



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.

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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.

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