Mapping the van der Waals state space

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We show that the metric structures of the thermodynamic state space enables us to uniquely decide if two thermodynamic states belong to the same phase or not, even in the presence of a critical point. While the method cannot classify one state in itself into a definite phase, coherent regions can be identified in the state space. The construction is demonstrated on the van der Waals gas.

I. INTRODUCTION

Most thermodynamic systems may exist in more than one phase. In a microscopic sense this means different possible patterns for the particles, leading to different behaviors under external influence. It was a great convenience to refer a particular state as belonging to one and only one of these phases, because then some general features would have been specified in a single word.

However, serious problems arise if one wants to do this. According to common opinion, no phase transition happens above the critical temperature, so there are not different phases. It is worthwhile to cite a statement from the standard literature.[1]

"At pressures higher than the critical pressure, the liquid can be heated from a low temperature to a high one without any discontinuity in the process. Ebulliation does not occur as at lower pressures, and no other event makes a change from the liquid phase to the vapor phase. The distinction between the two phases is therefore arbitrary." Applying this *mutatis mutandis* to temperatures, one can conclude that the two phases are distinguishable only below T_{cr} and above this there is not physical difference.

While this statement is true, it has serious consequences for distinguishing the phases even below T_{cr}. To see this, let us follow Landau and Lifshic.[2] They say (in our own translation; Chap. 83); "When a critical point exists, a continuous transition can be realized between any two states of the matter, during which phase separation does not happen in any point; this can be done by changing the state of the matter along a curve circumventing the critical point without crossing the phase equilibrium curve. In this sense, the existence of a critical point questions the notion of different phases, and one cannot always tell which states belong to the first and second phase, respectively. In the strict sense, two phases can be mentioned only when they coexist in contact, i.e., on the phase equilibrium curve." (On that curve a thermodynamic measurement shows that the intensives are homogeneous in the system, but the extensive densities are not; the disjoint regions of different densities are the different phases.[3] When the intensives differ too, from the difference of densities alone one cannot conclude to differences of phases.)

So (i) the proper way to compare conjectured different phases is to move one to the other in the state space; if during this or at the end a phase separation is inevitable, we may say that they belonged to different phases indeed. However, (ii) since there is no phase distinction above T_{cr}, the result is not unique. As Ref. 2 emphasizes, one may choose different paths for the translation with and without a phase transition on the path. Maybe a circumventing path seems unnatural between low temperature states, but in any case, *if one wants to speak about distinguishable phases*, or anything related to phases, some principle must single out a path for the construction.

A popular prescription is the use of *isotherms*. This accepted, phases (or at least *regions* related to phases) can only be defined by isotherms if we introduce the critical isotherm as a borderline, above which the states can be called, e.g., *gaseous* (being permanent gas in the usual sense,[4]) and then one can uniquely classify the states into these three regions, however, three problems arise. First, the different boundaries of the regions are highly different for physical meaning. A serious structural change happens when crossing the phase boundary (manifested in bubble or droplet formation), while nothing observable happens crossing the critical isotherm. Second, *generally*, i.e., when the states to be compared are of different temperatures, one cannot choose an isothermal path. Finally, the choice of isotherms is uninterpretable from the viewpoint of the Riemannian structure of state space, introduced by Weinhold.[5] There is no preferred coordinate system in a Riemannian space, and obviously isotherms are the coordinate lines only if T is one of the coordinates. If one takes seriously the Riemannian structure, and wants to exploit its advantages, they must not attribute physical meaning to special coordinates.

However, the Riemannian structure does yield something preferred, namely such *paths* between any pairs of thermodynamic states, the shortest ones called *geodesics*. Here we show that the comparison of states can be based on geodesics instead of isotherms, so one can indeed uniquely decide if there is phase boundary between any two states or not. By collecting all the points mutually geodesically connected, one again obtains some regions which inherit certain properties of the liquid, vapor, and gas regions of the noninvariant classification. In this paper, we demonstrate this construction using a van der Waals system; then a fourth region appears too, near the critical point.

II. THE METRIC

Riemannian structure of the thermodynamic state space is defined by the second derivatives of a thermodynamic po-

tential density as a metric tensor. With extensive densities as coordinates, one can use either energy[5] or entropy[6] density as the potential and these two descriptions are thermodynamically (but no metrically) equivalent. Here we turn to the second possibility, because then the meaning of the distance, measured in units of average fluctuations,[7] is very transparent. When some extensives are substituted by intensives, the potential is a Massieu function. For a van der Waals gas, the variables (here and henceforth) are the dimensionless density x and dimensionless temperature y defined as

$$x = n/n_0, \quad y = T/an_0^2, \tag{2.1}$$

where the parameters n_0 and a are defined via the equations of state

$$p = nn_0T/(n_0 - n) - an^2,$$
$$\epsilon = (3/2)nT - an^2. \tag{2.2}$$

The physical state space is

$$y \geqslant 0, \quad 0 \leqslant x \leqslant 1. \tag{2.3}$$

Using the dimensionless variables of Eq. (2.1), the equation of state (2.2), in the way described in Refs. 6 and 7, leads to the line element

$$ds^2 = [x^{-1}(1-x)^{-2} - 2e^z]dx^2 + (3/2)xdz^2, \tag{2.4}$$

where we have introduced a new variable

$$z = -\ln(y). \tag{2.5}$$

For comparison, the line element of the ideal gas is

$$ds^2 = x^{-1}dx^2 + (3/2)xdz^2. \tag{2.6}$$

The formulas suggest that for diluted hot states, the van der Waals *metric* goes to that of the ideal gas. However, this is not exactly true for the Riemannian *curvature*. For the necessary Riemann geometry formulas, see Ref. 8.

It is worthwhile to consider first the invariant curvature and symmetries. For an ideal gas, the curvature vanishes and the space has three independent Killing vectors

$$K_1^i = [x^{1/2}\sin(qz),(2/3)^{1/2}x^{-1/2}\cos(qz)], \tag{2.7}$$

$$K_2^i = [x^{1/2}\cos(qz), -(2/3)^{1/2}x^{-1/2}\sin(qz)], \tag{2.8}$$

$$K_3^i = (0,1), \tag{2.9}$$

$$q = (3/8)^{1/2}$$

with an $E(2)$ commutation. On the other hand, the line element (2.4) leads to the scalar curvature

$$R = (1/3)[4x(1-x)^4e^{2z} + (1-x)^2(3x^2 - 6x - 1)e^z$$
$$- 3(1-x)] \times [1 - 2x(1-x)^2e^z]^{-2}, \tag{2.10}$$

which is the only algebraical curvature invariant[8,9] in two dimensions and, since the Riemann tensor has only one independent component, it completely describes the invariant curvature. There is a line singularity in the curvature at

$$e^{-z} = 2x(1-x)^2 \tag{2.11}$$

and it is the only curvature singularity. There $g_{xx} = 0$ [cf. Eq. (2.4)]. Hence, at this line, the density fluctuations are infinite, therefore this curvature singularity is just the line of thermodynamical instability. Therefore the real physical manifold of stable states is the region

$$0 \leqslant x \leqslant 1, \quad y > 2x(1-x)^2.$$

The meaning of the boundaries is as follows: Line $x = 0$ is the vanishing particle number density. In this direction, the space is not complete. The problems here are connected with the fact that there it is possible to get complete vacuum by fluctuations in a given subvolume of a very dilute gas. The problem could be eliminated by using quantum statistics including antiparticles, but it is better not to do this here; for some more discussion, see Chap. 5.

Line $x = 1$ is the maximum possible density of the van der Waals gas. According to line element (2.4), this line is in the infinity. The lower boundary is the singularity, which can be reached; world lines may end on a singularity without making the space extendible. Finally, the manifold is extended to infinity upwards (at high temperatures).

The singularities of g_{ik} at $x = 0$ and $x = 1$ are only coordinate singularities. In the conjectured ideal gas limit $x \to 0$, $z \to -\infty$, $R \to -1$, so indeed this asymptotic region is not flat, thus the ideal gas geometry has not been recovered. (By restoring the correct dimensions, the asymptotic curvature is $-1/n_0$.) In the limit $x \to 1$, the curvature vanishes, but this limit is obviously not an ideal gas.

By direct calculation, one can show that the Killing equation

$$K_{i;k} + K_{k;i} = 0 \tag{2.12}$$

has no solution, therefore, there are no symmetries for the van der Waals gas (there is one symmetry when the attraction is neglected[10]). However, one can hope that some symmetries are recovered approximately in some asymptotic regions, where

$$K_{i;k} + K_{k;i} \equiv Q_{ik} \to 0. \tag{2.13}$$

The quantities Q_{ik} should go to 0 in *some definite sense*. Although for this the general criteria are still unknown, in a true space of $(++)$ signature $Q_{rs}Q^{rs}/K^2 \to 0$ is sufficient. The K^{-2} factor scales out the effect of the freedom in the normalization[8] of the Killing field.

By applying the above definition of asymptotic symmetry, we can evaluate if and where the ideal gas symmetries (2.7)–(2.9) are approximate for a van der Waals gas. The results are K_3 of Eq. (2.9) generates an approximate symmetry in the region

$$x^{1/2}(1-x)^2e^z \ll 1. \tag{2.14}$$

Nevertheless, for K_1 and K_2 being asymptotic symmetries, the further condition

$$x \ll 1 \tag{2.15}$$

is also needed. In addition, observe that in our dimensionless coordinates the invariants are dimensionless. Requiring Q^2/K^2 to be at most 0.01, curves A and F of Fig. 1 are obtained as lower boundaries for the approximate symmetries. The only domain where all three ideal gas symmetries at least approximately hold is the hot dilute left-hand side of curve F. Still, even there R does not go to 0, therefore, there exist better approximate Killing vectors with SO(2,1) group structure. (Note that K_3 is an approximate symmetry anyway for high temperature.)
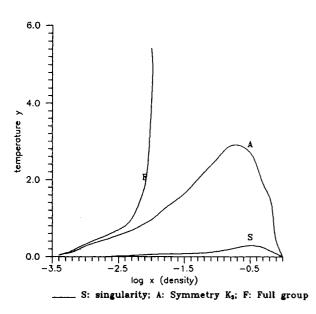
FIG. 1. Domains of approximate validity of the ideal gas symmetries in the van der Waals state space (above the respective curves). Details in the text.

III. GEODESIC STRUCTURE

Consider two points separated by a finite distance. Then various curves can be followed bewteen them. For the whole curve the length s is

$$s(1,2) = \int_1^2 \sqrt{g_{rs}(dx^r/dl)(dx^s/dl)}\,dl, \tag{3.1}$$

where l is any monotonous parameter along the curve. The curves of extreme length are called geodesics[8] and they are determined by the endpoints. In a curved space, therefore, geodesics play the role of straight lines. In affine parametrization $l = s$, Eq. (3.1) reduces to an identity

$$g_{rs}x^r x^s = 1 \tag{3.2}$$

where the prime denotes the derivative with respect to the affine parameter. The extremum condition for $s(1,2)$ yields the form

$$x^{i''} + \Gamma^i_{rs}x^r x^s = 0, \tag{3.3}$$

which needs two initial conditions.

Now, our starting problem was that the phase boundary was not able to separate the state space into two parts, because it did not exist at high temperatures. However, unstable states behind the singularity are not parts of the manifold. So the singularity line may be (and, as will be shown, is) concave in the sense that it does not contain *all* the chords of its boundary point pairs. Then some states are geodesically disconnected.

Now, by this means one could define disconnected states which may remind us of states separated by phase transition. We are going to show that indeed that the lack of geodesic connection can be physically interpreted in this way. Namely, when there is *no* geodesic connection, it means that the minimal curve would like to cross the singularity. Since the thermodynamic meaning of the singularity is the borderline of thermodynamic stability of states, such a path (if realized at all) would mean inevitable phase separation[3] at the border of the manifold. Then there is no *natural* path

between the initial and final states without phase transition. Therefore, here we accept the following:

Definition. Points 1 and 2 do not belong to the same phase if they are geodesically disconnected on the manifold. Here we used a criterion conform to common sense. A *finite* line is considered to be *between* two points if the shortest connecting path crosses it.

At the end of this section, we demonstrate that:

(i) our above definition is operative;

(ii) the results are nontrivial even for initial and final states of the same temperature;

(iii) it can be used even if there are problems with the usual "isothermal" criterion.

Item 1 is easy to demonstrate. A geodesic (line of extreme length) of fixed endpoints can be calculated by variational methods. Now we turn to item 2. Consider, e.g., two states at $y = 0.8$. In our dimensionless units $y_{cr} = 8/27$, we are well above any transition. Still, the geodesic has a tendency to incline. This phenomenon is displayed in Fig. 2. First the densities at the endpoints are 0.1 and 0.9 (curve a); observe the serious inclination. Shifting the densities to 0.05 and 0.95, the points cease to be geodesically connected, but during the variation there is a tendency to obtain "minimal" paths similar to curve b. The explanation is simple. Our task is to span a given density gap with the minimal number of average fluctuations. Now, at the singularity, the average *density* fluctuations is infinite. Therefore, it is profitable to go down first to the neighborhood of the critical point, thus increasing the possible horizontal steps. Of course, then later one has to go up again, therefore, this way is not a real gain if y_1 and y_2 are too high. The inclination is increasing when one has to abridge bigger and bigger density gaps.

Finally, item 3 can be demonstrated by choosing the following endpoints:

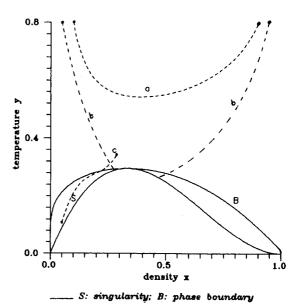$$x_1 = 0.05, \quad y_1 = 0.10; \quad x_2 = 0.29, \quad y_2 = 0.34.$$

FIG. 2. Some characteristic geodesics in the van der Waals state space. Note the tendency of inclination for "horizontal" curves and the opposite for "vertical" ones. Details in the text.

Now, here the initial temperature is below critical, while the final one is above. So, a thumb rule "no phase transition above T_{cr}" could not help us in any way even if accepted. Consequently now, in order to see if a phase transition exists or not between the two states, one must uniquely define the path, and the geodesic path is an operative definition. For clear demonstration, the endpoints have been so chosen that the straight line connecting them *on the* (n,T) *plane* crosses the instability, maybe suggesting a phase transition. However, the above points are geodesically connected, as curve c in Fig. 2 demonstrates.

By summarizing the results of this section, an invariant and purely thermodynamic definition has been given for two states belonging (or not belonging) to the same phase.

Still we cannot assign a particular phase to *a given* state (remaining in accordance with Landau's remark[2]). It seems that here *the question* itself is wrong in the given context. However, as will be shown in the next section, by invariant thermodynamic means in the state space one can construct *regions*, which are coherent units, inheriting the essential characteristics of *phases*.

IV. REGIONS

States *on* the phase boundary can be classified into *phases*.[2] Now, one could look for the maximal domain of the state space, which is coherent for geodesic connection and contains the, say, vapor part of the phase boundary. This domain would be called Vapor *region*. If this construction could be realized, then this region, defined by invariant thermodynamic expressions, would be just what is expected for the vapor "part" of the phase diagram: the maximal domain whose points are connected with every states recently created in evaporation, without a subsequent second phase transition. (Obviously, by the spirit of the construction, metastable states between the phase boundary and singularity are ignored; anyway, there stationary initial and final states are not expected, and this metastable domain could be similarly classified later.)

However, this idea can be realized *only in a restricted sense*. Namely, even the vapor part of the phase boundary is not geodesically connected as a whole unit (shown later). Then one has to choose a preference: which section of the vapor side of the phase boundary is the more substantial. Our physical argument is that the region must contain at least the asymptotically cold (and therefore dilute) phase equilibrium states as such ones most different from liquid states (*par excellence vapor*).

So we are now looking for the maximal coherent region of the state space, which contains the asymptotic vapor states and whose points are all mutually connected on the shortest lines (similarly for the liquid points). Then this maximal region is a whole coherent unit without referring any coordinate system and, since some part of it cannot be regarded as anything else than vapor, this is the Vapor *region* of the space defined by invariant means.

The direct way of constructing this region would be to take a sufficiently dense cluster of points and then to check geodesic connections. Here a more rapid way is followed. First the region is looked for, whose points are all geodesical-

ly connected with asymptotic vapor (or liquid) point, and then the mutual connectivities of the boundary points are checked. Obviously, if these points are mutually connected, interior points are too.

First we consider a general two-phase system with minimal complication, i.e., here we assume that the envelope of all geodesics starting from the asymptotic vapor (liquid) point and going to infinity does exist and is convex. If so, then there are only two different possible region structures. Take a point *on* one of the phase boundaries at low temperature and set geodesics going in every directions thence. Some of them will end on the singularity; collect those which will not and construct their envelopes. Then go down in temperature with the starting point along the phase boundary (asymptotic states of the phase); if the limit of the envelopes exists (assumed here), then it is the boundary of the region whose points are *all* geodesically connected with the asymptotic state. If this limiting envelope is convex (again assumed here), then this is a coherent region whose boundaries are the envelope and the boundaries of the manifold.

Now, there are two envelopes, so obviously two possibilities for their general shapes: they may or may not cross each other. If not, the state space separates into three regions. Two of them lie above the envelopes, are coherent units, and are geodesically connected with the asymptotic parts of the corresponding phases. Therefore, we call them Vapor and Liquid, respectively. The third region is not necessarily a coherent unit, defined here purely negatively, as the set of points geodesically disconnected with the asymptotic parts of any of the distinguishable phases. Since this region contains the vicinity of the critical point, it may be called Critical. In addition, this region is critical for distinction as well, since states in the neighborhood of the critical point are not expected to show clear characteristics of either a familiar vapor or such a liquid, and this ambiguity is reflected in the existence of an intermediate region (which may be even larger than the domain of critical behaviors as, e.g., opalescence).

The other possibility is when the two envelopes cross each other. Then Vapor is the coherent region whose points are *disconnected* with the asymptotic *liquid* states, but *connected* with the asymptotic *vapor* ones, Liquid is vice versa, Critical is the same as in the previous case, and Gas is again a coherent region whose points are geodesically connected with the asymptotic states of *both* regions, so being *above* the transition.

Our remaining task is to see if such a construction can be made for a van der Waals system; if so, which case is realized and where are the boundaries of the regions.

V. THE CALCULATION

Now we are starting to realize the above construction for the van der Waals system. First, very dilute and cold vapor and very dense and cold liquid states are to be chosen on the phase boundary. For these, we take
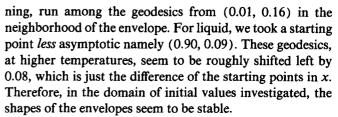
$$x_v = 0.01, \quad y_v = 0.16;$$

$$x_f = 0.98, \quad y_f = 0.0196.$$

The corresponding envelopes of geodesics avoiding the sin-

gularity (so remaining on the manifold up to arbitrarily high temperatures) are displayed in Fig. 3. The envelopes cross each other, thus four regions have been obtained.

Before discussing the shapes and locations of the regions, first we should have to verify that these envelopes approximate those of the asymptotic construction. However, there are problems of both numerical technique and principles. When going to $y = 0$ on the phase boundary, the surviving geodesics start more and more vertically, and various terms in the second-order geodesic equation start to diverge. Furthermore, the $x \ll 1$ part of the phase boundary is almost vertical, so only the very close neighborhood of $x = 0$ would be really low in temperature. In addition, ideal gas geodesics have the tendency to become horizontal after traversing some fundamental section in y. So there is a part of the phase boundary, very cold nevertheless well above the singularity (which is possible only for $x \ll 1$), where one might expect complications. Here we do not investigate this question from two reasons. First, ideal gas geodesics may possess strange shapes, but this phenomenon is clearly independent of any phase transition, so we do not have anything to do with it in the present context. Second, it is well-known that the ideal gas equation of state is aphysical for very low temperatures (e.g., violating Third Law). The same is true for a very dilute cold van der Waals gas. This trouble should and can be healed by using, e.g., quantum statistics; then at higher temperatures and moderate densities, the equation of state is practically unchanged, but the asymptotic dilute region is different.[11] Since here we deal with a classical phenomenological equation, this (very complicated) way will not be followed, however, strange features of the cold dilute states do not have to be taken literally.

So here we do not *prove* the exact asymptoticity of our envelopes; however, two checks have been made. For vapor, some geodesics have been calculated from the starting point (0.001, 0.123). They, except of course for the very begin-

ning, run among the geodesics from (0.01, 0.16) in the neighborhood of the envelope. For liquid, we took a starting point *less* asymptotic namely (0.90, 0.09). These geodesics, at higher temperatures, seem to be roughly shifted left by 0.08, which is just the difference of the starting points in x. Therefore, in the domain of initial values investigated, the shapes of the envelopes seem to be stable.

Now we are in the position to define the regions of the state space. For display, cf. Fig. 3. Still, the (n,T) coordinates, though advantageous for drawing geodesics, are not the most familiar ones for phase diagrams. So we transform this diagram to the usual one in (p,v) coordinates on Fig. 4, where p is the (dimensionless) pressure from Eq. (2.2) and $v \equiv 1/x$. Here we have been forced to use logarithmic scale on the p axis, because the crossing of envelopes is located high above critical pressure. We will return to this point in the Conclusion.

Still we have to verify that the Vapor, Liquid, and Gas regions are coherent (i.e., the points of any of these three regions are mutually geodesically connected). In order to see this, we checked the convexity of the above-defined boundaries (which is *sufficient* condition). At all investigated point pairs, the boundaries turned out to be convex; some examples for demonstration are given on Fig. 5.

It is interesting that geodesics moving in the neighborhood of the instability show a gravitational lens type reconverging (cf. Fig. 6), caused by the repulsive property of the singularity. This is the reason for the envelopes not being geodesics.

VI. CONCLUSIONS

We have investigated systems possessing more than one phase and a critical point, for which there are serious problems when classifying states into phases, and have demonstrated that some classification can be done by means of the metric thermodynamics of Weinhold and Ruppeiner in a
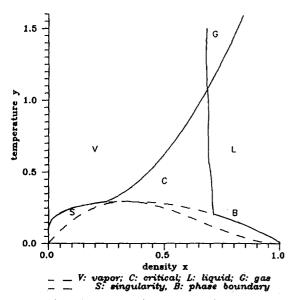

FIG. 3. The region structure for van der Waals gas. Very asymptotic cold vapor states have not been explicitly investigated, because there Third Law is violated.
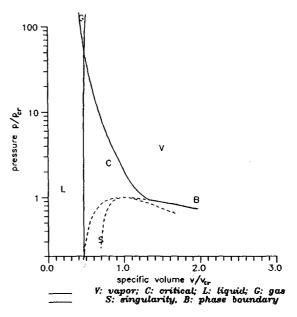

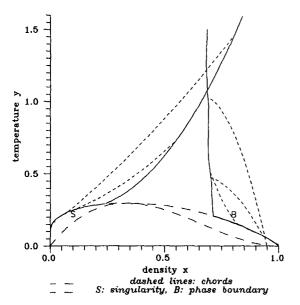FIG. 4. As Fig. 3, but on the (p,v) diagram. Pressure scale is logarithmic.

FIG. 5. Chords of the left (vapor) and right (liquid) region boundaries of van der Waals gas, respectively, demonstrating the convexity of the boundaries.

natural way. By this, one can uniquely decide if there is a phase transition *between* two given states. However, even then one cannot assign a definite phase to *one* given state. Still, a more modest aim can be achieved, namely we can recognize coherent regions in the state space, inheriting the fundamental characteristics of phases. For van der Waals gas, three *coherent* regions have been found, call Vapor, Liquid, and Gas; the remaining part of the state space seems to be the region of the attraction of the critical point.

The resulted region structure, while *qualitatively* not unreasonable, possesses three strange quantitative features, more or less interconnected. First, the left boundary of the Liquid region does not approach the neighborhood of the
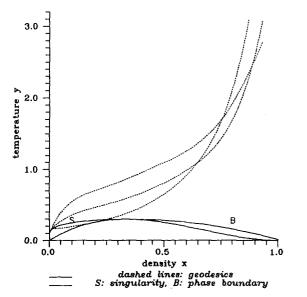

FIG. 6. "Gravitational lens effect" in the neighborhood of the critical point. Due to the repulsion at the upper part of the singularity, the geodesics cross each other in two points.

critical density; the border is rather vertical. This is not a numerical error as shown in the Appendix. Second, the Gas region is rather rudimentary and again does not extend below approximately the *double* of critical density, rather strangely for a permanent gas. Again, this is connected with the vertical nature of the Liquid envelope. Third, the Critical region (whose internal structure has not been investigated here) extends too high (up to approximately three times critical temperature). These strange features lead to the particular shape of Fig. 4. There the Critical region in *pressure* extends one and half orders of magnitude above the critical pressure, and this peak is located at approximately double the critical density. So, the intermediate (Critical) region is rather extended.

However, our guess is that these particularities are not characteristic for *real* systems, which are here approximated by the van der Waals gas; they seem to be the consequence of a particular approximation. Namely, the existence of a high minimal gas density directly comes from the fact that *all* van der Waals liquid geodesics turn back to high densities. Now, this is caused solely by the *high density* behavior of the system, where the van der Waals equation of state is not the general approximation for real "gases." So here we could only demonstrate how an invariant classifying method works. Our conjecture is that a realistic high density equation of state could be selected according to the more conventional shape of the resulted regions. This question would deserve further investigation.

ACKNOWLEDGMENTS

APPENDIX: THE GEODESIC EQUATION

Here we start from Eqs. (3.2) and (3.3). Equation (3.3) gives the second derivatives of x and z on a geodesic, but Eq. (3.2) is a first integral. The remaining equations can be evaluated by writing

$$z = z(x) \tag{A1}$$

and then we get

$$z^{**} = -\{z^* + (2/3)e^z\}/x - (1-x)^2 z^*$$
$$\times [1 - 2x(1-x)^2 e^z]^{-1}\{(1-3x)/[2x(1-x)^3]$$
$$+ 2xz^* e^z + 3xz^{*2}/4\}, \tag{A2}$$

where

$$z^* \equiv dz/dx. \tag{A3}$$

This is the equation for geodesic paths.

Now, from direct calculation, one learns that, starting from $z \ll -1$ and $1 - x \ll 1$, the geodesics tend to be vertical at moderate $x - s$ and $z - s$. We must check if this is a numerical error or not. Accepting *first* the phenomenon, one may conclude that for $|z^*| \gg 1$, the leading term of the right-hand side of Eq. (A2) is the last one. Thus, there

$$z^{**} \approx -(3/4)(1-x)^2 x[1 - 2x(1-x)^2 e^z]^{-1} z^{*3}. \tag{A4}$$

Now, the prefactor of the new right-hand side is moderate and negative, so

$$z^{**} \approx - C^2 z^{*3}, \tag{A5}$$

but this rough approximation can be integrated as

$$z^{*-2} \approx C^2(x - x_{\min}) \rightarrow (dz/dx) \approx [C(x - x_{\min})]^{-1/2}, \tag{A6}$$

$$x_{\min} < 1,$$

whence

$$z \approx z_1 + (2/C)(x - x_{\min})^{1/2}. \tag{A7}$$

This is just the shape obtained in numerical calculation; $x_{\min}$ depends on the initial point and slope, but for $(1 - x_0) \ll 1$, its absolute minimum seems to be ~ 0.70.

Similar geodesics can be analytically obtained from the restricted van der Waals system[10]

$$ds^2 = [x(1 - x)]^{-2} dx^2 + (3/2)x dz^2 \tag{A8}$$

in which there is no attraction. Then

$$z^{**} = - (3 - 5x)[2x(1 - x)]^{-1} z^*$$
$$- (3/4)x(1 - x)^2 z^{*3}. \tag{A9}$$

It can be integrated as

$$z^* = Q\{x(1 - x)[x - (2/3)Q^2]\}^{-1/2}, \tag{A10}$$

$$z = z_Q + \sqrt{3/8}\,\arctan\sqrt{(3x/2Q^2) - 1} + Q[1 - (2/3)Q^2]^{-1/2}$$
$$\times \ln[\sqrt{1 - (2/3)Q^2} + \sqrt{x - (2/3)Q^2}]/[\sqrt{1 - (2/3)Q^2} - \sqrt{x - (2/3)Q^2}], \tag{A11}$$

where Q is a constant of integration. Now, at

$$x_Q = (2/3)Q^2, \tag{A12}$$

dz/dx diverges, but z does not. Since $x - (2/3)Q^2$ must not become negative (cf. the square roots), beyond (x_Q, z_Q) the path continues with $x > x_Q$, i.e., turns back. Therefore, asymptotic liquid geodesics cannot extend below critical density for a van der Waals system.

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