Phase Transitions For Dilute Particle Systems with Lennard-Jones Potential

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Abstract: We consider a classical dilute particle system in a large box with pair-interaction given by a Lennard-Jones-type potential. The inverse temperature is picked proportionally to the logarithm of the particle density. We identify the free energy per particle in terms of a variational formula and show that this formula exhibits a cascade of phase transitions as the temperature parameter ranges from zero to infinity. Loosely speaking, the particle system separates into spatially distant components in such a way that within each phase all components are of the same size, which is the larger the lower the temperature. The main tool in our proof is a new large deviation principle for sparse point configurations.

1. Introduction

1.1. Motivation. One of the basic themes of equilibrium statistical mechanics is the study of interacting many-body systems in the thermodynamic limit. A major problem in this area, which has not been mathematically solved so far, is to understand the transition between the gaseous and the solid phase at positive temperature and particle density. In the present paper we discuss the simpler situation when these two quantities vanish asymptotically with the relation between them fixed on the critical scale. We investigate a classical dilute system interacting via a pair potential of Lennard-Jones type, which includes attraction as well as repulsion. In this model we obtain that the temperature-density plane can be divided into separate phases, corresponding to the formation of clusters of different sizes. Within each phase all clusters have the same size. On the lines separating the phases, we encounter nondifferentiability of the free energy of the system, so that we may speak of first-order phase transitions.

At fixed positive temperature, in a dilute system, the minimal inter-particle distance diverges and the system does not feel the interaction. At zero temperature, however, the minimisation of energy leads to the emergence of a macroscopic rigid crystalline structure, see [Th06]. We study the transition between these two scenarios by letting the
Fig. 1. Blow-up near the origin in the temperature-density plane. The schematic phase diagram is for the case of three phase transitions, \( \eta = 3 \): Phase I (single points), Phase II (finite clusters with more than one point), Phase III (larger finite clusters), Phase IV (infinite clusters). Phases I-III are gaseous phases, Phase IV may be interpreted as a fluid or solid phase.

temperature depend on the particle density in a critical way and thus zooming into the crucial region near the origin in the temperature-density plane (Fig. 1).

We now turn to a detailed description of the model. We consider the following pair-interaction energy of \( N \)-point configurations in \( \mathbb{R}^d \),

\[
V_N(x_1, \ldots, x_N) = \sum_{\substack{i,j=1 \atop i \neq j}}^N v(|x_i - x_j|), \quad \text{for } x_1, \ldots, x_N \in \mathbb{R}^d.
\]  

Here the pair-interaction potential \( v : [0, \infty) \to (-\infty, \infty] \) is assumed to be of Lennard-Jones type, by which we mean that it explodes close to zero, has a nondegenerate negative part and vanishes at infinity. Additionally, we always assume that \( v \) has compact support. We allow the possibility that \( v = \infty \) in some interval \([0, v_0]\) to represent hard core interaction. Assumption (V) below also ensures that the potential is stable, i.e., the energy \( V_N \) is of order \( N \), see Lemma 1.1 below.

We consider \( N \) particles in a centred cube \( \Lambda \subset \mathbb{R}^d \), such that the particle density is \( \rho := \frac{N}{|\Lambda|} \), where \( |\Lambda| \) is the Lebesgue measure of \( \Lambda \). The main object of our study is the partition function

\[
Z_N(\beta, \rho) := \frac{1}{N!} \int_{\Lambda^N} dx_1 \ldots dx_N 
\times \exp \{-\beta V_N(x_1, \ldots, x_N)\}, \quad \text{for } \beta, \rho \in (0, \infty), \quad N \in \mathbb{N}.
\]

We derive a variational characterisation of the limiting free energy per particle,

\[
\Xi(c) := - \lim_{N \to \infty} \frac{1}{\beta_N N} \log Z_N(\beta_N, \rho_N),
\]

for \( \beta_N \to \infty, \rho_N \to 0 \) such that \( -\frac{1}{\beta_N} \log \rho_N = c \) is constant. This relation implies that the energetic and entropic contributions to the partition function are on the same scale, and their competition determines the behaviour of the system.