOD*.

IN a previous paper (Phil. Mag. July 1900, p. 148) I have shown the forms of the wave-fronts reflected from spherical surfaces, by means of geometrical constructions, and photographs of the actual waves. In the present paper I shall discuss somewhat more fully the case of the reflexion of a plane wave by a hemispherical mirror, where we have a reflected wave of a form which I have likened to a volcanic cone. A superficial examination of the forms might lead one to imagine that the bowl of the crater collapsed to a point at the principal focus of the mirror. This can of course only be

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