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Nucleation in physical and nonphysical systems

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Abstract

The aggregation of particles out of an initially homogeneous situation is well known in physics. Depending on the system under consideration and its control parameters, the cluster formation in a supersaturated (metastable or unstable) situation has been observed in nucleation physics as well as in other branches. We investigate the well-known example of condensation (formation of liquid droplets) in an undercooled vapour to conclude that the formation of bound states as a phase transition is related to transportation science. We present a comparison of nucleation in an isothermal–isochoric container with traffic congestion on a circular one-lane freeway. The analysis is based, in both cases, on the probabilistic description by stochastic master equations.

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1. Introduction

The term cluster, as a group of similar things, is used in science in many different fields. It is common on all scales from subatomic physics up to astronomy. The existence of bound states of atoms or molecules as clusters with different sizes in gases, liquids and solid matter is an intermediate step between the elementary isolated particle and the macroscopic condensed state. The formation of bound states as an aggregation process is related to self-organization phenomena (Haken, 1983; Schmelzer et al., 1999). In general, the properties of clusters, especially the binding energy, depend on the cluster size and

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shape (Haberland, 1994; Jellinek, 1999). The nucleation and growth of atomic and molecular clusters is one of the basic topics in nucleation theory (Schmelzer et al., 1999; Wu, 1997). An example of experimental verification is given in Schmelzer et al. (2000).

The formation of clusters takes place on different scales in physical (nucleation of droplets, condensation of clouds) and nonphysical systems (insect societies, socio-configurations, transport communities). Nonphysical systems are generally a reflection of the interaction of people or animals. We, however, do not discuss here the social aspects of human interaction. We are particularly interested in traffic flow theory where the car drivers (or, formally, the vehicles) are considered as interacting particles. Physical systems like spin glasses are one of the most investigated complex systems to understand the clustering of states. In chemically reacting systems, the domain formation is simulated by Monte Carlo experiments and by lattice–gas automata. Monte Carlo methods are well established in statistical physics (Heermann, 1990; Newman and Barkema, 1999).

The clustering behaviour can be considered as a phase transition between different states of matter. In dependence on the boundary conditions, a quenched system, for instance, an undercooled vapour or an overcrowded road, undergoes a relaxation process to the new phase. The theoretical understanding of the physical mechanism for the dynamics of the aggregation phenomenon has important implications for the more general task of realizing relaxation phenomena in equilibrium and nonequilibrium complex systems (Schmelzer et al., 1999).

The modelling of such supersaturated (metastable or unstable) systems is dominated by a very complicated energy landscape with many local minima and can be done by different means. Having in mind the homogeneous or heterogeneous (e.g., by electrical charges) nucleation and condensation process, we divide the following theoretical and computational methods (Mahnke, 1998):

1. Molecular dynamics: based on the classical many particle Hamiltonian with well-known Lennard Jones interaction, the integration of the equations of motions shows the clustering process quite obvious.
2. Master equation approach: in this Monte Carlo simulation technique, the master equation for the chemical reactions of the attachment and the detachment of elementary particles (monomers) on or out of clusters is solved with phenomenologically motivated transition probabilities. This method will be used later on.
3. Monte Carlo simulation technique: the formation process of clusters on a two-dimensional lattice can be modelled by a so-called nucleation automaton with a well-explained energy function. The relaxation to a one-big-cluster-state as the equilibrium situation is a searching process on the energy landscape to find a minimum in a very high dimensional situation.
4. Cellular automata models: chemically reacting systems with phase separations like the well-known Schlögl model can be simulated by probabilistic lattice–gas automaton models where space, time and particle velocities are discrete. Each molecule (occupied site) can undergo elastic and reactive collisions and depending on the updating rule, interesting spatiotemporal configurations of particles emerge.

5. Deterministic nonlinear dynamical systems: the Becker–Döring cluster equations and other kinetic equations of such type provide a very famous dynamical model for the growth, shrinkage, coagulation and fragmentation of clusters (droplets) in a condensing vapour. The trends to equilibrium can be studied in dependence on the kinetic coefficients. Especially for the late Ostwald ripening regime, a number of dynamic systems as coupled nonlinear sets of equations exist.

It should be mentioned that nonphysical systems, like traffic flow or economics, can also be described by methods of statistical thermodynamics. Such an approach, based on the use of state function entropy and its maximization principle, has been presented by [Montroll and Badger \(1974\)](#), [Reiss and Huang \(1971\)](#) and [Reiss et al. \(1986\)](#). Although our present investigation of traffic flow does not involve the entropy maximization principle, it clearly supports the idea that nonphysical systems like traffic flow and physical systems like supersaturated vapour can be treated similarly.

The aim of the present paper is to give a comparison between aggregation in supersaturated vapour and in traffic flow by providing a unique description of these two phenomena within the stochastic master equation approach. We emphasize that phase transitions, which are well known and investigated by statistical physics and thermodynamics take place in nonphysical systems too, as already pointed out by [Montroll and Badger \(1974\)](#). We concentrate here on vehicular traffic, but other fields like cancer growth and stock market development behave similarly.

2. Stochastic master equation approach

Stochastic processes enter into many physical descriptions of nature. Historically, first, the motion of a heavy particle in a fluid of light molecules has been observed. The path of such Brownian particles consists of stochastic displacements due to random collisions. Such motion was studied by the Scottish botanist Robert Brown (1773–1858). In 1828, he discovered that the microscopically small particles into which the pollen of plants decay in an aqueous solution are in permanent irregular motion. Such a stochastic process is called Brownian motion and can be interpreted as discrete random walk or continuous diffusion movement. The intuitive background to describe the irregular motion completely as stochastic process is to measure values $x_1, x_2, \dots, x_n, \dots$ at time moments $t_1, t_2, \dots, t_n, \dots$ of a well-defined time-dependent random variable $x(t)$ and assume that a set of joint probability densities or distributions

$$p_n(x_1, t_1; x_2, t_2; \dots; x_n, t_n) \quad \text{for } n = 1, 2, \dots \quad (1)$$

exists.

This stochastic description in terms of macroscopic variables is called mesoscopic. Typical systems encountered in everyday life like gases, liquids, solids, biological organisms, human or technical objects consist of about 10^{23} interacting atoms. The macroscopic properties of matter are usually the result of collective behaviour of a large number of atoms and molecules acting under the laws of quantum mechanics. To understand and control these collective macroscopic phenomena, the complete knowledge

based upon the known fundamental laws of microscopic physics is useless because the problem of interacting particles is much beyond the capabilities of the largest recent and future computers. The understanding of complex macroscopic systems consisting of many basic particles (in the order of atomic sizes: 10^{-10} m) requires the formulation of new concepts. One of the methods is the stochastic description taking into account the statistical behaviour. Since the macroscopic features are averages over time of a large number of microscopic interactions, the stochastic description links both approaches, the microscopic and the macroscopic one, together to give probabilistic results (Gardiner, 1990; Honerkamp, 1994; van Kampen, 1992).

Speaking about a stochastic process from the physical point of view, we always refer to stochastic variables (random events) changing in time. A realization of a stochastic process is a trajectory $x(t)$ as function of time.

A stochastic process without any dynamics (like a coin throw or any hazard game) is called a temporally uncorrelated process and the normalized distribution $p_1(x_1, t_1)$ describes the process totally.

Introducing dynamics via correlations between two different time moments, this assumption enables us to define the Markov process by two quantities totally, namely the first-order $p_1(x_1, t_1)$ and the second-order probability density $p_2(x_1, t_1; x_2, t_2)$, or equivalently by the joint probability $p_1(x_1, t_1)$ and the conditional probability $p_2(x_2, t_2 | x_1, t_1)$ to find the value x_2 at time t_2 , given that its value at previous time $t_1 (t_1 < t_2)$ is x_1 . In contradiction to uncorellated processes, Markov processes are characterized by the following temporal relationship

$$p_2(x_1, t_1; x_2, t_2) = p_2(x_2, t_2 | x_1, t_1)p_1(x_1, t_1). \quad (2)$$

This Markov property enables us to calculate all higher-order joint probabilities p_n for $n > 2$. To determine the fundamental equation of stochastic processes of Markov type, we start with the third-order distribution ($t_1 < t_2 < t_3$)

$$p_3(x_1, t_1; x_2, t_2; x_3, t_3) = p_2(x_3, t_3 | x_2, t_2)p_2(x_2, t_2 | x_1, t_1)p_1(x_1, t_1) \quad (3)$$

and integrate this identity over x_2 and divide both sides by $p_1(x_1, t_1)$. We get the following result for the conditional probabilities defining a Markov process

$$p_2(x_3, t_3 | x_1, t_1) = \int p_2(x_3, t_3 | x_2, t_2)p_2(x_2, t_2 | x_1, t_1)dx_2, \quad (4)$$

called Chapman–Kolmogorov equation. As already stated, the Markov process is uniquely determined through the distribution $p_1(x, t)$ at time t and the conditional probability $p_2(x', t' | x, t)$, also called transition probability from x at t to x' at later t' , to determine the whole hierarchy p_n ($n \geq 3$) by the Markov property (Eq. (2)).

The memory in a Markov process is very short, only one time interval from t to t' plays any role. If the trajectory has reached x at time t , the past is forgotten, and it moves toward x' at t' with a probability depending on x, t and x', t' only. The entire information relevant for the future is thus contained in the present. This gives sense to transform the Chapman–Kolmogorov equation (Eq. (4)) in an equivalent differential equation in the short time limit $t' = t + \tau$ with small τ tending to zero. The short time

behaviour of the transition probability $p_2(\cdot|\cdot)$ should be written as a series expansion with respect to time interval τ in the form

$$p_2(x, t + \tau | x'', t) = [1 - \bar{w}(x, t)\tau]\delta(x - x'') + \tau w(x, x'', t) + \mathcal{O}(\tau^2). \tag{5}$$

The new quantity $w(x, x'', t) \geq 0$ is the transition rate, the probability per time unit, for a jump from x'' to $x \neq x''$ at time t . This transition probability multiplied by the time step τ gives the second term in the series expansion describing transitions from an other state x'' to x . The first term (with the delta function) is the probability that no transitions takes place during time interval τ .

Inserting Eq. (5) in the right-hand side of the Chapman–Kolmogorov equation (Eq. (4)) and integrating over x' (taking into account the normalization conditions for probabilities), we obtain the differential formulation of the Chapman–Kolmogorov equation

$$\frac{\partial}{\partial t} p_1(x, t) = \int w(x, x', t) p_1(x', t) dx' - \int w(x', x, t) p_1(x, t) dx' \tag{6}$$

called master equation in the (physical) literature (Gardiner, 1990; Honerkamp, 1994; van Kampen, 1992). The name ‘master equation’ for the above probability balance equation is used in a sense that this differential expression is a general, fundamental or basic equation. For a homogeneous in time process, the transition rates $w(x, x', t)$ are independent of time t . The short time transition rates w have to be known from the physical context, often like a clever ansatz, or have to be formulated based on a reasonable hypothesis or approximation. With known transition rates w the master equation (Eq. (6)) gives the resulting evolution of the probability p_1 over a long time period.

The master equation can be written in different ways. Since we are particularly interested in the case where the stochastic variable has discrete values (natural numbers) within a finite range $0 \leq n \leq N$, the master equation for the time evolution of the probabilities $p_1(x, t)$, now $P(n, t)$, is then written as

$$\frac{dP(n, t)}{dt} = \sum_{n' \neq n} \{w(n, n')P(n', t) - w(n', n)P(n, t)\}, \tag{7}$$

where $w(n', n) \geq 0$ are rate constants for transitions from n to other $n' \neq n$. Together with the initial probabilities $P(n, 0)$ ($n=0, 1, 2, \dots, N$) and the boundary conditions at $n=0$ and $n=N$, this set of equations governing the time evolution of $P(n, t)$ from the beginning at $t=0$ to the long-time limit $t \rightarrow \infty$ has to be solved. The meaning of both terms is clear. The first (positive) term is the inflow probability current to state n due to transitions from other states n' , and the second (negative) term is the outflow current due to opposite transitions from n to n' .

Defining stationarity, sometimes called steady state, as a time-independent distribution $P^{st}(n)$ by the condition $dP(n, t)/dt|_{P=P^{st}}=0$, the stationary master equation is given by

$$0 = \sum_{n' \neq n} \{w(n, n')P^{st}(n') - w(n', n)P^{st}(n)\}. \tag{8}$$

This equation states the obvious fact, that in the stationary or steady state regime, the sum of all transitions into any state n must be balanced by the sum of all transitions from n

into other states n' . Based on the properties of the transition rates per unit time, the probabilities $P(n, t)$ tend in the long-time limit to the uniquely defined stationary distribution $P^{\text{st}}(n)$. In open systems, a constant probability flow is possible. This fundamental property of the master equation may be stated as

$$\lim_{t \rightarrow \infty} P(n, t) = P^{\text{st}}(n). \quad (9)$$

Let us shortly discuss the question of equilibrium in a system without external exchange. The condition of equilibrium in closed isolated systems is much more stronger than the former condition of stationarity (Eq. (8)). Here we demand a balance between each pair of states n and n' separately. This so-called detailed balance relation is written for the equilibrium distribution $P^{\text{eq}}(n)$ as

$$0 = w(n, n')P^{\text{eq}}(n') - w(n', n)P^{\text{eq}}(n). \quad (10)$$

Of course, each equilibrium state is by definition also stationary. If the initial probability vector $P(n, 0)$ is strongly nonequilibrium, many probabilities $P(n, t)$ change rapidly as soon as the evolution starts (short-time regime), and then relax more slowly towards equilibrium (long-time behaviour). The final (thermodynamic) equilibrium is reached in the limit $t \rightarrow \infty$. As a particular example of such a behaviour, the relaxation process in atomic clusters has been studied in [Miller et al. \(1999\)](#).

We are speaking about a one-dimensional stochastic process if the state space is characterized by one variable only. As in our investigations, this discrete variable is a particle number $n \geq 0$ describing the amount of molecules or the size of an aggregate. In chemical physics, such aggregation phenomena like formation and/or decay of clusters are of great interest. Examples are the formation of a crystal or glass upon cooling a liquid or the condensation of a droplet out of a supersaturated vapour. To determine the relaxation dynamics of model clusters, we take a particularly simple Markov process with transitions between neighbouring states n and $n' = n \pm 1$. This situation is called a one-step process. In biophysics, if the variable n represents the number of living individuals of a particular species, the one-step process is often called birth-and-death process to investigate problems in population dynamics. The random walk with displacements to left and right by one step is well known in physics and often plays a role as an introductory example and has been recently revisited and applied to new fields like econophysics ([Paul and Baschnagel, 1999](#)).

Setting the transition rates $w(n, n-1) = w_+(n-1)$, $w(n, n+1) = w_-(n+1)$, and therefore also $w(n+1, n) = w_+(n)$, $w(n-1, n) = w_-(n)$, the master equation (Eq. (7)) reads

$$\frac{dP(n, t)}{dt} = w_+(n-1)P(n-1, t) + w_-(n+1)P(n+1, t) - [w_+(n) + w_-(n)]P(n, t). \quad (11)$$

In general, the forward and backward transition rates $w_+(n)$, $w_-(n)$ are nonlinear functions of the random variable n ; the physical dimension is one over time (s^{-1}). We pay attention to particles as aggregates in a closed box or vehicular jams on a circular road. Therefore, in finite systems the range of the discrete variable n is bounded between 0 and N ($n = 0, 1, 2, \dots, N$).

The general one-step master equation (Eq. (11)) is valid for $n=1, 2, \dots, N-1$, but meaningless at the boundaries $n=0$ and $n=N$. Therefore, we have to add two boundary equations as closure conditions

$$\frac{dP(0, t)}{dt} = w_-(1)P(1, t) - w_+(0)P(0, t), \tag{12}$$

$$\frac{dP(N, t)}{dt} = w_+(N-1)P(N-1, t) - w_-(N)P(N, t). \tag{13}$$

In finite systems with $n=0, 1, 2, \dots, N$ one finds a situation which corresponds to steady state with a detailed balance relationship similar to Eq. (10). Therefore, the stationary distribution $P^{st}(n)$ fulfills the recurrence relation

$$P^{st}(n) = \frac{w_+(n-1)}{w_-(n)} P^{st}(n-1). \tag{14}$$

By applying the iteration successively and taking into account the normalization condition (the sum of all the probabilities must be equal to 1), the stationary probability distribution $P^{st}(n)$ in finite systems is finally written as

$$P^{st}(n) = \begin{cases} \frac{\prod_{m=1}^n \frac{w_+(m-1)}{w_-(m)}}{1 + \sum_{k=1}^N \prod_{m=1}^k \frac{w_+(m-1)}{w_-(m)}} & n = 1, 2, \dots, N \\ \frac{1}{1 + \sum_{k=1}^N \prod_{m=1}^k \frac{w_+(m-1)}{w_-(m)}} & n = 0. \end{cases} \tag{15}$$

The obtained result is a unique solution for the stationary probability distribution in finite systems with closed boundaries. For an isolated system the stationary solution of the master equation P^{st} is identical with the thermodynamic equilibrium P^{eq} , where the detailed balance holds, which for one-step processes reads

$$w_-(n)P^{eq}(n) = w_+(n-1)P^{eq}(n-1). \tag{16}$$

The condition of detailed balance states a physical principle. If the distribution P^{eq} is known from equilibrium statistical mechanics and one of the transition rates is also known (e.g., by a reasonable ansatz w_+), the equation (Eq. (16)) provides the opportunity to formulate the opposite transition rate w_- in a consistent way. By this procedure, the nonequilibrium behaviour is adequately described by a sequence of (quasi-) equilibrium states. The relaxation from any initial nonequilibrium distribution tends always to the known final equilibrium. In physical systems, the equilibrium distribution usually is represented in an exponential form

$$P^{eq}(n) \propto \exp[-\Omega(n)/(k_B T)] \tag{17}$$

where $\Omega(n)$ is the thermodynamic potential depending on the stochastic variable n , k_B is the Boltzmann constant, and T is the temperature (Münster, 1969).

3. Nucleation in supersaturated vapours

If we consider a vapour at equilibrium then a certain change of the thermodynamic parameters enables us to remove the system into a nonequilibrium state. The vapour becomes supersaturated. The basic quantity describing the situation is the cluster distribution \mathbf{N} at time t ,

$$\mathbf{N}(t) = (N_0, N_1, N_2, \dots, N_n, \dots, N_N) \quad (18)$$

which gives the number of clusters N_n of size n . The free particles (molecules) are called monomers of size $n=0$. It is supposed that N_1 molecules are excited. These molecules may be named as precluster of size $n=1$. The bound states are clusters of size $n \geq 2$. Investigating a finite system, the overall number of particles N_{total} as well as the volume V and the temperature T are fixed. The particle conservation law

$$N_{\text{total}} = N_0 + N_1 + \sum_{n=2}^N nN_n = \text{const} \quad (19)$$

takes into account that particles are either free, excited, or bounded in clusters. There is always some difficulty to describe the initial stage of formation of a cluster. We have introduced the precluster as an intermediate state between free and bounded states to provide an easy and unified description of the aggregation process, which is valid both in supersaturated vapour and in traffic flow discussed later on.

A simple example of a system of many particles is a gas consisting of identical molecules called monomers. If the gas is dilute (the density as number of molecules per unit volume is small), the average separation length between the monomers is large and correspondingly, their interaction is negligible. The gas is said to be ideal, if the average separation length is much larger than the de Broglie wavelength. We treat the monomers as undistinguishable particles moving in a closed volume and making reactive collisions to form aggregates called molecular clusters. Further on, we consider a simplified case where only one single cluster of size n (i.e., $N_n = 1$) coexists with $N_0 = N_{\text{total}} - n$ unbounded (free) particles, which means that the cluster distribution (Eq. (18)) reduces to

$$\mathbf{N}(t) = (N_0, 0, \dots, 0, N_n = 1, 0, \dots, 0) \quad (20)$$

and the overall particle conservation (Eq. (19)) to

$$N_{\text{total}} = N_0 + n \cdot 1 = \text{const}, \quad (21)$$

where the stochastic variable $n = n(t)$ is the number of particles bounded in the cluster at time t . The nucleation box (volume V) embedded in a heat bath (temperature T) displaying the situation schematically is shown in Fig. 1.

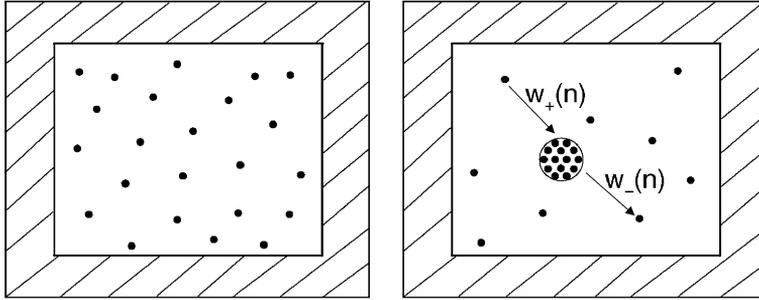


Fig. 1. Isothermal–isochoric nucleation in supersaturated vapour: free molecules (black dots) called monomers in the initial stage (left) of the aggregation process form a cluster (spherical droplet) of certain size n , coexisting with gas of free molecules, afterwards (right).

The starting point is the one-dimensional one-step master equation (Eq. (11)) describing condensation and evaporation of a single particle on or from a molecular cluster, where $w_+(n)$ and $w_-(n)$ are transition rates of condensation and evaporation, respectively, which have to be formulated now.

The attachment probability per time of a monomer to a (spherical) cluster of size n is proportional to cluster surface $A(n)$ and to density of free monomers N_0/V , i.e.,

$$w_+(n) = \alpha A(n)(N_{\text{total}} - n)/V, \quad 1 \leq n \leq N_{\text{total}}. \quad (22)$$

The coefficient α up to now is not specified (interpretation: velocity of sticking). The surface of spherical droplet is given by

$$A(n) = 4\pi r^2 = 4\pi(c_{\text{clust}}4\pi/3)^{-2/3} n^{2/3} \sim n^{2/3} \quad (23)$$

with known incompressible particle density inside the cluster $c_{\text{clust}} = \text{const}$ (liquid density as given experimental value). A special case is the formation of a precluster $n = 1$ out of an elementary particle ($n = 0$). The precluster can be understood as an excited monomer, which is able to react with some other monomer to form a dimer ($n = 2$). In the free particle state $n = 0$, any of the N_{total} monomers can become excited, so that the percentage in analogy to the traffic flow, we can write

$$w_+(0) = \frac{p}{\tau} N_{\text{total}} \quad (24)$$

where the parameter p in this case means the excitation probability per time multiplied by the time constant τ .

By using the detailed balance relation (Eq. (16)), the evaporation rate $w_-(n)$ of a monomer from a cluster of size n is calculated from the known attachment rate (Eq. (22)), as shown in Appendix A, i.e.,

$$w_-(n) = \alpha A(n) \frac{1}{\lambda_0^3} \exp\left(\frac{f_n - f_{n-1}}{k_B T}\right). \quad (25)$$

Here $f_n - f_{n-1}$ is the difference of binding energies between clusters of size n and $n - 1$ and $\lambda_0(T)$ is de Broglie wavelength of a monomer (particle of mass m) given by

$$\lambda_0 = h / (2\pi m k_B T)^{1/2} \approx 10^{-10} \text{ m.} \quad (26)$$

This is the wavelength of a quantum-mechanical free particle with energy $E = p^2 / 2m = \hbar^2 k^2 / 2m$, where k is the wave number related to the wavelength λ_0 .

Clusters as bound states of elementary particles (monomers) have negative potential energy, which is the so-called binding energy. The potential function $f_n(T)$ is well known from atomic and nuclear theory and also the Bethe–Weizsäcker formula (Schmelzer et al., 1999, 2000; Wu, 1997), which in a simple nonlinear approximation reads

$$f_n(T) = \mu_\infty(T)n + \sigma A(n). \quad (27)$$

The binding energy consists of a negative volume term ($\mu_\infty < 0$) and a positive surface contribution. The quantity $\mu_\infty(T)$ is the chemical potential of one monomer or, in other words, the energy necessary for taking away one elementary particle (monomer) from a cluster with a flat surface. The parameter σ can be understood as the surface tension of a flat surface. Ansatz (Eq. (27)) is a good approximation for large enough sizes n and also provides correct normalization condition $f_0 = 0$ for a free particle ($n = 0$). Substituting Eq. (27) into the detachment rate (Eq. (25)), we obtain the approximation

$$\begin{aligned} w_-(n) &= \alpha A(n) \frac{1}{\lambda_0^3} \exp\left\{ \frac{\mu_\infty(T) + \sigma[A(n) - A(n-1)]}{k_B T} \right\} \\ &\approx \alpha A(n) \frac{1}{\lambda_0^3} \exp\left(\frac{\mu_\infty(T)}{k_B T} \right) \exp\left(\frac{2\sigma k(n)}{c_{\text{clust}} k_B T} \right). \end{aligned} \quad (28)$$

This result is valid for large enough clusters (starting with $n \approx 10$) and contains the curvature $k(n)$ of a size n droplet

$$k(n) = 1/r = (c_{\text{clust}} 4\pi/3)^{1/3} n^{-1/3}. \quad (29)$$

The difference of surface areas $A(n) - A(n-1)$ in Eq. (28) can be evaluated by using a series of expansions of $A(n-1)$ around n and retaining the leading term only, i.e.,

$$n^{2/3} - (n-1)^{2/3} \approx n^{2/3} - n^{2/3} \left(1 - \frac{2}{3n} \right) \sim n^{-1/3}. \quad (30)$$

Taking into account the ideal gas model, the chemical potential μ_∞ is related in a simple way to the equilibrium density (concentration) $c_{\text{eq}}(\infty)$ of monomers for flat interface ($r \rightarrow \infty$) between liquid phase (droplet) and gaseous phase (free monomers). Thus, we have

$$\mu_\infty(T) = k_B T \ln[\lambda_0^3 c_{\text{eq}}(\infty)]. \quad (31)$$

However in reality, due to spherical droplets, the interface is curved, therefore the concentration of free monomers in equilibrium is larger than $c_{\text{eq}}(\infty)$.

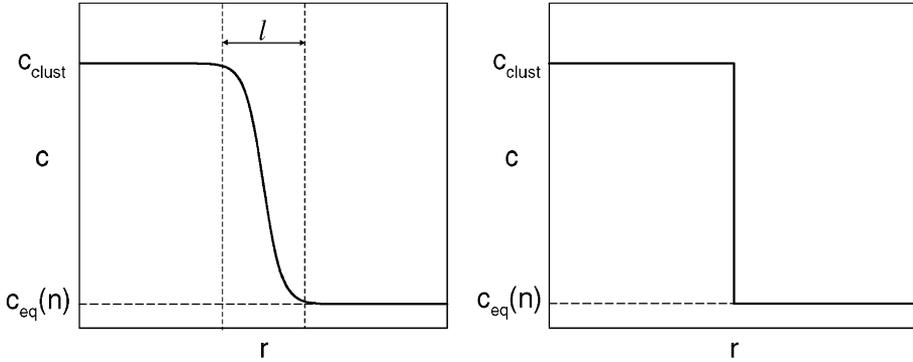


Fig. 2. Particle concentration c , depending on the distance r from the center of cluster. The left picture shows a real density profile, whereas the right one approximates the profile corresponding to a model of cluster with sharp border. The length l shows the width of the interface between the dense phase (c_{clust}) and the dilute surrounding ($c_{\text{eq}}(n)$) over a size n droplet.

For large enough clusters, the detachment probability

$$w_-(n) = \alpha A(n) c_{\text{eq}}(\infty) \exp(\ell k(n)) \tag{32}$$

is obtained by inserting Eq. (31) into Eq. (28), where the length $\ell = \ell(T)$ defined as

$$\ell(T) = \frac{2\sigma}{c_{\text{clust}} k_B T}, \tag{33}$$

is explained and visualised in Fig. 2.

Considering the cluster sizes $n(t)$ as a continuous variable which can be measured experimentally, the equation of motion dn/dt with a given velocity function $v(n)$, showing the time evolution of the cluster size, is well known. Putting forward phenomenological arguments like Fick’s law, the dynamical equation of reaction limited aggregation reads

$$\frac{dn}{dt} = v(n) \text{ with } v(n) = \frac{D}{\ell} A(n) (c_{\text{free}} - c_{\text{eq}}(n)), \tag{34}$$

where $c_{\text{free}} = N_0/V = (N_{\text{total}} - n)/V = c - n/V$ is the density of free particles, and $c = N_{\text{total}}/V$ is the total density of particles. The constant D is called diffusion coefficient; the coefficient ℓ called capillary length is a small interface thickness defined by Eq. (33).

In the stochastic approach, an equation of the same type as Eq. (34) can be obtained for the average cluster size $\langle n \rangle$. Based on the master equation (Eq. (11)), we get a deterministic equation for the mean value

$$\frac{d}{dt} \langle n \rangle = \frac{d}{dt} \sum_n n P(n, t) = \langle w^+(n) \rangle - \langle w^-(n) \rangle, \tag{35}$$

which can be written in a certain approximation as follows

$$\frac{d}{dt} \langle n \rangle \approx w^+(\langle n \rangle) - w^-(\langle n \rangle), \tag{36}$$

describing the time evolution of the average cluster size $\langle n \rangle$. According to the definitions of the transition frequencies, Eqs. (22) and (32), the time evolution of the mean cluster size (Eq. (36)) can be written in the same form as Eq. (34),

$$\frac{d}{dt} \langle n \rangle = \alpha A(\langle n \rangle) \left[\frac{N_{\text{total}} - \langle n \rangle}{V} - c_{\text{eq}}(\infty) e^{\ell k(\langle n \rangle)} \right]. \quad (37)$$

By comparing these two equations, we find the up to now unknown coefficient α and the equilibrium concentration $c_{\text{eq}}(n)$, i.e.,

$$\alpha = D/\ell \quad (38)$$

and

$$c_{\text{eq}}(n) = c_{\text{eq}}(\infty) e^{\ell k(n)}. \quad (39)$$

The only difference between Eqs. (34) and (37) is that in the latter case, we always have the average value of the cluster size $\langle n \rangle$ instead of n . Rewriting Eq. (37), we finally get

$$\frac{d\langle n \rangle}{dt} = \frac{D}{\ell} A(\langle n \rangle) \left(c - \frac{\langle n \rangle}{V} - c_{\text{eq}}(\infty) e^{\ell k(\langle n \rangle)} \right). \quad (40)$$

In the stationary state, $d\langle n \rangle/dt = 0$ holds. Eq. (40) is valid at large enough n only, whereas at $\langle n \rangle \rightarrow 0$ it should be modified to ensure that the transition rates and, therefore, the expression in the brackets does not diverge. Then we obtain three stationary solutions. The homogeneous situation without any cluster corresponds to $A(\langle n \rangle_{\text{st}}) = 0$, or to zero value of the stationary cluster size $\langle n \rangle_{\text{st}} = 0$. The other two solutions, describing the heterogeneous situation, originate from the identity $c_{\text{freec}}(\langle n \rangle_{\text{st}}) = c_{\text{eq}}(\langle n \rangle_{\text{st}})$ or in extended version

$$c - \frac{\langle n \rangle_{\text{st}}}{V} = c_{\text{eq}}(\infty) \exp[\ell(c_{\text{clust}} 4\pi/3)^{1/3} \langle n \rangle_{\text{st}}^{-1/3}]. \quad (41)$$

From this equation, we can find the stationary cluster size $\langle n \rangle_{\text{st}}$ as a function of the total density c . This is a nonlinear equation that cannot be solved analytically. However, it can be easily analysed (solved) graphically. Fig. 3 terms on the l.h.s. (thick straight line) and on the r.h.s. (curved line) vs. $\langle n \rangle$ are shown. The two crossing points $\langle n \rangle = n_{\text{cr}}$ and $\langle n \rangle = n_{\text{stable}}$ correspond to two different solutions of Eq. (41). The quantity n_{cr} is known as the critical cluster size in nucleation theory, whereas n_{stable} represents the stable stationary cluster size. Their meaning will be clarified in further discussion. The crossing points exist only if the total concentration c exceeds some critical value $c > c_1$, which corresponds to a bifurcation point where both solutions merge into one, as it is shown by thin straight line which has only one common point with the curved line at the marginal (largest possible) value of the critical cluster size $\langle n \rangle_{\text{st}} = n_{\text{cr}}^*$. At $c > c_1$ three different regions can be distinguished for the cluster size $\langle n \rangle_{\text{st}}$:

- I. At $\langle n \rangle < n_{\text{cr}}$, we have $d\langle n \rangle/dt < 0$, which means that the cluster dissolves.
- II. At $n_{\text{cr}} < \langle n \rangle < n_{\text{stable}}$, we have $d\langle n \rangle/dt > 0$, which means that the cluster grows until it reaches the stable stationary size n_{stable} .
- III. At $\langle n \rangle > n_{\text{stable}}$, we have $d\langle n \rangle/dt < 0$, which means that the cluster reduces its size (dissolves) to the stationary value n_{stable} .

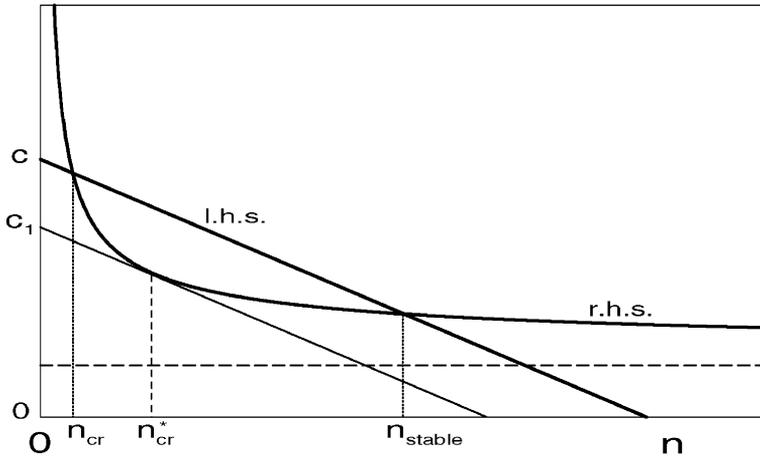


Fig. 3. Terms on the l.h.s. (straight lines) and on the r.h.s. (curved line) of Eq. (41) depending on the cluster size n . The two crossing points at $n = n_{\text{stable}}$ (stable cluster size) and $n = n_{\text{cr}}$ (unstable or critical cluster size) correspond to two different solutions of Eq. (41). The thin straight line related to the critical density c_1 has a single common point with the curved line at $n = n_{\text{cr}}^*$. The horizontal dashed line shows the value of equilibrium concentration $c_{\text{eq}}(\infty)$.

According to this, the solution $\langle n \rangle = n_{\text{stable}}(c)$ corresponds to a stable cluster size, whereas the solution $\langle n \rangle = n_{\text{cr}}(c)$ to an unstable stationary cluster size.

Expansion of the exponent in Eq. (39), retaining the linear term only, yields

$$c_{\text{eq}}(\langle n \rangle) = c_{\text{eq}}(\infty)(1 + \ell k(\langle n \rangle)). \tag{42}$$

By using this linearization around the critical cluster size n_{cr} , Eq. (40) can be written in the well-known form (Schmelzer et al., 1999)

$$\frac{d\langle n \rangle}{dt} = Dc_{\text{eq}}(\infty)A(\langle n \rangle)[k(n_{\text{cr}}) - k(\langle n \rangle)]. \tag{43}$$

From this equation, the above discussed property that clusters with an overcritical size ($n > n_{\text{cr}}$, i.e., $k(n) < k(n_{\text{cr}})$) grow, whereas those with an undercritical size ($n < n_{\text{cr}}$, i.e., $k(n) > k(n_{\text{cr}})$) dissolve, is obvious. In the actual bistable situation, the growth from an undercritical to an overcritical cluster size cannot be described by deterministic equations of motion like Eq. (43). This phenomenon of noise-induced transitions over the critical value of cluster size can be treated in the stochastic approach only.

We have simulated by Monte Carlo method and have presented in Fig. 4 three different stochastic trajectories showing the time evolution, i.e., the cluster size n vs. the dimensionless time $t^* = (\alpha A(1)/V) t$, of the system with $N_{\text{total}} = 1000$ particles starting with n values around the critical cluster size $n_{\text{cr}} \approx 54$ (the lower dashed line). The parameters of the system are chosen such that $\sigma A(1)/(k_B T) = 10$ and $Vc_{\text{eq}}(\infty) = 160$. In one of the cases, the cluster dissolves, whereas in the other two cases, it grows over the critical size. Besides, in distinction to the prediction of the deterministic equation (Eq. (40)), in one of

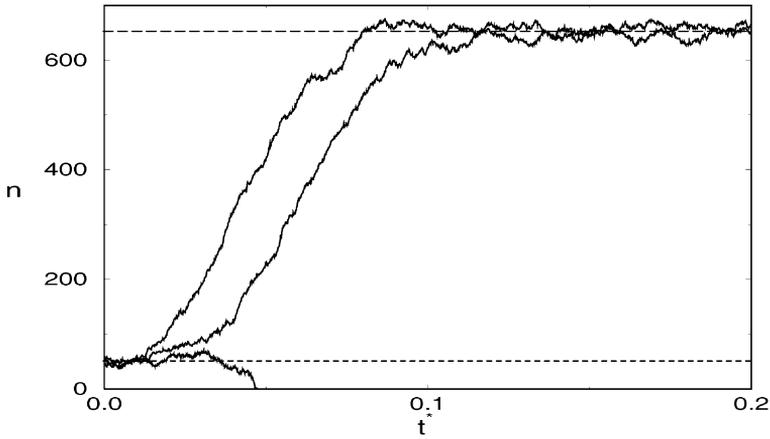


Fig. 4. Three different stochastic trajectories showing the time evolution of the cluster size n vs. the dimensionless time t^* . The lower dashed line indicates the critical cluster size $n_{cr} = 54$; the upper dashed line represents the stable cluster size $n_{stable} = 650$.

the cases, the growth up to the stable cluster size $n \approx 650$ (the upper dashed line) occurs starting with $n = 45 < n_{cr}$. The probability distribution at three different time moments, i.e., $t^* = 0.003, 0.04$ and 0.3 , have been calculated by averaging over a large number of stochastic trajectories starting with the $n = n_{cr} = 54$. The results are shown in Fig. 5. The probability maximum moves towards larger values of the cluster size n with increasing

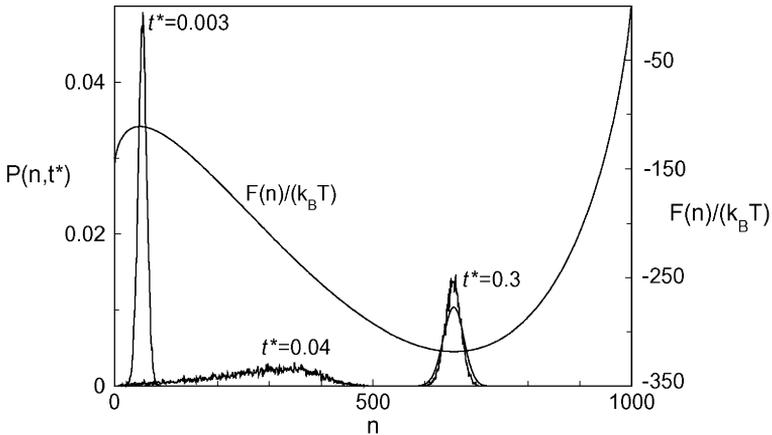


Fig. 5. The probability distribution $P(n, t^*)$ at three different dimensionless time moments $t^* = 0.003$ (left), $t^* = 0.04$ (middle), and $t^* = 0.3$ (right) calculated by averaging over 20,000 stochastic trajectories simulated by the Monte Carlo method. The equilibrium distribution is shown by a smooth solid line. The maximum of the equilibrium distribution corresponds to the minimum of free energy, i.e., $F(n)/(k_B T)$ (smooth curve).

time, and at $t^* = 0.3$ the probability distribution agrees approximately with the equilibrium distribution $P^{\text{eq}}(n) \propto \exp(-F(n)/(k_B T))$ (smooth solid line). The maximum of the equilibrium distribution corresponds to the minimum of free energy, whereas the critical cluster size to the local maximum of free energy, as shown in Fig. 5.

4. Car cluster formation on roads

The aggregation of particles out of an initially homogeneous situation is well known and it takes place in physical and in nonphysical systems, like traffic flow, and can be described similarly (Kaupužs and Mahnke, 2000b; Mahnke, 2000). Traffic flow theory has a long history (Prigogine and Herman, 1971) and is still alive (Helbing, 1997). Theoretical approaches based on deterministic car-following models (Bando et al., 1994) and particle-hopping models (Chowdhury et al., 2000) are well known. An experimental study of phase transitions in traffic flow has been presented by Kerner (2000), the stochastic description is provided in Kaupužs and Mahnke (2000a), Mahnke and Kaupužs (1999), Mahnke and Pieret (1997).

In analogy to the droplet formation in supersaturated vapour, we consider a model of traffic flow on a one-lane road according to which N cars are moving along a circle of length L , as illustrated in Fig. 6 where two different regimes of traffic flow are shown, i.e., free flow (left) and congested traffic flow with two car clusters (right). For simplicity, we have restricted our further analysis to the simplest model where only one car cluster (jam) can exist. If a road is crowded by cars, each car requires some minimal space or length which, obviously, is larger than the real length of a car. We call this the effective length ℓ of a car. The maximal velocity of each car is v_{max} . Following the idea of Bando et al. (1994), the behaviour of individual drivers is described by the optimal velocity model. The desired (optimal) velocity v_{opt} , depending on the distance between two cars Δx , is given in

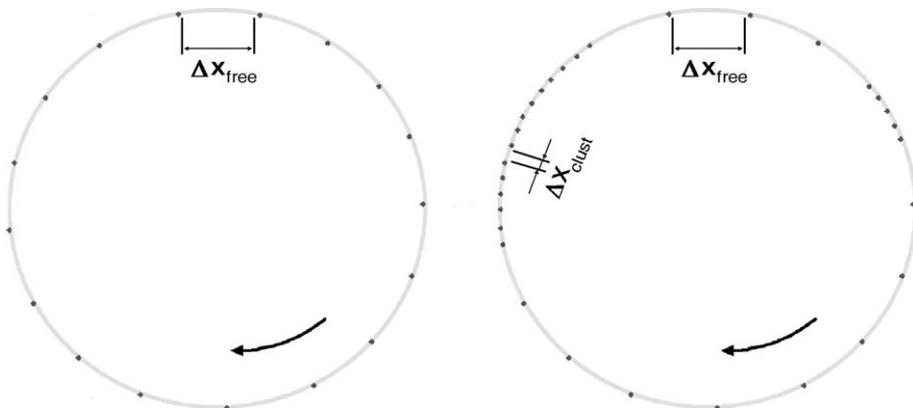


Fig. 6. Free traffic flow (left) and congested traffic flow (right) on the one-lane circular road. Each black dot represents a car and its direction of motion is indicated by the arrow.

dimensionless variables $w_{\text{opt}} = v_{\text{opt}}/v_{\text{max}}$ and $\Delta y = \Delta x/\ell$ by the formula (Mahnke and Kaupužs, 1999; Mahnke and Pieret, 1997):

$$w_{\text{opt}}(\Delta y) = \frac{(\Delta y)^2}{d^2 + (\Delta y)^2}, \quad (44)$$

where the parameter $d = D/\ell$ is the interaction distance. D is the distance between two cars corresponding to the velocity value $v_{\text{max}}/2$.

Measurements on highways have shown that the density c_{clust} of cars in congested traffic is independent of the size of the dense phase (jam). As a consequence the distance between jammed cars, the spacing $\Delta x_{\text{clust}} = \ell \Delta y_{\text{clust}} = \text{const} \geq 0$, is well known and has to be treated as a given measured quantity.

The length of the cluster (jam) depending on the number of congested cars n is defined by $L_{\text{clust}} = \ell n + (n-1)\Delta x_{\text{clust}}$. According to this, the average distance $\Delta x_{\text{free}} = \ell \Delta y_{\text{free}}$ between two cars outside the jam (or free cars) distributed over the free part of the road with length $L_{\text{free}} = L - L_{\text{clust}}$ is given by

$$\Delta y_{\text{free}}(n) = \frac{L/\ell - N - S(n)\Delta y_{\text{clust}}}{N - S(n)}, \quad (45)$$

where N is the total number of cars on the road (circle of length L) and $S(n) = n - 1 + \delta_{n,0}$ is the number of fixed spacings Δx_{clust} between cars in jam.

The traffic flow is described as a stochastic process where adding a vehicle to a car cluster of size n is characterized by a transition frequency (attachment probability per time unit) $w_+(n)$ and the opposite process by a frequency $w_-(n)$. The number n of cars in the cluster is the stochastic variable, which may have values from 0 to N . The basic equation for the evolution of the probability distribution $P(n, t)$ to find a cluster of size n at time t with probability P is known as master equation (Eq. (11)). The one-dimensional stochastic equation reads:

$$\frac{1}{\tau} \frac{dP(n, T)}{dT} = w_+(n-1)P(n-1, T) - [w_+(n) + w_-(n)]P(n, T) + w_-(n+1)P(n+1, T). \quad (46)$$

where $T = t/\tau$ is the dimensionless time. The time constant τ will be specified below.

The main task is to formulate expressions for both transition probabilities w_+ and w_- . We have assumed that the detachment frequency $w_-(n)$ or the average number of cars leaving the cluster per time unit is a constant independent of cluster size n . The ansatz for $w_+(n)$ is now formulated allowing for Δx_{clust} to be nonzero. Our general assumption is that a vehicle changes the velocity from $v_{\text{opt}}(\Delta x_{\text{free}})$ in free flow to $v_{\text{opt}}(\Delta x_{\text{clust}})$ in jam and approaches the cluster as soon as the distance to the next car (the last car in the cluster) reduces from Δx_{free} to Δx_{clust} . This assumption allows one to calculate the average number of cars joining the cluster per time unit or the attachment frequency to an existing cluster $w_+(n)$. The case $w_+(0)$ have to be considered separately. This is a probability per time of a stochastic event that a driver randomly reduces the velocity of his car to $v_{\text{opt}}(\Delta x_{\text{clust}})$ without obvious reason, thus forming a precluster or cluster of size $n=1$. An ansatz for

$w_+(0)$ similar to that we have used in the case of supersaturated vapour is appropriate. Thus, we have the ansatz which in dimensionless quantities reads

$$w_+(0) = \frac{p}{\tau} N \tag{47}$$

$$w_+(n) = \frac{b}{\tau} \frac{w_{\text{opt}}(\Delta y_{\text{free}}(n)) - w_{\text{opt}}(\Delta y_{\text{clust}})}{\Delta y_{\text{free}}(n) - \Delta y_{\text{clust}}} \tag{48}$$

$$w_-(n) = 1/\tau = \text{const}, \tag{49}$$

where $b = v_{\text{max}}\tau/\ell$ denotes a dimensionless parameter and p is the stochasticity. The parameter τ is a time constant, which can be understood as the waiting time for the escape (detachment) of first car out of the jam into free flow (Mahnke and Kaupužs, 1999).

The master equation (Eq. (46)) has been solved in Mahnke and Kaupužs (1999), Mahnke and Pieret (1997) with an aim to extract from this solution, information about the formation of traffic jams and about the various possible regimes of traffic flow depending on the parameters of the system, as well as to calculate the flux–density relationship, called fundamental diagram of traffic flow. Our purpose is to study the dynamics of the cluster (jam) growth and dissolution by finding stable and unstable stationary states, and compare the results with aggregation in supersaturated vapour.

Like in the case of the cluster growth in supersaturated vapour, the deterministic equation (Eq. (35)) for growth of a single car cluster on the road is written as Eq. (36). The stationary cluster size $\langle n \rangle_{\text{st}}$ can be calculated from the condition $d\langle n \rangle/dt = 0$ or

$$\frac{w_+(\langle n \rangle)}{w_-(\langle n \rangle)} = b \frac{w_{\text{opt}}(\Delta y_{\text{free}}(\langle n \rangle)) - w_{\text{opt}}(\Delta y_{\text{clust}})}{\Delta y_{\text{free}}(\langle n \rangle) - \Delta y_{\text{clust}}} = 1 \tag{50}$$

consistent with the ansatz for transition probabilities Eqs. (48) and (49). By using the definition (Eq. (44)) of the optimum velocity function $w_{\text{opt}}(\Delta y)$ we obtain the equation

$$b \left[\frac{(\Delta y_{\text{free}}(\langle n \rangle))^2}{d^2 + (\Delta y_{\text{free}}(\langle n \rangle))^2} - \frac{(\Delta y_{\text{clust}})^2}{d^2 + (\Delta y_{\text{clust}})^2} \right] = \Delta y_{\text{free}}(\langle n \rangle) - \Delta y_{\text{clust}}, \tag{51}$$

which can be solved with respect to Δy_{free} . One solution of the third-order equation (Eq. (51)) is trivial $\Delta y_{\text{free}} = \Delta y_{\text{clust}}$. The other two solutions, which have certain physical meaning, read

$$\Delta y_{\text{free}}^{(1,2)} = \frac{d}{2[d^2 + (\Delta y_{\text{clust}})^2]} \times \left\{ bd \pm \sqrt{b^2 d^2 + 4b \Delta y_{\text{clust}} [d^2 + (\Delta y_{\text{clust}})^2] - 4[d^2 + (\Delta y_{\text{clust}})^2]^2} \right\}. \tag{52}$$

According to Eq. (52), the headway Δy_{free} between cars in a free flow coexisting with a single cluster has constant value depending merely on the control parameters of the model.

Now, by means of Eq. (45), which states the relation between Δy_{free} and n , we are able to calculate the stationary cluster size $\langle n \rangle_{\text{st}}$. As already pointed out, we set $S(n) = n - 1 + \delta_{n,0} \approx n$, assuming that the cluster (if it exists) contains a large number of cars. This leads to the equation

$$\frac{\langle n \rangle_{\text{st}}}{L/\ell} = \frac{c(1 + \Delta y_{\text{free}}^{(1,2)}) - 1}{\Delta y_{\text{free}}^{(1,2)} - \Delta y_{\text{clust}}}, \quad (53)$$

where $c = \ell N/L$ is the total density of cars and the term on the left hand side of the equation, in fact, is the relative part of the road crowded by cars. In this case $\Delta y_{\text{free}}^{(1,2)}$ has a constant value given by Eq. (52). The results of Eq. (53) make sense at large enough densities where it provides a positive value of $\langle n \rangle_{\text{st}}$. The solution with the largest value $\Delta y_{\text{free}}^{(1)}$ (positive sign in Eq. (52)) gives the average stationary size of a stable cluster depending on the total density c within the region $c > c_1$, where

$$c_1 = \frac{1}{1 + \Delta y_{\text{free}}^{(1)}} \quad (54)$$

is the critical density having the same meaning as in the case of cluster growth in supersaturated vapour. There is another critical density c_2 , given by

$$c_2 = \frac{1}{1 + \Delta y_{\text{free}}^{(2)}}, \quad (55)$$

which defines the region $c > c_2$ where an unstable car cluster corresponding to the solution (Eq. (53)) with the smallest value $\Delta y_{\text{free}}^{(2)}$ of the headway can exist. In a special case of vanishing bumper-to-bumper distance in jam $\Delta y_{\text{clust}} = 0$, our result (Eq. (52)) reduces to

$$\Delta y_{\text{free}}^{(1,2)} = \frac{b}{2} \pm \sqrt{\frac{b^2}{4} - d^2}, \quad (56)$$

and Eq. (53) to

$$\frac{\langle n \rangle_{\text{st}}}{L/\ell} = c + \frac{c - 1}{\frac{b}{2} \pm \sqrt{\frac{b^2}{4} - d^2}}. \quad (57)$$

This result, obtained in the simple one-cluster model discussed here remains true in the multicluster model, outlined in (Kaupužs and Mahnke, 2000b) and discussed in detail in (Kaupužs and Mahnke, 2000a), if the size of the system is large ($N \rightarrow \infty$) and stochasticity p is small. Note only that n , in general, is defined as the total number of congested cars.

The value of $\langle n \rangle_{\text{st}} \ell / L$ with sign ‘+’ in Eq. (57) corresponds to the stable, whereas that with sign ‘-’, to the unstable stationary cluster size. Like in the case of supersaturated vapour, the growth of the car cluster starting with the undercritical (i.e., smaller than the unstable) cluster size can be described within a stochastic approach only. Fig. 7 presents a typical stochastic trajectory showing a noise-induced switching from free flow with n values

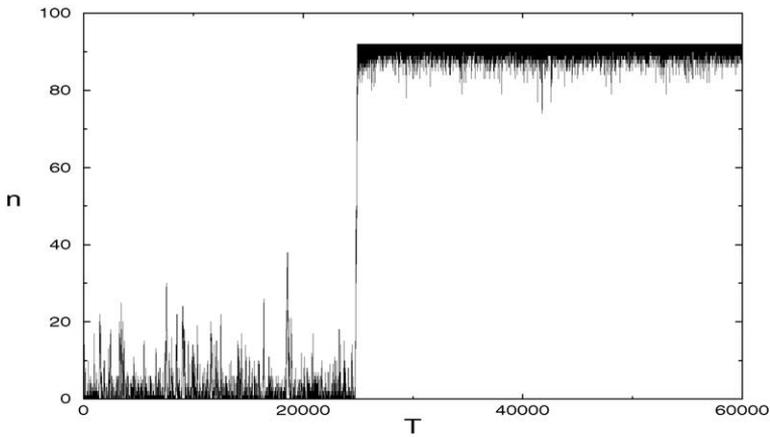


Fig. 7. A stochastic trajectory showing the total number of congested cars n vs. dimensionless time T .

fluctuating below the unstable cluster size (in this example $N=92$, $c=0.7886$, $b=8.5$, $d=13/6$, $\Delta y_{\text{clust}}=1/6$, which corresponds to the critical cluster size about 53 and the stable cluster size about 91) to the state with large stable cluster including almost all cars.

5. Discussion

A comparison between aggregation processes in supersaturated vapour and in traffic flow is illustrated in Figs. 8 and 9. In Fig. 8, we have shown both solutions of Eq. (41)

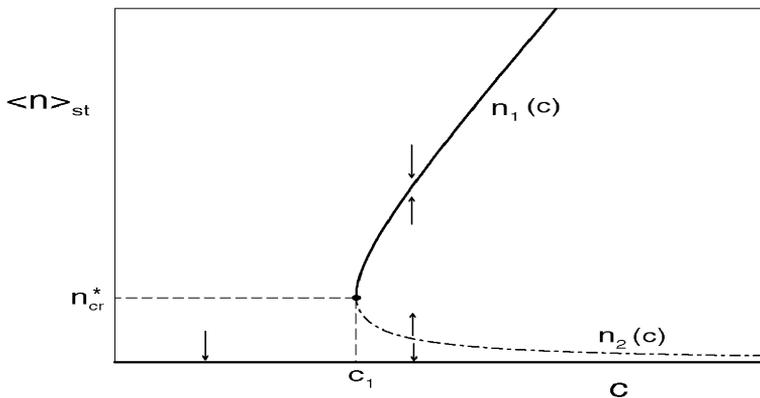


Fig. 8. The stationary cluster size $\langle n \rangle_{\text{st}}$ depending on the total density c of particles in a supersaturated vapour. The stable cluster size (the horizontal line and the branch $n_1(c)$) is shown by thick solid lines, whereas the unstable cluster size (the branch $n_2(c)$) is shown by dot-dashed line. Arrows indicate the time evolution of $\langle n \rangle$.

(branches $n_1(c)$ and $n_2(c)$), providing the stationary cluster size in a supersaturated vapour as a function of total density c . The diagram shown in Fig. 9 relates the stationary cluster size $\langle n \rangle_{st}$ to the total density of cars c in the case of the aggregation in traffic flow at vanishing Δy_{clust} . In analogy to the case of supersaturated vapour, the two branches given by Eq. (57) (with ‘+’ and ‘-’, respectively) are denoted by $n_1(c)$ and $n_2(c)$.

In Figs. 8 and 9, branches depicted by thick solid lines correspond to stable cluster size, whereas those indicated by dot–dashed lines correspond to unstable cluster size. Several trajectories showing the time evolution of $\langle n \rangle$ to one of the stable stationary values (thick lines) are indicated by arrows. In both figures, $n_1(c)$ corresponds to the stable cluster size and $n_2(c)$ to the unstable (critical) cluster size. Note, however, that we have two different kinds of bifurcations at $c=c_1$. In distinction to the traffic flow, in the case of the supersaturated vapour, there is a jump in the cluster size. Besides, in the traffic flow, we do not have the critical cluster size at intermediate densities $c_1 < c < c_2$, which means that even a very small car cluster at the initial time moment has a tendency to grow up to the stationary size. At large densities ($c > c_2$), the critical cluster size $n_2(c)$ appears as well in traffic flow.

Apart from the abovementioned similar features, there is an essential difference between the aggregation in supersaturated vapour and in traffic flow. If we allow a coexistence of many clusters, then in supersaturated vapour the difference in surface curvature makes larger clusters more stable (i.e., the probability that they survive during a given time interval increases) as compared to smaller clusters. In essence, the traffic flow is one-dimensional, therefore such effect cannot be, in principle, observed. As a result, in the supersaturated vapour the final stage of aggregation is one large cluster, whereas in traffic flow there are several smaller clusters. However, this difference does not appear in the one-cluster model discussed here in detail.

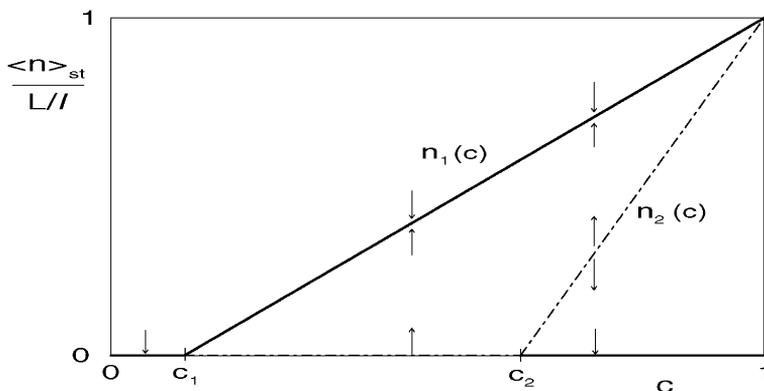


Fig. 9. The stationary cluster size $\langle n \rangle_{st}$ normalized to L/l (i.e., the relative part of the road crowded by cars) depending on the total density of cars c . The stable cluster size (branch $n_1(c)$ and horizontal lines) is shown by thick solid lines, whereas the unstable cluster size (branch $n_2(c)$ and a horizontal line) is shown by dot–dashed lines. Arrows indicate the time evolution of $\langle n \rangle$. Parameters: $b=8.5$, $d=13/6$, and $\Delta y_{clust}=0$.

To conclude this paper, we recall the key points of the developed approach. It has been shown that both supersaturated vapour and traffic flow can be described by stochastic master equations. Solutions of the master equation in each of the cases have shown the existence of phase transition from initially homogeneous state to a heterogeneous state where some of the particles (molecules or cars) are bounded in a cluster. The cluster growth dynamics in supersaturated vapour and in traffic flow has been studied in view of both deterministic and stochastic theory. Finally, the comparison of results has been made showing that, on the one hand, at certain conditions the nucleation in traffic flow is similar to that in supersaturated vapour (small, i.e., undercritical, clusters tend to dissolve, whereas those of overcritical size tend to grow) and, on the other hand, there are also some essential differences between both cases, in particular, the absence of critical cluster size in traffic flow at intermediate densities.

Appendix A

Our system is described by the cluster distribution \mathbf{N} defined by Eq. (18). The total Hamiltonian $H(\mathbf{N})$ reads

$$H = \sum_{n=0}^N H_n \quad (58)$$

with the contribution H_n for the N_n clusters of size n at coordinates $\mathbf{r}_i^{(n)}$ and momentum $\mathbf{p}_i^{(n)}$ written as kinetic energy and interaction potential

$$H_n(\mathbf{p}^{(n)}, \mathbf{r}^{(n)}) = \sum_i \frac{(p_i^{(n)})^2}{2m_i^{(n)}} + \sum_{i<j} U_{ij}^{(n,n)}(|\mathbf{r}_i - \mathbf{r}_j|). \quad (59)$$

The mass $m_i^{(n)}$ of a cluster containing n monomers ($n \geq 1$) is given by

$$m_i^{(n)} \equiv m_n = nm \quad (60)$$

where $m \equiv m_0$ is the mass of one monomer. The canonical partition function, i.e., the statistical integral, is an integral over all space and momentum coordinates. In the semiclassical approximation it reads (Münster, 1969)

$$Z(T, V, \mathbf{N}) = \prod_{n=0}^N \frac{1}{N_n! h^{3N_n}} \int d^{3N_n} p d^{3N_n} q \exp(-\beta H_n), \quad (61)$$

where $\beta = 1/(k_B T)$. This partition function can be divided in two factors, one of which represents an ideal part due to the kinetic energy

$$Z_{\text{ideal}}(T, V, \mathbf{N}) = \prod_{n=0}^N \frac{V^{N_n}}{N_n! h^{3N_n}} (\sqrt{2\pi m_n k_B T})^{3N_n} \quad (62)$$

and the second part $Z_{\text{binding}}(T, V, \mathbf{N})$ is responsible for the energy stored in clusters. In a certain approximation, both terms together read

$$Z(T, V, \mathbf{N}) = \prod_{n=0}^N \frac{V^{N_n}}{N_n!} \left[\left(\frac{\sqrt{2\pi m_n k_B T}}{h} \right)^3 \exp\left(-\frac{f_n}{k_B T}\right) \right]^{N_n} \quad (63)$$

where the binding energy $f_n(T)$ is the minimum value of the potential energy searched over all spatial arrangements of the n bounded monomers

$$f_n(T) = \min_{\mathbf{r}} \sum_{i < j} U_{ij}^{(n,n)}(|\mathbf{r}_i - \mathbf{r}_j|). \quad (64)$$

From the canonical partition function, we can calculate the thermodynamic quantities using the relation to state function free energy

$$F(T, V, \mathbf{N}) = -k_B T \ln Z(T, V, \mathbf{N}). \quad (65)$$

According to Eqs. (63) and (65), in the isothermal–isochoric situation we obtain

$$F(T, V, \mathbf{N}) = k_B T \sum_{n=0}^N [N_n \ln(\lambda_n(T)^3/V) + \ln N_n!] + \sum_{n=0}^N N_n f_n(T) \quad (66)$$

with de Broglie wavelength $\lambda_n(T) = n^{-1/2} \lambda_0(T) = n^{-1/2} (h^2/(2\pi m k_B T))^{1/2}$ (at $n \geq 1$). Using Stirling formula $\ln N_n! \approx N_n \ln N_n - N_n$ in Eq. (66) we obtain an approximation for large cluster numbers N_n (Mahnke, 2000)

$$F(T, V, \mathbf{N}) = k_B T \sum_{n=0}^N N_n [\ln(\lambda_n(T)^3 N_n/V) - 1] + \sum_{n=0}^N N_n f_n(T). \quad (67)$$

In the case of one cluster of size n only (see Eq. (20)) and at $N_0 = N_{\text{total}} - n \rightarrow \infty$ (i.e., in the thermodynamic limit by expansion of $\ln N_0!$) the free energy (Eq. (66)) reads

$$F(T, V, n) = k_B T \{ (N_{\text{total}} - n) [\ln(\lambda_0(T)^3 (N_{\text{total}} - n)/V) - 1] + (1 - \delta_{n,0}) \ln(\lambda_n(T)^3/V) \} + f_n(T). \quad (68)$$

For the equilibrium cluster distribution, the most probable value of the cluster size n corresponds to the minimum of the thermodynamic potential, in this case free energy F , as it is evident from Eq. (17). The latter equation (with $\Omega \equiv F$) combined with the detailed balance condition (Eq. (16)) allows to find the relation between transition rates $w(\mathbf{N}'|\mathbf{N})$

and $w(\mathbf{N}|\mathbf{N}')$ of opposite stochastic events (transition from state \mathbf{N} to state \mathbf{N}' and vice versa), i.e.,

$$\frac{w(\mathbf{N}'|\mathbf{N})}{w(\mathbf{N}|\mathbf{N}')} = \exp\left(\frac{F(T, V, \mathbf{N}) - F(T, V, \mathbf{N}')}{k_{\text{B}}T}\right). \quad (69)$$

In our special case, where only one cluster of size n is possible, Eq. (69) in the thermodynamic limit reduces to

$$\frac{w_-(n)}{w_+(n-1)} = \frac{V(1-1/n)^{3/2}}{\lambda_0^3(T)(N_{\text{total}}-n)} \exp\left(\frac{f_n(T) - f_{n-1}(T)}{k_{\text{B}}T}\right) : n \geq 2 \quad (70)$$

$$\frac{w_-(1)}{w_+(0)} = \frac{1}{N_{\text{total}}} \exp\left(\frac{f_1(T)}{k_{\text{B}}T}\right). \quad (71)$$

From Eq. (70), we obtain an approximation

$$\frac{w_-(n)}{w_+(n)} = \frac{V}{\lambda_0^3(T)(N_{\text{total}}-n)} \exp\left(\frac{f_n(T) - f_{n-1}(T)}{k_{\text{B}}T}\right), \quad (72)$$

consistent with Eqs. (22) and (25), which is true for large enough n . In a rough approximation, we have assumed that Eq. (72) can be extrapolated up to $n=1$. Based on Eq. (71), the stochasticity parameter p in Eq. (24) can be written as

$$\frac{p}{\tau} = w_-(1) \exp\left(-\frac{f_1(T)}{k_{\text{B}}T}\right). \quad (73)$$

By Eqs. (22), (25) and (73) all the transition rates are well defined in a way consistent with the basic principles of statistical mechanics.

References

- Bando, M., Hasebe, K., Nakayama, A., Shibata, A., Sugiyama, Y., 1994. Structure stability of congestion in traffic dynamics. *Jpn. J. Ind. Appl. Math.* 11, 203.
- Chowdhury, D., Santen, L., Schadschneider, A., 2000. Statistical physics of vehicular traffic and some related systems. *Phys. Rep.* 329, 199.
- Gardiner, C.W., 1990. *Handbook of Stochastic Methods*. Springer, Berlin, 1983 (1st ed.), 1985.
- Haberland, H. 1994. *Clusters of Atoms and Molecules*. Springer, Berlin.
- Haken, H., 1983. *Synergetics. An Introduction*. Springer, Berlin, 1978 (1st ed.).
- Heermann, D.W., 1990. *Computer Simulation Methods in Theoretical Physics*. Springer, Berlin.
- Helbing, D., 1997. *Verkehrsdynamik. Neue physikalische Modellierungskonzepte*. Springer, Berlin.
- Honerkamp, J., 1990. *Stochastische Dynamische Systeme*. VCH Verlagsgesellschaft. Weinheim, 1994; *Stochastic Dynamical Systems*. VCH, New York.
- Jellinek, J. 1999. *Theory of Atomic and Molecular Clusters*. Springer, Berlin.
- Kaupužs, J., Mahnke, R., 2000a. A stochastic multi-cluster model of freeway traffic. *Eur. Phys. J.*, B 14, 793.
- Kaupužs, J., Mahnke, R., 2000b. Nucleation on roads. In: Hale, B., Kulmala, M. *Nucleation and Atmospheric Aerosols 2000*. AIP Conference Proceedings, vol. 535. American Institute of Physics, New York, p. 221.

- Kerner, B.S., 2000. Phase transitions in traffic flow. In: Helbing, D., Hermann, H.J., Schreckenberg, M., Wolf, D.E. Traffic and Granular Flow '99. Springer, Berlin, p. 253.
- Mahnke, R., 1998. Aggregation phenomena to a single cluster regime under different boundary conditions. *Z. Phys. Chem.* 204, 85.
- Mahnke, R., 2000. Nucleation in physical and non-physical systems. In: Hale, B., Kulmala, M. Nucleation and Atmospheric Aerosols 2000. AIP Conference Proceedings, vol. 535. American Institute of Physics, New York, p. 229.
- Mahnke, R., Kaupužs, J., 1999. Stochastic theory of freeway traffic. *Phys. Rev., E* 59, 117.
- Mahnke, R., Pieret, N., 1997. Stochastic master-equation approach to aggregation in freeway traffic. *Phys. Rev., E* 56, 2666.
- Miller, M.A., Doye, J.P.K., Wales, D.J., 1999. Structural relaxation in atomic clusters: master equation dynamics. *Phys. Rev., E* 60, 3701.
- Montroll, E.W., Badger, W.W., 1974. Introduction to Quantitative Aspects of Social Phenomena. Gordon and Breach, New York.
- Münster, A., 1969. Statistical Thermodynamics, vol. I. Springer, Berlin.
- Newman, M.E.J., Barkema, G.T., 1999. Monte Carlo Methods in Statistical Physics. Clarendon Press, Oxford.
- Paul, W., Baschnagel, J., 1999. Stochastic Processes. From Physics to Finance. Springer, Berlin.
- Prigogine, I., Herman, R., 1971. Kinematic Theory of Vehicular Traffic. Elsevier, New York.
- Reiss, H., Huang, C., 1971. Statistical thermodynamic formalism in the solution of information theory problems. *J. Stat. Phys.* 3, 191.
- Reiss, H., Hammerich, A.D., Montroll, E.W., 1986. Thermodynamic treatment of nonphysical systems: formalism and an example (single-lane traffic). *J. Stat. Phys.* 42, 647.
- Schmelzer, J., Röpke, G., Mahnke, R., 1999. Aggregation Phenomena in Complex Systems. Wiley-VCH, Weinheim.
- Schmelzer Jr., J., Lembke, U., Kranold, R., 2000. Nucleation and growth of AgCl clusters in a sodium borate glass: numerical analysis and SAXS results. *J. Chem. Phys.* 113, 1268.
- van Kampen, N.G., 1992. Stochastic Processes in Physics and Chemistry. North-Holland, Amsterdam, 1981.
- Wu, D.T., 1997. Nucleation theory. In: Ehrenreich, H., Spaepen, F. Solid State Physics, vol. 50. Academic Press, San Diego, p. 37.