# SCHEMATIC MODELLING OF SUPERIONIC CONDUCTION

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**Abstract**

Some main properties of driven lattice gases as observed in a series of Monte Carlo simulations are briefly reviewed. The lattice is either two- or quasi-two dimensional. Particles jump according to an irreversible rule which induces a net steady current for appropriate boundaries, and a sharp linear interface occurs in some circumpstances. Several nonequilibrium phase transitions are described. The relation with conduction in soild electrolytes is briefly discussed.

## 1 Introduction

Stochastic lattice gases are suited to study ordering phenomena in open systems, e.g. pattern formation, self-organization, and morphogenesis. In the *driven lattice gas* (DLG) [1] particles jump stochastically to a NN hole under competition between a heat bath at temperature $T$ and a driving external field, $E\hat{\mathsf{x}}$, of constant intensity $E > 0$. The steady state is then characterized by a net particle current along the field direction, $+\hat{\mathsf{x}}$, if permitted by boundary conditions. A familiar case corresponds to $L_x \times L_y$ rectangles with toroidal boundaries, particle density $\rho$, and the bath implemented by the Metropolis algorithm. The latter implies that the probability per unit time for the exchange of a particle and a hole is $\min\{1, \exp(-\delta H/k_B T)\}$. Here, $\delta H$ represents the associated *energy cost,* which is computed assuming that energy corresponds to the Ising Hamiltonian with NN particle attractions, and adding to this the work done by the field (in the case of exchanges along either $+\hat{\mathsf{x}}$ or $-\hat{\mathsf{x}}$). This system is denoted $\lambda_E$ hereafter. The case $\lambda_0$ in which the field has been *switched off* corresponds to the celebrated equilibrium system solved by Onsager for the *infinite* lattice, i.e., $L_x \to \infty$ and $L_y \to \infty$ [15]. Consider also $\Lambda_E$ consisting of two NN adjacent $\lambda_E$ planes both perpendicular to the $\hat{\mathsf{z}}$ axis. That is, any site in $\Lambda_E$ has five NN's with one of them in the other plane. Any particle interacts only with the ones at NN sites within the same plane (there are no interplane bonds) but may hop to the other plane according to the same rule as for $\hat{\mathsf{y}}$-jumps, i.e., the Metropolis algorithm with no field; cf. Ref.[12, 14] for more details. The symbols $\lambda_\infty$ and $\Lambda_\infty$ stand hereafter for $\lambda_E$ and $\Lambda_E$, respectively, when the field is *saturating* which means that no particle may jump $-\hat{\mathsf{x}}$.

Monte Carlo (MC) simulations have been a main source of information on the DLG. These (together with mean-field approximations [8, 14]) have revealed a rich variety of nonequilibrium phenomena as one varies the values of $T$, $\rho$ and $E$, and considers either two- ($\lambda_E$) or quasi-two- ($\Lambda_E$) dimensional lattices. Therefore, the DLG provides an introduction to the study of basic questions in nonequilibrium statistical physics (where a general theory is lacking) which is simple, natural and mathematically well-defined; in fact, it has been used to test theory, and to obtain phenomenological information to be incorporated by theory.

*Figure 1:* Computer and corresponding experimental results.

The model versatility has also allowed for a meaningful comparison between computer results and observations on real substances [6, 10]. Such comparisons have suggested that the DLG may contain some of the essential features of ionic conductivity in solid electrolytes. *Figure 1* illustrates the close similarity computer and experimental results may sometimes exhibit. The (negative of the) logarithm of the current (number of actual $+\hat{\mathsf{x}}$-jumps per site per unit time) *versus* the inverse temperature in $\lambda_\infty$ -main graph- is compared in *figure 1* with the corresponding quantity [16] in $RbAg_4I_5$ -upper inset- and in $KHg_4I_5$ -lower inset-. The similarity is also close if one compares (not shown) the *specific heat* (e.g., temperature derivative of the density of particle-hole bonds) in the model, on one hand, and in $Ag_2Se$ and in $AgI$ [17], for example, on the other. Concerning these similarities, it may be remarked that, as in $\lambda_E$ and $\Lambda_E$, substances are often characterized by low-dimensional conductivity. That is, it has been reported that the sample geometry often compels free ions to move within a few layers only, or else within quasi-one dimensional channels.

Further practical interest on the DLG is a consequence of the fact that appropriate versions of it have been found useful to represent several phenomena. These range from dynamics of macromolecules such as DNA fragments undergoing field-inversion gel-electrophoresis, to staging in layered compounds, and growth of surfaces by hexagonal packing of discs [14]. On the other hand, allowing for two planes, as in $\Lambda_E$, not only reveals novel phenomena but also has some computational interest. This is due to the fact that a large amount of computer time is required to obtain reliable quantitative results by the MC method concerning the phase transitions in $\lambda_0$. The reason is that, besides critical slowing down, a system exhibits slow relaxation toward ordered steady states if the only mechanism is NN exchanges, i.e., diffusion of particles, which conserves density. One may perhaps obtain in this case statistically good enough stationary mean values for short-range order parameters, for instance, but (e.g.) the structure function stabilizes very rarely if at all within actual computer runs. However, $\Lambda_E$ incorporates an additional degree of freedom, i.e., the particles can hop to other lattice and, consequently, (slow) diffusion within the plane is not the only relaxational mechanism, which helps to obtain good data [18].

Some of the properties of the DLG are reviewed below, mainly as obtained from the MC study of $\Lambda_\infty$. A comment on the differences of behaviour between $\Lambda_\infty$ and $\lambda_\infty$ is made when necessary. I refer to the original papers [2]-[8], and to a recent review in Ref. [14] for further details.

## 2 Phase Transitions

$\lambda_E$ is observed to behave for any $E \neq 0$ essentially differently from the equilibrium case $\lambda_0$. Some of the differences are illustrated in *figure 2*. The upper curve represents the transition temperature in $\lambda_0$ as a function of particle density $\rho$; below is the corresponding result for $\lambda_\infty$. The observed critical temperature is $t_\infty = 1.38 \pm 0.01$ for the infinite lattice in units of $t_0$, the equilibrium Onsager critical temperature. The shaded region corresponds to metastable states, i.e., the phase transition is discontinuous (at least) for $\rho \geq 0.2$. The segregation is into *liquid* (particle-rich) and *gas* (particle-poor) phases. Unlike for $\lambda_0$, however, the gas is anisotropic, namely, microscopic clusters occur which are lengthened along $\hat{x}$ both above and below the transition temperature. Moreover, the liquid phase is striped defining a sharp interface parallel to $\hat{x}$ all along the system. The fluctuations or width of the interface diverge as one approaches $t_\infty$.

*Figure 2:* Phase diagrams in two dimensions.

The origin for the differences between $\lambda_0$ and $\lambda_\infty$ is, formally, that dynamics induces (for any $E \neq 0$) a preferential hopping in the field direction that impedes detailed balance except locally. In fact, no *well-defined*, e.g., short-range Hamiltonian which represents the energy exists that allows one to write a canonical formula for the steady state. This is reflected in the existence of a net steady (dissipative) current of matter throughout the system (for periodic boundary conditions) if $E \neq 0$. The fact that $t_\infty \gg t_0$ is a nonequilibrium anisotropic feature, which is to be associated to the action of the field on correlations and on the existence of the interface [8].

*Figure 3:* The two phase transitions in $\Lambda_\infty$ for varying $\rho$.

$\Lambda_\infty$ exhibits some novel behaviour as compared to $\lambda$. For $\rho = \frac{1}{2}$, a continuous phase transition occurs at $T_\infty = 1.30 \pm 0.01$ which is similar to the one in $\lambda_\infty$. However, a liquid stripe forms now at each plane *one on top of the other*. The observation $t_\infty > T_\infty$ is consistent with the fact that dynamics in $\lambda_\infty$ combines the thermal, random process along $\hat{\mathbf{y}}$ with the action of the field, while extra randomness (along $\hat{\mathbf{z}}$) adds to this in $\Lambda_\infty$. It makes $\Lambda_\infty$, say, less anisotropic than $\lambda_\infty$. This argument also implies that no new symmetries are introduced by dynamics in $\Lambda_\infty$ (as compared to those in $\lambda_\infty$), which suggests one to expect the same critical behaviour for both systems. It has indeed been confirmed by MC simulations (and can be proved for $E = 0$ [18]).

*Figure 4:* The correlation between planes for $\Lambda_\infty$.

As $T$ is further decreased, $\Lambda_\infty$ exhibits a new phase transition at $T_\infty^* < T_\infty$. The striped liquid phase coagulates in one of the planes only for any $T < T_\infty^*$. $T$wo abrupt changes of slope in the curve for the current as a function of temperature that are evident in *figure 3* reveal the existence of the two phase transitions in $\Lambda_\infty$; *figure 4* for the two-site correlation function between planes (for the only possible value of distance, $r = 1$) as a function of temperature provides further evidence. The latter indicates $T_\infty \simeq 1.3$ and $T_\infty^* \simeq 0.95$ for $\rho = \frac{1}{2}$ ($T$ is alwys in units of $t_0$).

*Figure 5:* Phase diagrams for $\Lambda_\infty$ $(- - -)$ and $\lambda_0$ (——).

Another fact in *figure 3* is that the phase transition in $T_\infty^*(\rho)$ is discontinuous for any $\rho$ while the one at $T_\infty(\rho)$ is continuous for $\rho = \frac{1}{2}$ but discontinuous for $\rho \leq 0.35$. The resulting phase diagram is in *figure 5.* The low-temperature phase transition at $T_\infty^*$ for $\rho = \frac{1}{2}$ happens to become continuous as one decreases sufficiently the value of the field (e.g., for $E = 1$). No actual interface occurs in this case given that one plane holds gas and the other liquid only. Interesting enough, one measures then the equilibrium critical exponent $\beta = \frac{1}{8}$ in the presence of a steady current of matter throughout the system. The phase diagrams of $\Lambda_\infty$ and $\lambda_0$ are compared in *figure 5.* The error bars here represent limits of metastability.

Another important issue is the critical behaviour in $T_\infty$ (for $\rho = \frac{1}{2}$). Unlike in $T_E^*$ for $E = 1$ and $\rho = \frac{1}{2}$, where $\beta = \frac{1}{8}$, one measures $\beta \simeq 0.3$ (actually, $\beta = 0.27 \pm 0.02$) both in $T_\infty$ for $\Lambda_\infty$ and in $t_\infty$ for $\lambda_\infty$ ($\rho = \frac{1}{2}$ in both cases).

*Figure 6:* The short-range order parameter for $\Lambda_\infty$.

The fact that $\beta \neq \frac{1}{2}$ is indicated in *figure 6.* This represents the temperature variation of the short-range order parameter defined [19] as

$$\sigma = \left\langle \frac{n_{++}n_{--}}{n_{+-}^2} \right\rangle$$

where $n_{++}$, $n_{--}$, and $n_{+-}$ stand, respectively, for the density of particle-particle, hole-hole and particle-hole bonds, and $\langle \cdots \rangle$ is the stationary average. One has

$$\sigma \sim \epsilon^{1-\alpha} + const.\epsilon^{2\beta}$$

as the critical point is approached, i.e., $\epsilon \to 0$, so that the situation in *figure 6* discards the possibility of having classical critical behaviour.

The fact that $\frac{1}{8} < \beta < \frac{1}{2}$ is further demonstrated in *figure 7* for the temperature variation of the order parameter [14] for $\Lambda_\infty$. Two familiar methods to estimate $\beta$ are illustrated in *figure 7*; any reasonable manipulation of data indicates $\beta \simeq 0.3$. The observation that $\beta$ differs from the equilibrium value should probably be associated to the presence of a peculiar interface in both $\Lambda_\infty$ and $\lambda_\infty$.

*Figure 7:* Study of order-parameter critical-exponent for $\Lambda_\infty$.

Let us mention again on the possible relevance of the DLG to understanding some properties of superionic conductors. These materials are characterized by large ionic conductivities at low temperature which are imputed to mobility *in a liquid-like fashion* of one type of ions (e.g., $Ag^+$) through a solid lattice set up by another type of ions (e.g., $I^-$). Qualitative differences have been reported between different materials concerning the temperature variation of the conductivity in the region in which the changeover occurs. This is illustrated in *figure 8* which collects a series of experimental results (the horizontal axis here corresponds to $T_m/T$ where $T_m$ is the associated melting temperature).

*Figure 8:* Temperature dependence of conductivity [20].

It has been remarked [20] that one may classify all these cases in only three distinct classes. Then it is interesting the observation [10] that these classes may correspond to three basic types of behaviour in the model. That is, one observes discontinuities in *figure 8* reminiscent of the phase transitions of first order reported above for small $\rho$ (i.e., when many empty sites are available for ionic diffusion), and one observes a rather continuous behaviour, as in the model second-order phase transition for $\rho \approx \frac{1}{2}$ (near half occupation of available sites). It is also observed in the semi-logarithmic plot of *figure 8* that conductivity varies linearly in some cases. This corresponds to the absence of a phase transition, as in some one-dimensional versions of the DLG in which a continuous changeover from low to high conductivity occurs for some values of the parameters. *Figure 9* illustrates this (different curves here correspond to $\rho$ increasing to $\rho = \frac{1}{2}$ from top to bottom).

*Figure 9:* Particle current for the one-dimensional DLG.

# 3 Correlations

The two-site correlation function, $G(r)$, confirms the existence of ordering phenomena (e.g., *figure 4*), and reflects further interesting properties of the DLG. In particular, it evidences that the density of the nonequilibrium gas phase, $\rho_{\infty}(T)$, differs from the corresponding one in equilibrium, $\rho_0(T)$. This is illustrated in *figure 10* for $T = 0.8 < T_{\infty}^{*}$; here, the values of $G(r)$ for large $r$ are $\rho_{\infty}^2 = (0.959)^2$ and $\rho_0^2 = (0.955)^2$, respectively ($\bigcirc$ and $*$ stand for $\hat{\mathsf{x}}$ and $\hat{\mathsf{y}}$ nonequilibrium correlations, respectively).

*Figure 10:* Spatial variation of two-site correlations for $\rho = \frac{1}{2}$.

Most intriguing is the question about correlation lengths. One might argue [11] that two independent lengths are needed to describe the anisotropic clusters which characterize the DLG. Indeed, it is suggested by configurations such as the ones presented in *figure 11.* Let us assume this is correct, and denote the two lengths by $\xi_{\hat{\mathsf{x}}}$ and $\xi_{\hat{\mathsf{y}}}$, respectively. They would correspond to the mean displacement along $\hat{\mathsf{x}}$ and $\hat{\mathsf{y}}$, respectively, of a hole (particle) within the liquid (gas) phase during time interval $\Delta t$. Assuming the two processes are independent, one should probably expect that $\xi_{\hat{\mathsf{x}}} \sim \Delta t$, as for a pure driving process, and $\xi_{\hat{\mathsf{y}}}^2 \sim \Delta t$, as for a pure random walk. Therefore, the expectation is that one should always expect that $\xi_{\hat{\mathsf{x}}} \sim \xi_{\hat{\mathsf{y}}}^2$ against the hypothesis.

*Figure 11:* Typical configurations at high $T$ for large $E$ (two on the left, [12]), and low $T$ for small $E$ (right, [21]).

The simplest and most accurate way to estimate these lengths is probably to compute $G(r)$ for the high-$T$ gas phase. With this aim, one should have in mind the fact that spatial correlations in this system (with conserved density) exhibit slow, power-law decay with distance at high $T$ [22, 12]. This means that one may expect

$$G(x,y) = \frac{ax^2 - by^2}{(x^2+y^2)^2}$$

to be a good description for $r = (x, y)$ large enough. This is in contrast with the exponential relaxation with $r$ that characterizes the equilibrium systems except at criticality. Then $a$ and $b$ are a measure of the two lengths, respectively. More explicitly, one may use the phenomenological formulae

$$G(x) \sim \frac{1}{1+\left(\frac{x}{\xi_{\hat{\mathsf{x}}}}\right)^2}, \quad G(y) \sim \frac{1}{1+\left(\frac{y}{\xi_{\hat{\mathsf{y}}}}\right)^2}.$$

Such study has confirmed that the lengths $\xi_{\hat{\mathsf{x}}}$ and $\xi_{\hat{\mathsf{y}}}$ are indeed well defined [12]. Furthermore, the expectation above that $\xi_{\hat{\mathsf{x}}} \sim \xi_{\hat{\mathsf{y}}}^2$ is nicely confirmed within rather general conditions, as illustrated in *figure 12.*

The above indicates that only one length is independent and should therefore matter for critical behaviour, e.g.,

$$\xi \sim \sqrt{\xi_{\hat{\mathsf{x}}}\xi_{\hat{\mathsf{y}}}} \sim \xi_{\hat{\mathsf{y}}}^{\frac{3}{2}}.$$

It seems that one has here self-affinity (as in various interface phenomena). That is, the clusters shape (but not its size) is given (e.g.) for each $E$, and the relation between the two lengths is maintained as $T$ is varied [13]. Would this be the case, $\xi_{\hat{\mathsf{x}}}$ would not participate in critical properties which would instead be dominated by $\xi_{\hat{\mathsf{y}}}^{\zeta}$, with $\zeta \approx \frac{3}{2}$. This length would then be mediated by the existence of the peculiar, linear interface along $\hat{\mathsf{x}}$.

*Figure 12:* The relation between two phenomenological lengths.

This explains also the old observation [5] that a unique length suffices to characterize the scaling behaviour of the DLG. Under this hypothesis, one is led to expect [5, 13] that the order parameter of the DLG satisfies

$$m \sim \begin{cases} L^{-\beta/\nu}\left(B\,x^{\beta} - B_s\,x^{\beta-\nu}\right), & T < T_C \\ B_s'\,x^{-\omega\nu}, & T > T_C\ . \end{cases}$$

Here, $\epsilon = \left|(T - T_C)\,T_C^{-1}\right|$, $T_C$ represents either $t_\infty$ or $T_\infty$, and $x = \epsilon L^{1/\nu}$ for $L \times L$ and $2 \times L \times L$ lattices; cf. Ref.[13] for a generalization of this to rectangular lattices. This behaviour has recently been (re)confirmed for both two- and quasi-two-dimensional lattices with $\beta = 0.27$, $\nu = 0.7$; the parameter $\omega$ is model dependent, as expected, and it was estimated to be $\omega = 0.2$ and 0.3 for $\lambda_\infty$ and $\Lambda_\infty$, respectively. The same values for $\beta$ and $\nu$ have been reported for several other nonequilibrium anisotropic systems in which a peculiar interface occurs [13].

The prediction that the DLG has classical behaviour, e.g., $\beta = \frac{1}{2}$, is not borne out [13]. Furthermore, it has repeatedly been demonstrated [7, 12, 23] that the DLG does not behave isotropically if one fixes the ratio $L_x^{\mu} L_y^{-1}$, where $\mu = \nu_x/\nu_y$. The latter two predictions come from a field-theoretic proposal in which two lengths are involved which diverge independently with $\nu_x$ and $\nu_y$, respectively, at $T_C$ [11]. It seems that a continuous version of the DLG should not consider $E$ as a relevant parameter but rather focus on the influence of the interface.

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