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Equilibrium versus random sequential addition of dimers on a lattice

G Fiumara† and P V Giaquinta‡

† Dottorato di Ricerca in Fisica, Università degli Studi di Messina, Casella Postale 50, Villaggio S Agata, 98166 Messina, Italy

‡ Dipartimento di Fisica, Università degli Studi di Messina, Casella Postale 50, Villaggio S Agata, 98166 Messina, Italy

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Abstract. The statistical-mechanical properties of particles forming dimers are compared with the results obtained on a two-dimensional lattice through a random sequential addition (RSA) experiment. The relation between the most likely fraction of dimers filling the lattice at equilibrium in the disordered phase and the corresponding non-equilibrium jamming limit attained through RSA is explored. Some implications relevant for the physics of the liquid state are also discussed.

1. Introduction

A variety of experimental situations in many diverse fields such as physics, chemistry and biology can be described as processes of random sequential addition (RSA) of non-overlapping 'objects' onto a volume [1]. In the standard RSA model the objects, once inserted, are clamped at their positions. As a result, the filling process is intrinsically irreversible and saturates when no more holes large enough to fit another particle are left over. Clearly, the average density attained at 'jamming' is systematically smaller than the density of the system at close packing.

Because of the absence of thermal relaxation channels, RSA-jammed configurations constitute a subset only of the whole spectrum that a system exhibits at thermodynamic equilibrium. Widom proved that the probability densities associated with the RSA and the equilibrium sampling of hard spheres are indistinguishable through the third cluster integral, and deviate thereafter [2]. In the same paper Widom also speculated on a potential relation of the RSA-jamming threshold with some characteristic density of the fluid at equilibrium, possibly in a metastable state.

Indeed, the problem concerning the random filling of space yields useful hints for a deeper understanding of the nature of the liquid state as already appreciated by Bernal who, in his attempt to build up a 'statistical geometry' of liquids, envisioned that RSA might be considered as 'the model for a liquid approaching its limit of coherence at, or above, the critical point' [3]. This original intuition can be tested, for instance, by switching on a weak and short-ranged attraction between hard spheres in a perturbative way (thus leaving substantially unchanged the underlying structural scenario) so as to monitor the onset of thermodynamic coexistence between a gas and a liquid phase in the density–temperature plane [4]. In fact, if a negative Yukawa tail is superimposed to the otherwise merely repulsive hard-core interaction (a case that is amenable to a complete analytical treatment in the mean spherical approximation), a gas–liquid critical point eventually springs up at a density which falls extremely close to the current numerical estimate of the hard-sphere jamming limit, i.e. at a volume that is roughly twice that occupied by the particles in a close-packed arrangement [5]. A signature of such a 'critical' packing threshold is also present in the *equilibrium* structure and dynamics of the reference hard-sphere fluid, as emphasized by Giaquinta and Giunta in the framework provided by the multiparticle-correlation expansion of the statistical entropy [6]. Therefore, it appears that the existence of such an intrinsic 'watershed' between low and high densities, which becomes manifest both in an equilibrium and non-equilibrium description of the system, does indeed substantiate Bernal's *structural* definition of liquids as '*homogeneous, coherent* and *essentially* irregular assemblages of molecules containing no crystalline regions or holes large enough to admit another molecule' [3].

At a basically descriptive level, a systematic comparison between the RSA and equilibrium formalisms was recently pursued for continuous systems by Tarjus and co-workers who showed that a distribution-function approach can be set up to study also RSA configurations in a manner which closely parallels the statistical-mechanical treatment of equilibrium configurations [7].

As far as lattice-gas models are concerned, the relation between maximal filling thresholds and *order–disorder* transition densities has been discussed by Baram and Kutasov [8].

In this paper we aim at exploring such a relation for a lattice-gas Hamiltonian which was introduced by Parrinello and Tosatti (PT) to simulate the saturation of a molecular (diatomic) bond through classical monatomic interactions [9]. For arbitrary space dimension the PT Hamiltonian reads [10]

$$\mathcal{H} - \mu N = -(J/2)\sum_{(i,j)}\left[\prod_{k(i)}(1-c_k)\right]c_i c_j\left[\prod_{l(j)}(1-c_l)\right] - \mu\sum_i c_i \qquad (1)$$

where i, j are nearest-neighbour sites on the lattice, $k(i)$ labels the first neighbours of site i which are different from j, and similarly, $l(j)$ labels the first neighbours of site j different from i. The site-occupancy variable c_i takes on the value zero or one for an empty or filled site, respectively, and thus determines the fluctuating number of occupied sites N for a given value of the chemical potential μ. The projectors which appear within square brackets on both sides of the Ising-type term $c_i c_j$ allow the formation of a bond between two neighbouring particles if and only if all of the residual nearest-neighbour sites are vacant. This constraint implies interactions which are clearly non-local and irreducibly many-body.

The phase diagram generated by the PT Hamiltonian in one dimension and on a plane square lattice has been discussed in a number of papers [9–12]. Here we just note that, apart from the 'chemical' saturation force leading to the formation of dimers with energy $-J$ (with $J > 0$), no extra attractive interaction between particles is currently postulated. Therefore, the model does not exhibit either an atomic or a molecular gas–liquid phase transition. Still, in 2D, as a result of the energy–entropy balance, the system undergoes an order–disorder phase transition from a molecular-fluid (MF) to a molecular-crystal (MC) phase [10]. On a square lattice, the half-filled MC ground state is made up by staggered rows of parallel dimers and can also be described as a close-packed structure of *hexagonal* tiles. A finite-size-scaling analysis of the Monte Carlo data shows that the transition is first order [12]. For high enough values of the chemical potential and for temperatures lower than a 'critical' value T_{MC}, dimers eventually dissociate to form an atomic phase

(AP). The corresponding transition is again discontinuous. On a 32×32 square lattice, $T_{MC} \simeq 0.306J/k_B$, where k_B is Boltzmann's constant†.

In this paper we shall be concerned with the properties of the model along the MF–MC line only of the phase diagram. In particular, we intend to compare some results on the dense molecular-fluid phase that were obtained through two conceptually different numerical experiments, viz an equilibrium sampling of the PT Hamiltonian carried out through a Monte Carlo technique and an irreversible deposition of dimers onto the lattice.

2. The equilibrium experiment

We performed standard Monte Carlo simulations on square lattices with linear size $L = 4n$ ($n \leqslant 8$), under periodic boundary conditions. Each move consisted of an attempt at removing an existing particle or at inserting a new one at an empty lattice site. Along each run we accumulated the histogram $\mathcal{N}_{(\beta,\mu)}(N, N_b)$, i.e. the number of configurations produced for each value of the number of particles N and number of bonds $N_b = -E/J$ (where E is the energy) in the thermodynamic state characterized by the chemical potential μ and by the reciprocal temperature $\beta = 1/k_BT$. As discussed in detail in [12], such histograms typically show two peaks that are originated by the bunching of liquid-like and solid-like configurations, respectively, in two distinct regions of the (N, N_b) plane. The change in the relative weights (volume underneath the peaks) of the two maxima monitors the transition from the MF to the MC phase.

Here, we shall focus on the maximum associated with liquid-like configurations and, in particular, on its position $\widetilde{N}_b(\beta, \mu; L)$ along the N_b axis. In figure 1 we plot $\widetilde{N}_b(\beta, \mu; L)$ as a function of the chemical potential for $\beta = 3.5$‡. It is quite manifest that for all the sizes investigated the number of dimers filling the lattice at a given temperature in the most likely fluid configuration does not depend in a sensitive way on the value of the chemical potential over a wide range of states. The scaled quantity $\widetilde{N}_b(\beta, \mu; L)/L^2$ is also largely independent on the size of the lattice as shown in the inset of figure 1. The relative deviations observed in the distribution of the data points are all within the numerical error of the calculation. In fact, they correspond to variations of one or two dimers at the most for any size.

On average, an increase of μ simply turns into an increased number of atoms filling up the residual sites available in the lattice (viz the sites lying outside the dimeric exclusion shells) until the fluid freezes into the molecular-crystal phase. Even then, as can be appreciated from the arrows drawn in figure 1, the smaller and smaller remnant of the 'liquid' peak in the probability distribution function of the finite system keeps stably centred about the same reference value until the peak itself is eventually washed out when moving deeply inside the bulk of the MC phase.

Indeed, a finer analysis reveals a slightly re-entrant behaviour of the liquid-peak position for temperatures approaching T_{MC} ($\beta \lesssim 3.5$): in fact, as shown in figure 2, a growing chemical potential initially drives an increase, although weak, of $\widetilde{N}_b(\beta, \mu; L)$ up to a turnover point where the external-bath pressure becomes so high that even a small fraction of molecular bonds dissociate to the advantage of the re-populating atomic phase. Whatever the case, we take the quantity $\Theta_b(\beta) \equiv \max_\mu \left\{\widetilde{N}_b(\beta, \mu; L)/L^2\right\}$ as a reference uppermost threshold for the most likely population of dimers which are supported in a disordered configuration at a given temperature.

† In the following, the numerical values for the thermodinamic quantities (energy, temperature, chemical potential) will be expressed in 'reduced' units of J and k_B.

‡ The corresponding histograms for a 32×32 lattice are shown in figure 2 of [12].

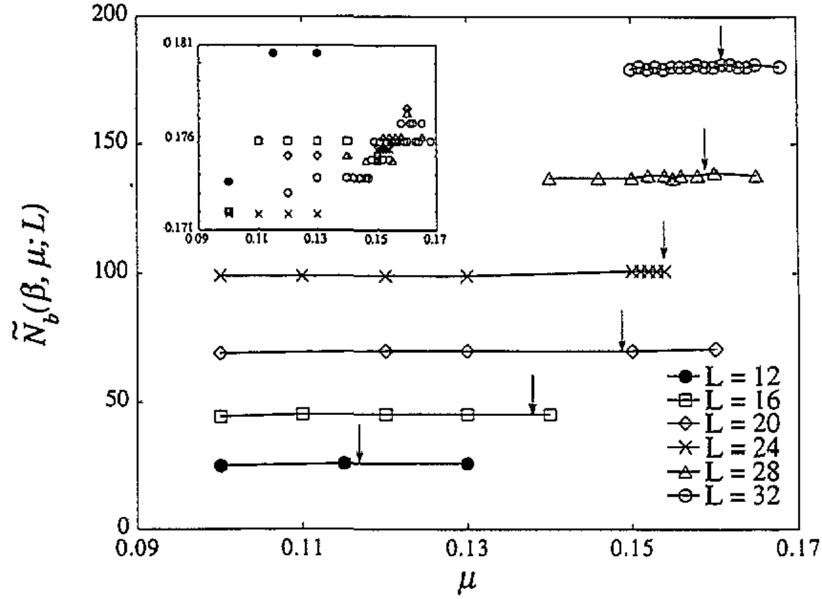

Figure 1. Position of the 'liquid' peak in the configuration histogram plotted as a function of the chemical potential, for a number of lattice sizes, at a reduced reciprocal temperature $\beta = 3.5$. The arrows indicate the transition points in the finite systems. The same data but for the scaled quantity $\tilde{N}_b(\beta, \mu; L)/L^2$ are shown as an inset.

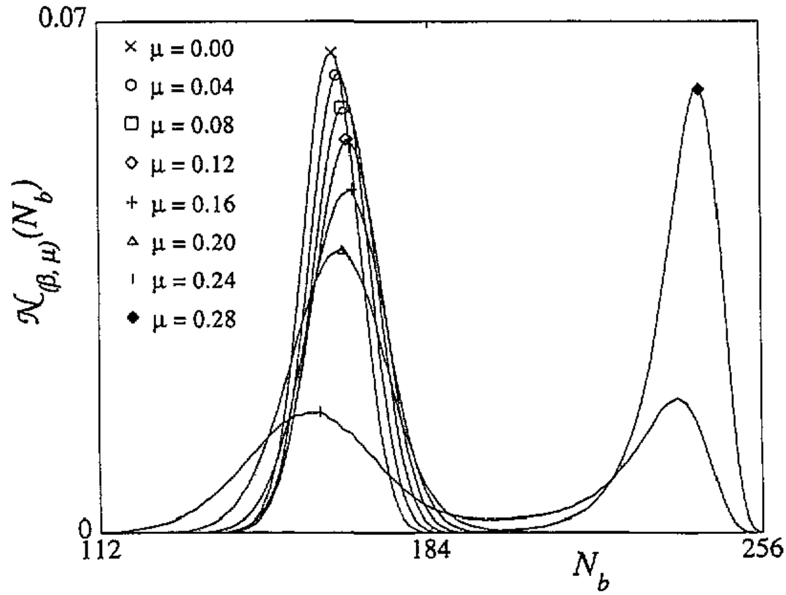

Figure 2. The bond-state histogram $\mathcal{N}_{(\beta,\mu)}(N_b) \equiv \sum_N \mathcal{N}_{(\beta,\mu)}(N, N_b)$ computed for a 32×32 lattice at reduced reciprocal temperature $\beta = 3.3$. The histogram, that is properly normalized to one, is plotted for a number of values of the reduced chemical potential which refer to states lying on both sides of the transition point.

3. The RSA experiment

In addition to the Monte Carlo sampling of the PT Hamiltonian, we carried out a number of RSA numerical experiments. The earliest irreversible filling studies for simplified models of rigid dimers with no extended exclusion shell on one- and two-dimensional lattices date back to the original papers by Flory and Roberts, respectively [13, 14]. Recently, a more sophisticated model (the so-called '8-site model') was proposed by Brundle and co-workers [15] in order to explain the formation of some non-equilibrium ordered structures on certain metal surfaces as a result of the dissociative adsorption of oxygen [16, 17]. This model bears some similarity with the PT model in that dimers are assumed to adsorb randomly at *diagonally* adjacent (next-nearest-neighbour) sites of a plane square lattice under the constraint that all of their six nearest-neighbour sites are empty†.

In the present RSA numerical experiment unoriented dimers with an exclusion core which precisely complies with the PT constraint were sequentially dropped onto a square lattice. At variance with the equilibrium experiment, we did not allow for the presence of non-bonded particles. Notwithstanding this simplification, a typical RSA experiment still ends up in a jammed configuration which also contains a fraction of vacant sites falling outside the exclusion shells of the deposited dimers. Virtually, the occupation of such 'free' sites by isolated particles (monomers) would not destroy any pre-existing PT bond. We found for the average RSA fraction Θ_b^{RSA} (the ratio of the maximum number of dimers filling the lattice to the number of sites) a value of 0.161 ± 0.002 with a fraction of free sites Θ_f^{RSA} equal to 0.063 ± 0.006‡.

4. Discussion

The equilibrium results obtained on a 32×32 lattice for the 'maximal' bond fraction are plotted in figure 3 against the RSA benchmark. As expected, $\Theta_b(\beta)$ decreases with increasing temperatures. However, the feature we want to focus on here is that for $T \simeq T_{MC}$ the above quantity becomes equal to Θ_b^{RSA}. We note that at this temperature there is also a fair correspondence between the fraction of unbonded particles Θ_a reckoned in the fluid-peak state and the RSA fraction of free sites. In fact, $\Theta_a \simeq 0.08$ for $\beta = 3.27$, a value only just higher than Θ_f^{RSA}. This small discrepancy may be justified by the presence, at equilibrium, of atomic clusters (formed by more than two neighbouring particles), apart from monomers and dimers. Such dense local arrangements, which become more and more likely with increasing temperatures, have no analogue in the free-volume patches of a frozen RSA configuration since the RSA algorithm cannot produce but isolated vacancies outside the molecular exclusion shells.

We cannot exclude that the correspondence noted above for the PT model between RSA and equilibrium properties is accidental. It is altogether tempting to argue on the rationale that would justify this phenomenological observation, also taking advantage of the potential analogies with the 3D hard-sphere case.

We suggest that the outcome of a random-filling experiment can be re-read under a different but, somehow, complementary perspective. The standard RSA is a 'blind'

† In this case the unit cell is a *rectangle* (45° tilted relatively to the lattice-site frame) giving rise to a $c(2\times2)$-ordered structure at close packing, with an ideal coverage of $\frac{1}{2}$ as in the PT model [17].

‡ As might have been expected, the *bond* saturation coverage attained by PT dimers is slightly less than that found for the 8-site model (0.181) [18]. In fact, it seems rather intuitive that hexagons, when dropped at random over the lattice, do ultimately 'waste' more space than rectangles.

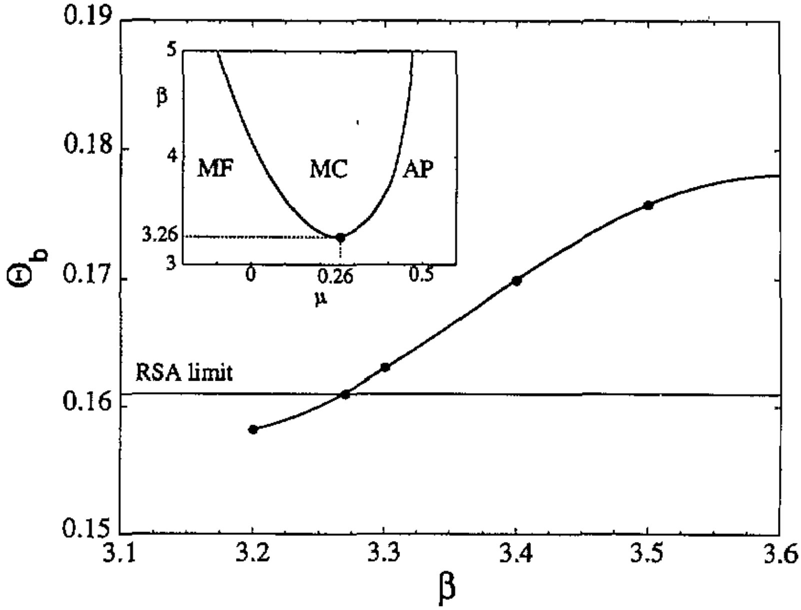

Figure 3. The quantity $\Theta_b(\beta)$ computed for the 32 × 32 lattice and plotted as a function of the reduced reciprocal temperature β. The horizontal line marks the RSA jamming limit. The phase diagram of the PT model in the (μ, T) plane is also sketched in the inset: the labels identify the molecular-fluid region (MF), the molecular-crystal phase (MC), and the atomic phase (AP), respectively. The reduced thermodynamic coordinates shown for the 'critical' end-point do also pertain to the 32 × 32 lattice size. As discussed in the text, the data for $\Theta_b(\beta)$ refer to the MF–MC boundary region.

(and, thus inefficient) space-sampling procedure. The average-limit coverage achieved in a jammed configuration defines a threshold that can be crossed only by resorting to a *cooperative* dynamical process (even stochastic, and not necessarily leading to thermodynamic equilibrium) which, through some *correlated* readjustment of the particle positions, may actually drive the system to closer-packing states. Obviously, a correlated aggregation process gives rise to a pattern with some degree of spatial *coherence* in the relative distribution of the particles, coherence which would typically show up in the spatial profiles of the pair and higher-order correlation functions. Hence, retrospectively, the RSA limit appears as a lower threshold of minimal coherence, i.e. as the most dilute state in which *all* the particles do start 'feeling' each other through the 'passive' constraints arising from their mutual hindrance effects.

Let us move now to the equilibrium scene, by ideally coupling the jammed system to a thermal bath. It is not difficult to realize that the existence of an underlying structural background as that described above may represent a sort of marginal condition for the onset of large-scale condensation phenomena. In fact, at such a point a (structurally assisted) phase transformation can be readily triggered out by 'switching on' an even faint extra attraction between particles. This turns out to be the case for a condensing 3D fluid of hard spheres. The driving mechanism appears to be substantially analogous for the PT dimers: in this case, it is the bonding energy that competes with the lattice-gas entropy. Again, the marginal RSA condition is seen to correspond to the 'critical' end-point that is located on top of the molecular liquid–solid coexistence region. We conclude that the condition $\Theta_b(T_{MC}) = \Theta_b^{RSA}$ witnesses the existence of a unique critical threshold beyond which the molecular-liquid phase does eventually acquire a well defined 'identity' both on a structural and a thermodynamical ground. In fact, as is seen from figure 3, below the critical temperature T_{MC} the lattice progressively accommodates more and more dimers—as compared to the reference RSA threshold—in an average configuration that is still globally disordered. The increase of Θ_b is made possible by the growth of correlations on a local scale, consistently with the discussion developed above on the interplay between spatial coherence and correlations. The resulting phase is thus characterized by an increasing degree (with decreasing temperatures) of *short-range order* which is the distinguishing feature, at a structural level, of a liquid with respect to a gas†. On the other hand, the phase below T_{MC} also acquires a sharp thermodynamic identity by contrast to the long-range-ordered phase.

5. Concluding remarks

The goal of this paper was to investigate the existence of a potential relation between the coverages attained through an irreversible deposition of dimers onto a square lattice and via their thermally mediated packing in the disordered phase at equilibrium. The lattice-gas Hamiltonian we have investigated is a rather complex one since it allows for the coexistence of atomic and molecular phases. The evidence presented in the paper appears to be consistent, at a phenomenological level, with the hypothesis of an underlying correspondence between RSA and the equilibrium properties of a Hamiltonian system. However, there is no doubt that a proof of the existence of such a connection for both discrete and continuum models still remains an open question.

A natural extension of this work would be to perform a comparative analysis of the spatial distribution functions in the two cases. As mentioned in the introduction, a hint in this direction has been already found in the expansion of the statistical entropy in terms of spatial correlations between n-tuples of particles [6]. In fact, an inspection of the resummed contribution to the entropy of the fluid arising from the correlations involving *more than two particles* shows that this intermediate quantity, at variance with the total excess entropy and the 'pair' term of the expansion, exhibits a non-monotonic behaviour as a function of the density, with a crossover from negative to positive values at high densities. The resulting minimum neatly separates a low-density from a high-density regime and falls at a value of the packing fraction which, for hard spheres, coincides with the RSA jamming limit of the model. In this case, the possibility of a fortuitous coincidence has been ruled out through a similar calculation carried out for a hard-core model in 2D, namely for a system of hard disks embedded onto the surface of a sphere [18–20]. As for hard particles in 3D, the signature found in the density dependence of the equilibrium multiparticle entropy happens to fall precisely at the RSA threshold of the 2D model [21, 22].

Summing up, we believe that we may provisionally state that the hypothesis of an underlying physical relation between the RSA jamming threshold of a system and its equilibrium phase diagram is presently supported by a number of independent observations which, notwithstanding the diversity of the models investigated, coherently fit into a reasonable theoretical framework.

The results of a study on the same theme, carried out for a binary mixture of hard particles in two dimensions, will be presented in a forthcoming paper [23].

† Order on a short range becomes manifest through the more and more frequent appearance of some typical arrangements as, for instance, *rings* formed by four dimers (each lying along a side of a 4×4 square) which encapsulate an empty core of four sites (the vertices of the inner 2×2 square). This particular configuration raises the local-bond fraction to $\frac{2}{9}$.

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