



Statistical complexity, virial expansion, and van der Waals equation



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HIGHLIGHTS

- We specialize the notion of statistical complexity for a real gas.
- We obtain van der Waals isotherms expressed in complexity terms.
- A complexity-like equation of state is obtained.

ARTICLE INFO

Article history:

Received 23 February 2016

Available online 19 April 2016

Keywords:

Statistical complexity

Real gas

Second virial coefficient

ABSTRACT

We investigate the notion of LMC statistical complexity with regards to a real gas and in terms of the second virial coefficient. The ensuing results are applied to the van der Waals equation. Interestingly enough, one finds a complexity-interpretation for the associated phase transition.

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1. Introduction: statistical complexity

Ascertaining the degree of unpredictability and randomness of a system does not automatically entail that one is adequately grasping the extant correlation-structures. Normally, the desideratum is to be able to capture the relationship amongst the components of a given physical system. These structures, of course, greatly influence the features of the specific probability distribution (PD) P that describes the physical process under study. The duet randomness–structural correlations does not have totally independent components. We are sure that the opposite extremes of (i) perfect order and (ii) maximal randomness do not display significant structural correlations [1]. In between these two extreme situations a great range of structural degrees may be present, that in turn should be reflected by the features of the PD we spoke about above. How? This is a complex problem. As Crutchfield noted in 1994, “Physics does have the tools for detecting and measuring complete order equilibria and fixed point or periodic behavior and ideal randomness via temperature and thermodynamic entropy or, in dynamical contexts, via the Shannon entropy rate and Kolmogorov complexity. What is still needed, though, is a definition of structure and a way to detect and to measure it” [2,3]. Seth Lloyd counted as many as 40 manners of defining complexity, none of them quite satisfactory.

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One would like that some appropriate functional $F[(P)]$ would capture correlations in similar fashion as Shannon's entropy captures randomness. A major breakthrough came from the definition proposed by López-Ruiz, Mancini and Calbet [1]. LMC's complexity clearly separated and quantified the contributions of entropy and structure, the latter being described by a concept called disequilibrium. LMC's suitable candidate for the desired functional has come to be called the statistical complexity (see, for instance, Refs. [1,4–9]). Our $F[(P)]$ should vanish in the two special extreme instances mentioned above.

In this effort we attempt a further validation of the LMC complexity notions by appeal to an example of exceptional importance: the van der Waals phase transition. For this purpose we will advance an LMC-complexity treatment for the real gas, in the second order virial approximation. After applying the ensuing results to the van der Waals equation, we will be able to provide a statistical complexity interpretation of the associated phase transition, a fact that, let us insist, gives in our opinion a strong validation to the use of the LMC measure.

The paper is organized as follows. Section 2 introduces preliminary materials. Our results are presented beginning with Section 3, devoted to the virial treatment of a real gas. Section 4 deals with the van der Waals gas and some conclusions are drawn in Section 5.

2. LMC statistical complexity in the canonical ensemble

We review in this preparatory section the basic ideas advanced by López-Ruiz in Ref. [10]. He refers, in a canonical ensemble-environment, to the behavior of the Statistical Complexity (SC) of an ideal gas in thermal equilibrium. For such a purpose, we consider first a classical ideal system of N identical particles, confined into a space of volume V , in thermal equilibrium at temperature T . The corresponding Boltzmann distribution in this scenario is [11]

$$\rho(\mathbf{r}, \mathbf{p}) = \frac{e^{-\beta H(\mathbf{r}, \mathbf{p})}}{Q_N^{(0)}(V, T)}, \quad (1)$$

where $\beta = 1/k_B T$, k_B the Boltzmann constant, $H(\mathbf{r}, \mathbf{p})$ is the Hamiltonian of the system, and \mathbf{r}, \mathbf{p} the pertinent phase space variables. The canonical partition function reads

$$Q_N^{(0)}(V, T) = \int d\Omega e^{-\beta H(\mathbf{r}, \mathbf{p})}, \quad (2)$$

with $d\Omega = d^{3N} \mathbf{r} d^{3N} \mathbf{p} / N! h^{3N}$. Connection with Helmholtz' free energy A_0 is established, according to Ref. [11], via

$$A_0(V, T) = -k_B T \ln Q_N^{(0)}(V, T). \quad (3)$$

R. López-Ruiz defines in Ref. [10] the disequilibrium-concept (in a canonical ensemble) as¹

$$D_0(V, T) = e^{2\beta [A_0(V, T) - A_0(V, T/2)]}. \quad (4)$$

Remember that the usual D -notation refers to the distance (in probability space) of the actual probability distribution to the uniform one [1]. In order to better appreciate the meaning of Eq. (4), we change T by $T/2$ in Eq. (3) and write

$$A_0(V, T/2) = -\frac{k_B T}{2} \ln Q_N^{(0)}(V, T/2). \quad (5)$$

Thus, replacing this into (4), it is easy to ascertain that

$$2\beta [A_0(V, T) - A_0(V, T/2)] = -2 \ln \left[Q_N^{(0)}(V, T) Q_N^{(0)-1/2}(V, T/2) \right], \quad (6)$$

which leads to

$$D_0(V, T) = \frac{Q_N^{(0)}(V, T/2)}{Q_N^{(0)2}(V, T)}, \quad (7)$$

a useful alternative expression for the disequilibrium, given in terms of the canonical partition function. We note that, by using definitions (1) and (2), the disequilibrium also can be written as

$$D_0(V, T) = \frac{\int d\Omega e^{-2\beta H(\mathbf{r}, \mathbf{p})}}{Q_N^{(0)2}(V, T)} = \int d\Omega \rho^2(\mathbf{r}, \mathbf{p}). \quad (8)$$

This alternative form is used in many applications (see, for example, Ref. [12]).

¹ For convenience, we use the subscript 0 for the ideal gas.

In addition, the LMC statistical complexity C_0 is defined as [1]

$$C_0(V, T) = D_0(V, T) S_0(V, T), \tag{9}$$

where $S_0(V, T)$ is the thermodynamic entropy of the system. Subsequently, the definition of statistical complexity was slightly modified by Catalan et al. in Ref. [13], in order to avoid putative negative values for C_0 . The new definition is applicable to systems described by either discrete or continuous probability distributions. In the canonical ensemble, the new C_0 is given by

$$C_0(V, T) = D_0(V, T) e^{S_0(V, T)}. \tag{10}$$

Hence, for the classical ideal gas whose Hamiltonian is $H(\mathbf{p}) = \sum_{i=1}^N p_i^2/2m$, the analytical expression for the partition function is [11]

$$Q_N^{(0)}(V, T) = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N, \tag{11}$$

with λ the particles' mean thermal wavelength $\lambda = h/(2\pi mk_B T)^{1/2}$ [11]. The Helmholtz free energy is, using Stirlings formula ($\ln N! \approx N \ln N - N$) [11], given by

$$A_0(V, T) = Nk_B T \left[\ln \left(\frac{N\lambda^3}{V} \right) - 1 \right]. \tag{12}$$

Thus, inserting Eq. (12) into definition (4), after a bit of algebra, we are led to

$$D_0(V, T) = \left(\frac{N\lambda^3}{V} \right)^N e^{-N} 2^{-3N/2} \equiv N! \left(\frac{\lambda^3}{V} \right)^N 2^{-3N/2}. \tag{13}$$

We know that here, as befits classical considerations, $N\lambda^3/V \ll 1$. Therefore, for $N \rightarrow \infty$ the disequilibrium $D_0(V, T)$ vanishes, as it should. Additionally, we have for the classical entropy the Sackur-Tetrode equation [11]

$$\frac{S_0(V, T)}{k_B} = \ln \left(\frac{V}{N\lambda^3} \right)^N + \frac{5N}{2}, \tag{14}$$

which is positive defined only if $V/(N\lambda^3) \gg 1$. In terms of the disequilibrium the entropy can be cast as

$$\frac{S_0(V, T)}{k_B} = \frac{3N}{2} - \ln [2^{3N/2} D_0(V, T)], \tag{15}$$

or, by inverting the above equation

$$D_0(V, T) = \left(\frac{e}{2} \right)^{3N/2} e^{-S_0(V, T)/k_B}. \tag{16}$$

The statistical complexity is

$$C_0(V, T) = \left(\frac{e}{2} \right)^{3N/2} \frac{S_0(V, T)}{k_B} e^{-S_0(V, T)/k_B}, \tag{17}$$

according to Eq. (6) of Ref. [1]. Explicitly, and after a little algebra, we can write the complexity in terms of V and T as

$$C_0(v, T) = N \left(\frac{e}{2} \right)^{-3N/2} \left(\frac{v e^{5/2}}{\lambda^3} \right)^{-N} \ln \left(\frac{v e^{5/2}}{\lambda^3} \right), \tag{18}$$

where $v = V/N$ denotes the volume per particle. We note $C_0(v, T)$ is positive if $v/\lambda^3 \gg 1$ (always true for a classical environment). It is easy to check that, for T tending to infinity, the statistical complexity vanishes [1], as it should.

3. Real gas and second virial coefficient

Here we start developing the new materials of this contribution. We consider a classical mono-atomic gas of N identical molecules, confined in a space of volume V , in equilibrium at temperature T . The Hamiltonian includes intermolecular interactions and is given by [11]

$$H(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i < j} u_{ij}, \tag{19}$$

where \mathbf{p}_i is the momentum of the i th particle and $u_{ij} = u(|\mathbf{r}_i - \mathbf{r}_j|)$ is the energy of interaction between the i th and j th particles, being a function of the inter-particle distance only, $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. The sum in the second right hand term of the Hamiltonian runs over the $N(N - 1)/2$ pairs of particles [11]. For such a system, the canonical partition function is [11]

$$Q_N(V, T) = Q_N^{(0)}(V, T) Z_N(V, T), \quad (20)$$

where $Z_N(V, T)$ is the so-called configuration integral, given by

$$Z_N(V, T) = \frac{1}{V^N} \int d^{3N} \mathbf{r} e^{-\beta \sum_{i < j} u_{ij}}. \quad (21)$$

Here, $Q_N^{(0)}(V, T)$ is the canonical partition function of the ideal gas given by Eq. (11) [11]. If the gas density $n = N/V$ is low enough, the partition function is approximated [14]

$$Q_N(V, T) = Q_N^{(0)}(V, T) \left(1 - \frac{N}{V} B_2(T)\right)^N, \quad (22)$$

where $B_2(T)$ is the second Virial coefficient, given by

$$B_2(T) = -\frac{1}{2} \int d^3 \mathbf{r} f(r), \quad (23)$$

and $f(r) = \exp(-\beta u(r)) - 1$ is usually called the Mayer function [11].

Let us consider now the disequilibrium. As shown above, it is given by

$$D(V, T) = \frac{Q_N(V, T/2)}{Q_N^2(V, T)}, \quad (24)$$

that in view of Eq. (22) becomes

$$D(V, T) = D_0(V, T) \frac{\left(1 - \frac{N}{V} B_2(T/2)\right)^N}{\left(1 - \frac{N}{V} B_2(T)\right)^{2N}}, \quad (25)$$

where we have identified the ideal disequilibrium using (8) as

$$D_0(V, T) = \frac{Q_N^{(0)}(V, T/2)}{Q_N^{(0)2}(V, T)} \equiv \left(\frac{Q_1^{(0)}(V, T/2)}{Q_1^{(0)2}(V, T)}\right)^N, \quad (26)$$

with $Q_1^{(0)}(V, T)$ the ideal partition function per particle. Expanding in terms of N/V , and neglecting terms of order N^2/V^2 , one obtains

$$D(V, T) = D_0(V, T) \left(1 + \frac{N}{V} (2B_2(T) - B_2(T/2))\right)^N. \quad (27)$$

It is convenient to define the disequilibrium per particle, so that (cf. (26)) one has

$$d(V, T) = \frac{D(V, T)}{N} = \frac{Q_1^{(0)}(V, T/2)}{Q_1^{(0)2}(V, T)} \left(1 + \frac{N}{V} (2B_2(T) - B_2(T/2))\right). \quad (28)$$

Furthermore, the entropy per particle (up to first order in the density n) is [14]

$$h(V, T) = \frac{S(V, T)}{Nk_B} = \frac{S_0(V, T)}{Nk_B} - \frac{N}{V} \frac{\partial}{\partial T} (TB_2(T)). \quad (29)$$

Hence, appealing to Eq. (10), we define the statistical complexity per particle as

$$c(V, T) = d(V, T) e^{h(V, T)}. \quad (30)$$

Replacing Eqs. (27) and (29) into Eq. (30), we cast the statistical complexity per particle of the real gas in the fashion

$$c(V, T) = c_0(V, T) \left(1 + \frac{N}{V} (2B_2(T) - B_2(T/2))\right) \exp\left(-\frac{N}{V} \frac{\partial}{\partial T} (TB_2(T))\right), \quad (31)$$

where

$$c_0(V, T) = d_0(V, T) e^{h_0(V, T)}, \quad (32)$$

with $h_0(V, T) = S_0(V, T)/Nk_B$.

4. Van del Waals gas

To illustrate the results of the previous section, we consider the following approximation for the intermolecular potential, given by

$$u(r) = \begin{cases} \infty & r < r_0 \\ e^{-\beta u(r)} \approx 1 - \beta u(r) & r > r_0, \end{cases} \quad (33)$$

where r_0 is the minimum possible separation between molecules [14]. It is easy then to compute the second virial coefficient by recourse to Eq. (23), that in this case becomes

$$B_2(T) = b - \beta a, \quad (34)$$

where

$$b = \frac{2}{3}\pi r_0^3, \quad (35)$$

is related to the volume of a hard-sphere molecule, and

$$a = \langle u(r) \rangle = 2\pi \int_{r_0}^{\infty} dr r^2 u(r), \quad (36)$$

is the mean potential energy. Given that

$$2B_2(T) - B_2(T/2) = b, \quad (37)$$

independent of temperature, and

$$\frac{\partial}{\partial T}(TB_2(T)) = b, \quad (38)$$

a constant, we finally obtain the statistical complexity per particle

$$c(V) = c_0(V) \left(1 + \frac{N}{V} b \right) \exp \left(-\frac{Nb}{V} \right), \quad (39)$$

which does not depend upon T . Expanding the exponential up to first order in N/V , with $Nb/V \ll 1$, we have $\exp(-Nb/V) \approx 1 - Nb/V$. Thus, we are led to

$$c(V) = c_0(V) \left(1 - \left(\frac{Nb}{V} \right)^2 \right), \quad (40)$$

or taking into account that $v = V/N$ is the volume-per-particle, we also get the relative statistical complexity

$$c_r(v) = \frac{c(v)}{c_0(v)} = 1 - \left(\frac{b}{v} \right)^2, \quad (41)$$

which is the virial expansion of the statistical complexity per particle up to first order in the density n , that is independent from T . In addition, from Eqs. (27), (37), and (38) we find the relative disequilibrium

$$d_r(v) = \frac{d(v)}{d_0(v)} = 1 + \frac{b}{v}, \quad (42)$$

which increases lineally with b/v . Note that:

1. If $b = 0$, this means that the mean volume per molecule is null and we recover the expression for the statistical complexity of the ideal gas, since $c(v) = c_0(v)$.
2. Since $b/v \ll 1$ (low particle-density), then $c(v) < c_0(v)$. The real gas statistical complexity is smaller than the ideal complexity. This indicates that the real gas represents a more ordered system than the ideal gas, which seems obvious.
3. In the non-realistic scenario $v = b$, then the statistical complexity vanishes, since the system becomes a “solid”.
4. The information entropy decreases for the real gas with respect to the ideal one, i.e., from Eq. (29) we get $h(v) < h_0(v)$.
5. On account of Eq. (41), $c_r(v)$ depends only upon the volume v . It can act then as a representative of the volume. This will be useful below in allowing for a Maxwell’s construction for the complexity.

We illustrate these comments in Fig. 1.

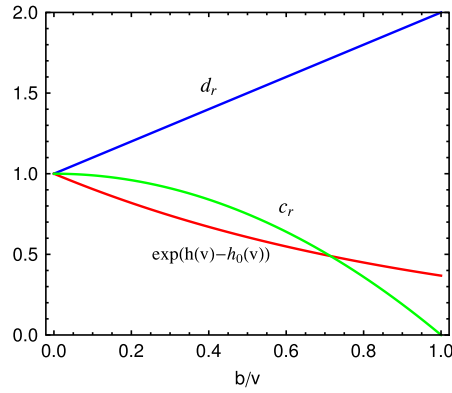


Fig. 1. Relative statistical complexity c_r (green line), relative disequilibrium d_r (blue line) and $\exp(h(v) - h_0(v))$ (red line), as a function of b/v . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.1. Van der Waals equation and statistical complexity

The thermodynamic equation of state advanced by Johannes Diderik van der Waals is of the form [15]

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT, \quad (43)$$

where P is the pressure of the fluid, v the total molar volume of the container, T is the absolute temperature of the system, and R is the universal gas constant.

Now, from Eq. (41) we easily get

$$v = b(1 - c_r)^{-1/2}, \quad (44)$$

that, replacing into van der Waals' equation (43), immediately leads to the pressure as a function of a ratio between complexities (real/ideal). We have

$$P = \frac{RT/b}{(1 - c_r)^{-1/2} - 1} - \frac{a}{b^2}(1 - c_r), \quad (45)$$

that we interpret as a complexity-like equation of state. We can recast it using critical variables, arising for the critical-point equations [16]

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0, \quad (46)$$

i.e., the critical isotherm on a $P - V$ diagram has a point of inflection. These two equations constitute a set of two equations in two unknowns, V , and T . Solving for them (see Ref. [16] for the pertinent details) yields the critical values referred to below, that allow one to recast the van der Waals equation into an invariant form, applicable to all fluids, by defining the following reduced variables

$$p_R = \frac{P}{P_c}, \quad (47)$$

$$v_R = \frac{v}{v_c}, \quad (48)$$

$$t_R = \frac{T}{T_c}, \quad (49)$$

where the critical values corresponds to the critical isotherm, given by the solutions to (46) (again, see Ref. [16])

$$P_c = \frac{a}{27b^2}, \quad (50)$$

$$v_c = 3b, \quad (51)$$

$$T_c = \frac{8a}{27Rb}. \quad (52)$$

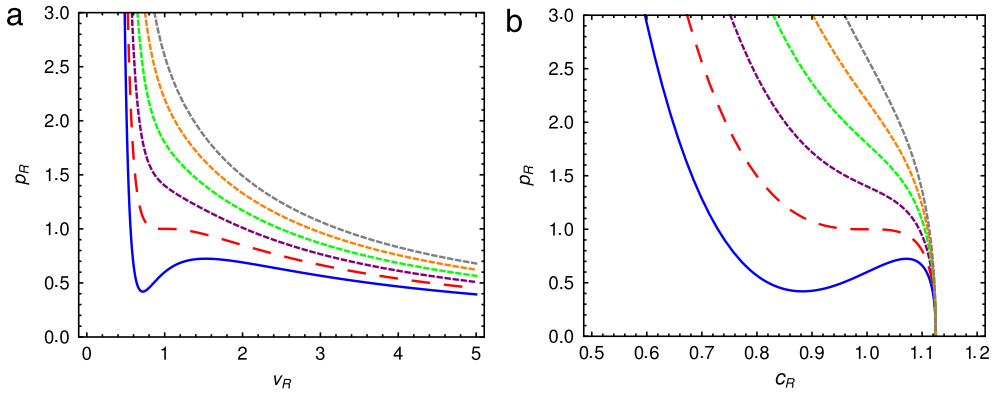


Fig. 2. (a) Reduced pressure p_R versus reduced volume v_R for different values of t_R . We take: $t_R = 0.9, 1.0, 1.1, 1.2, 1.3, 1.4$. In green color we display the critical isotherm. The blue line corresponds to the minimal value of t_R considered in this figure. (b) Reduced pressure p_R versus the ratio c_R for different values of t_R . We take also: $t_R = 0.9, 1.0, 1.1, 1.2, 1.3, 1.4$. Note the concavity change in the LMC statistical complexity in comparison with the critical isotherm given by the green line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Taking into account the definitions (47), (48), and (49) we get in natural fashion the relative statistical complexity in terms of reduced variables:

$$c_R = \frac{c_r}{c_{rc}}, \tag{53}$$

where $c_{rc} = 8/9$ is the critical value of the relative statistical complexity. Thus, we have

$$c_R = \frac{9}{8} \left(1 - \left(\frac{b}{v} \right)^2 \right). \tag{54}$$

Therefore, using reduced variables, we recast Eq. (45) in the fashion

$$p_R = \frac{8 t_R}{\left(1 - \frac{8}{9} c_R \right)^{-1/2} - 1} - 27 \left(1 - \frac{8}{9} c_R \right). \tag{55}$$

We depict in Fig. 2 Eqs. (43) and (55). In (a) we plot the typical cubical equation of state in terms of reduced variables. We compare this with Fig. (b) where we plot p_R as a function of the relative statistical complexity c_R in reduced variables.

One of our main results here is having encountered a complexity critical isotherm. Coexistence of phases is to be appreciated. Notice in Fig. 2 (b) that the gas phase lies at the right of the graph, since the real complexity there is close to that of the ideal gas. Instead, for smaller c_R ratios we enter a more ordered, liquid phase.

4.2. Remarks

From Eqs. (48) and (54) we easily obtain

$$c_R = \frac{9}{8} \left(1 - \frac{1}{9 v_R^2} \right). \tag{56}$$

Accordingly, for $v_R \mapsto \infty, c_R \mapsto 9/8 = 1.125$. The minimum complexity value is, of course, zero, that is attained for $v_R = 1/3 = 0.3333$ (as one gathers from (51) and (54)). This is illustrated in the graph given in Fig. 4.

Returning now to Eq. (55), in the limit $v_R \mapsto \infty, c_R = 9/8$ and the pressure vanishes (see Fig. 2(b)). This, the collapse there depicted at the right.

5. Conclusions

In this work we have studied features of the LMC statistical complexity for a dilute real gas using the virial coefficient B_2 and obtained some analytical results.

We obtained the statistical complexity per particle of the real gas in the fashion

$$c(V, T) = c_0(V, T) \left(1 + \frac{N}{V} (2B_2(T) - B_2(T/2)) \right) \exp \left(-\frac{N}{V} \frac{\partial}{\partial T} (TB_2(T)) \right),$$

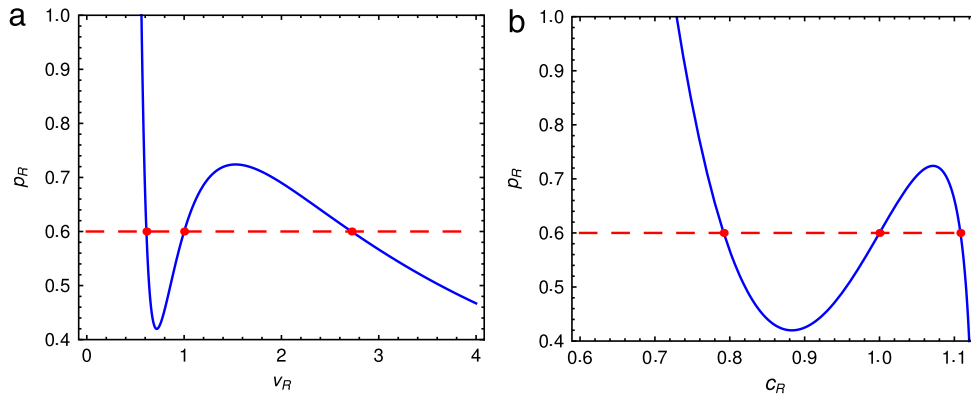


Fig. 3. Maxwell construction for a typical isotherm: (a) p_R vs. v_R for $t_R = 0.9$. (b) p_R vs. complexity-ratio c_R for $t_R = 0.9$.

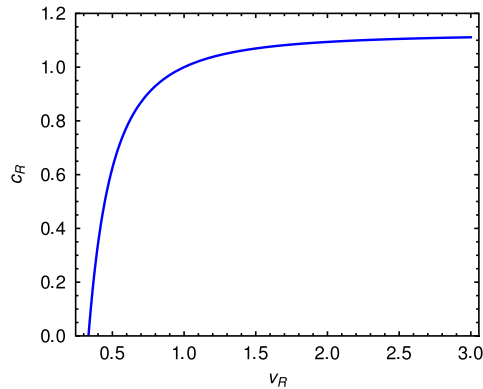


Fig. 4. Statistical complexity c_R versus v_R .

where

$$c_0(V, T) = d_0(V, T) e^{h_0(V, T)},$$

with $h_0(V, T) = S_0(V, T)/Nk_B$.

As for the van der Waals gas we have found that

1. If $b = 0$, the expression for the statistical complexity becomes that of the ideal gas.
2. The van der Waals statistical complexity is smaller than the ideal complexity since the van der Waals is of course a more ordered system.
3. In the non-realistic, but super-ordered $v = b$ case, the statistical complexity vanishes.
4. $c_r(v)$ depends only upon the volume v . It can act then as a representative of the volume.
5. We have encountered a complexity critical isotherm, where coexistence of phases is appreciated.

Summing up: the two body interaction produces an ordering effect and reduces the complexity with relation to that for the ideal gas. Application to the van der Waals gas allows one to see that the LMC complexity measure clearly distinguishes the two pertinent phases. The change takes place when the ratio between the real gas complexity and the ideal gas one ranges from 0.7 to 0.9 (Fig. 2). For $c_R \leq 0.8$ we encounter ourselves in a more ordered fluid phase than that of a gas (Fig. 3).

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