J. E. Purkinje University in Ústí nad Labem
Faculty of Science
Department of Physics

Abstract of the Doctoral Thesis

ON PERCOLATION IN MOLECULAR SIMULATIONS ON FINITE SYSTEMS

by

Mgr. Jiří Škvor

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Univerzita J. E. Purkyně v Ústí nad Labem
Přírodovědecká fakulta
Katedra fyziky

Autoreferát disertační práce

O PERKOLACI Z MOLEKULÁRNÍCH SIMULACÍ KONEČNÝCH SYSTÉMŮ

Mgr. Jiří Škvor

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Doktorand: Mgr. Jiří Škvor

Školitel: prof. RNDr. Ivo Nezbeda, DrSc.
Katedra chemie, PřF, UJEP
České mládeže 8, 400 96 Ústí nad Labem;
Termodynamická laboratoř E. Hály, ÚChP AV ČR
Rozvojová 2/135, 165 02 Praha 6 – Suchdol

Oponenti: doc. RNDr. Jiří Kolafa, CSc.
Ústav fyzikální chemie, VŠChT
Technická 5, 166 28 Praha 6 – Dejvice

Ing. Jan Hrubý, CSc.
Ústav termomechaniky AV ČR
Dolejškova 1402/5, 182 00 Praha 8

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Předseda OR: prof. RNDr. Rudolf Hrach, DrSc.
Katedra fyziky, PřF, UJEP
České mládeže 8, 400 96 Ústí nad Labem

Goals of the thesis

The problems addressed in the thesis are a part of a long-term research conducted in E. Hala Laboratory of Thermodynamics in the Institute of Chemical Process Fundamentals of the Academy of Sciences of the Czech Republic.

A general goal is to examine the effect of various definitions of a cluster and a percolating cluster on the percolation threshold and then to examine validity of the concept of universality. Particularly, using extensive Monte Carlo simulations,

1. to develop and implement an efficient numerical algorithm for the percolation threshold determination;

2. to discriminate between various definitions of the percolating cluster and find out general consequences of each of them;

3. to test the hypothesis of universality of the chosen percolation threshold parameters;

4. to locate the percolation line for different fluid models and different definitions of cluster.

Introduction

Percolation theory [1, 2] is, in general, a widely used method to explain and model quite a number of phenomena that are of scientific and industrial importance. It is associated with the occurrence of the so called percolating cluster and the list of applications is quite large not only in natural science but also in social science. The concept of percolation is used to characterize the effect of connectivity of microscopic elements (such as molecules, pores, conducting elements, people, etc.) in disordered systems (such as fluid, porous media, composite film, and society) on their macroscopic properties (such as condensation, flow of oil, flow of electric current, and information flow).

Dealing with fluids, then the most commonly accepted approach operates with molecules as the basic microscopic elements. From the macroscopic point of view, the fluid phase is homogeneous because its density is, in average, uniform throughout the system. However, on the microscopic level its particles (molecules) may form localized morphological structures called clusters. A cluster is, according to its local definition, a collection of particles such that there is a pass (via bonds) between a pair of particles and the entire problem is then reduced to the problem of an appropriate definition of bonds. As for bonds themselves, there are two basic concepts [3] to define an existence of a bond between a pair of particles, one based on their proximity in the configurational space (configurational clusters), and the other based on their proximity in the phase space (Hill [4] clusters).

The primary object of the percolation theory is the probability of occurrence of a percolating cluster (called also an infinite cluster or wrapping, spanning or crossing cluster), i.e., the cluster that spans the entire system. Dealing with fluids, this probability, R, depends on density, ρ, and the size, L, of the system at hand. The occurrence of a percolating cluster identifies a percolation transition. In the limit of an infinite fluid system, the percolating cluster occurs above a sharply defined density and does not occur below it. The goal is to find/determine this density, i.e. the percolation threshold density from results for finite systems. With the exception of special types of 2D and 3D lattice systems, it has not been determined theoretically (analytically).

The determination of the percolation threshold from results obtained for finite size systems is not unique and a number of various criteria have been

proposed and used. Although some authors claim that scaling corrections due to finite size effects are not essential [5], more accurate methods determining the percolation threshold density and other parameters are based on a finite-size scaling analysis. Extending results obtained originally for lattice systems to fluids it is assumed that, for large system size L, the function R exhibits near the percolation threshold the universal behavior as a function of the scaling variable $(\rho - \rho_c)\ L^{1/\nu}$ with ν, called the correlation length exponent, being a universal constant for the given dimensionality regardless of the thermodynamic conditions and the nature of systems considered [1, 6].

To verify different methods determining the percolation threshold parameters and draw some general conclusions, the molecular simulations are used as the only currently available tool. It is however necessary to bear in mind that (i) simulations operate only with finite systems and (ii) studies of the percolation transition on fluids are very time consuming in comparison with lattice systems. Furthermore, a number of different definitions of the percolating cluster and clusters themselves have been put forward and practically no generally accepted results are therefore available.

Results and discussion

In general, there are two main concepts to define a percolating cluster in a finite system for bulk fluids simulated in a (cubic) box with periodic boundary conditions identified as wrapping (having an infinite extent within the framework of the periodically repeating cells) and crossing (determined by the spatial extension only) clusters. Thus as a first step, different crossing and wrapping probabilities, R_{cr} and R_w, were examined as a function of the fluid density ρ for the configurational clusters in the square-well (SW) fluid with the attraction range parameter $\lambda = 1.25$ at three supercritical temperatures for a set of seven different system sizes characterized by the number of particles N, see Fig. 1 and paper [P1] for further details. Looking at R_w (right), two striking features are immediately discernible: (i) regardless of the system size, all the curves belonging to the same wrapping rule intersect at one point which is supposed to be the percolation threshold density ρ_c, and (ii) there is a unique ρ_c independent of the wrapping rule. In other words, it is observed that R_w becomes independent of the system size at a certain density, ρ_c.

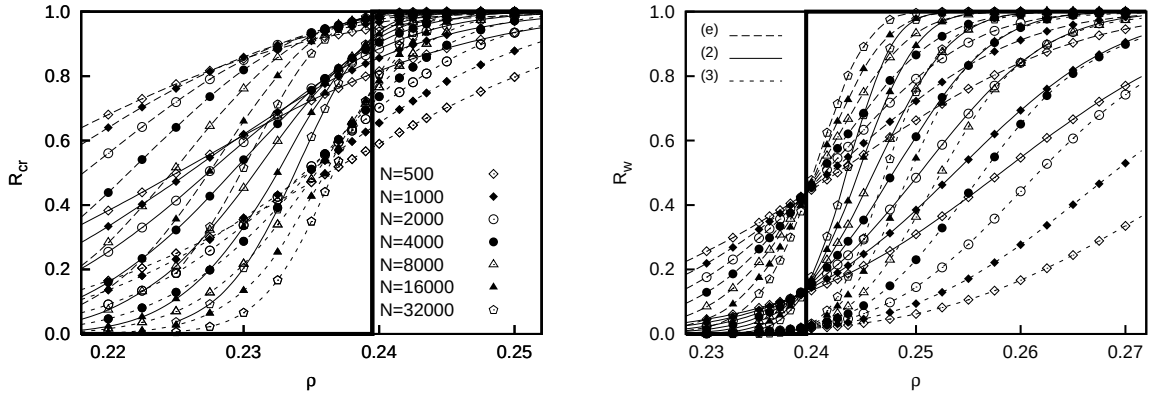

Figure 1: Crossing and wrapping probabilities, R_{cr} (left) and R_w (right), for the cluster which crosses/wraps system (the square-well fluid with parameter $\lambda = 1.25$ at supercritical temperature $T = 1.2$) at least in one$^{(e)}$, two$^{(2)}$ and three$^{(3)}$ dimensions, respectively, as a function of fluid density ρ. Different symbols correspond to different system sizes, number of particles N. The thick solid line represents the probability R for each spanning rule in the limit of an infinite system. The estimate of the percolation threshold fluid density is $\rho_c = 0.2395$.

Contrary to the wrapping probability, there is no such a common crossing point for R_{cr} (left) and thus it may be used for only a rough determination

of ρ_c or, to be specific, for a determination of the lower limit of ρ_c. It is also possible to estimate, intuitively, the percolation threshold via the inflection point of R_w. The inflection points of R_{cr} approach the percolation threshold with increasing L from the lower density side. The crossing probability $R_{cr}^{(e)}$, widely used in simulation studies, has the inflection point considerably below ρ_c even in the largest system studied.

Since three temperatures were considered, it was also possible to draw some conclusions on universality of the percolation exponent ν and the percolation probability $R_{w,c}$. Although this was not the goal of the research at this stage and we were aware of larger error bars, we concluded that the universality was satisfied [P1]. Furthermore, there was an open question, whether the results obtained for just one system, the SW fluid, might hold true also for other systems. We therefore continued in the research along the same line and considered a qualitatively different model, a primitive model of water, see paper [P2]. The obtained results confirmed the validity of the previously proposed method of determination of the percolation threshold in fluids and its characteristics, and further supported the hypothesis of universality, and efficiency and accuracy of the used method.

To summarize the results obtained till this point, it turns out that the most convenient way for the determination of ρ_c seems to be the probability for the cluster which wraps the system in any dimension, $R_w^{(e)}$. However, we have also been aware of two facts: (i) validity of the hypothesis of the universality was at the edge of accuracy of the results, and (ii) we used only one type of clusters, the configurational clusters. There was also another feature of the percolation line which should be brought in consideration: where does it end with lowering temperatures? Theoretical arguments suggest that it should terminate at the critical point but the simulation results have not indicated any such tendency. The same applies also to various literature data with one exception: When the Hill definition of the cluster is used, then the percolation line seems to go towards the critical point [7].

A further step of the project has aimed therefore at addressing all these issues. It means, (i) to consider both the configurational as well as Hill clusters, (ii) to consider a wider range of temperatures, (ii) to consider more fluid models and also a lattice model for comparison and verification of the generated results, and (iii) to pay great care to errors of simulations and their evaluation to be able to draw unambiguous conclusions.

The percolation of the configurational as well as Hill clusters in three different model fluids over a range of supercritical temperatures have been thus evaluated [P3]. In addition to the SW and primitive water fluids, the realistic continuous Lennard-Jones (LJ) model has also been included. To summarize, 35 differently defined systems were considered and three different system sizes have been used. Following the results obtained previously, we considered only wrapping clusters and the same behavior as before, namely, that all the curves for different system sizes intersect in one point which corresponds to the percolation threshold for the given system, has been observed. For a corresponding graph for one particular system see Fig. 2 (left).

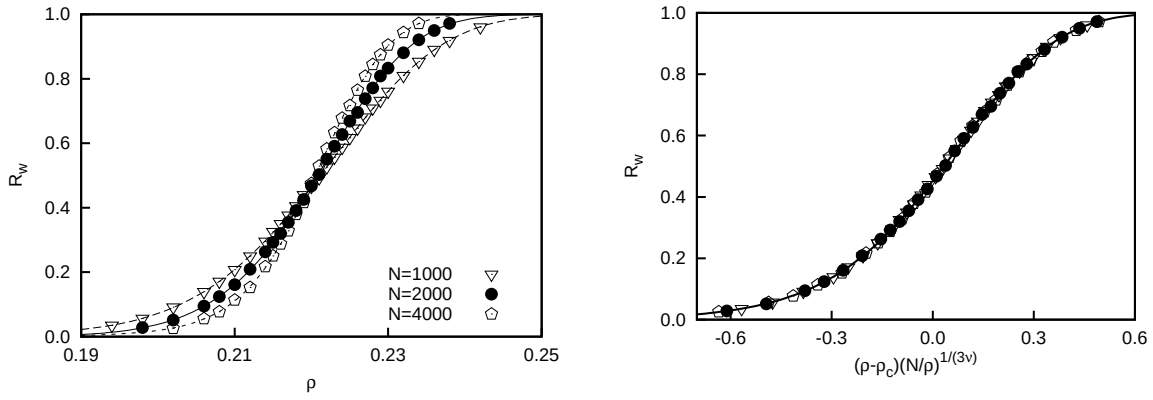

Figure 2: The wrapping probability $R_w^{(e)}$ as a function of fluid density (left) and as a function of the scaling variable (right) for the EPM5-4 model of water and configurational clusters at temperature $T = 0.25$ and different number of particles N.

Similarly, it has also been confirmed that $R_w^{(e)}$ exhibits the universal behavior as a function of the scaling variable even for relative small system sizes, see Fig. 2 (right). A nearly perfect collapse of all three curves into one may be considered as a convincing proof that the used numerical method (see paper [P3] for further details) for the determination of ρ_c, percolation exponent ν, and the critical wrapping probability $R_{w,c}^{(e)}$, is sufficiently accurate. However, the results for ν and $R_{w,c}^{(e)}$ (for LJ fluid listed in Table 1) do not seem to support the idea that these parameters are universal for a given dimensionality. The results show their rather a strong dependence on (i) the interparticle interaction, (ii) the temperature, and also (iii) the particular definition of cluster.

Table 1: Results for the percolation exponent ν and the wrapping probability at the percolation threshold $R_{w,c}^{(e)}$ for the Lennard-Jones fluid and two different definitions of cluster. Numbers in parenthesis denote the standard error of the mean of the last digits.

	configurational clusters		*Hill clusters*	
T	ν	$R_{w,c}^{(e)}$	ν	$R_{w,c}^{(e)}$
1.35	1.0943(23)	0.27327(62)	1.1046(26)	0.35266(66)
1.40	1.0759(15)	0.31902(44)	0.9799(12)	0.40706(36)
1.60	1.01078(66)	0.39003(19)	0.90414(43)	0.44393(13)
2.00	0.96331(40)	0.42299(12)	0.87972(51)	0.45109(15)
2.50	0.94563(33)	0.432922(99)	0.84206(98)	0.44799(34)

To further support the obtained results and check correctness of the used numerical method, we have applied our method also to a lattice system, specifically to the site percolation on simple cubic lattice, for which the data are known from literature. Using our method for the percolation threshold occupation probability p_c and the percolation exponent ν we get, respectively, $p_c = 0.3116004(35)$ and $\nu = 0.87555(49)$, which is in agreement with literature values $p_c = 0.3116080(4)$ [8], $p_c = 0.3116081(11)$ [9], and $p_c = 0.3115(3)$ [10], and the value $\nu = 0.877(12)$ [10]. From this comparison we dare to conclude that the used methodology is sufficiently accurate and efficient.

After having accurately determined the percolation threshold density ρ_c for three different model fluids over a range of supercritical temperatures and two different definitions of cluster, its temperature dependence may finally be discussed. The corresponding percolation line for the Lennard-Jones fluid is shown in Fig. 3. It is generally assumed (claimed) that the line of percolation originates from the critical point but without a convincing support and with a number of contradicting results.

For all three models we get completely different lines for the configurational and Hill clusters, and in the case of the LJ and SW fluids none of them seems to be going towards the critical point. This is clear without any doubt for the percolation line given by the configurational clusters. As for the line given by the Hill clusters, it gets very flat with lowering temperature. With respect to generally large fluctuations, and hence large errors, in vicinity of the critical point, a possibility that it eventually may approach the critical point cannot be ruled out. In fact, Campi et al. [7]

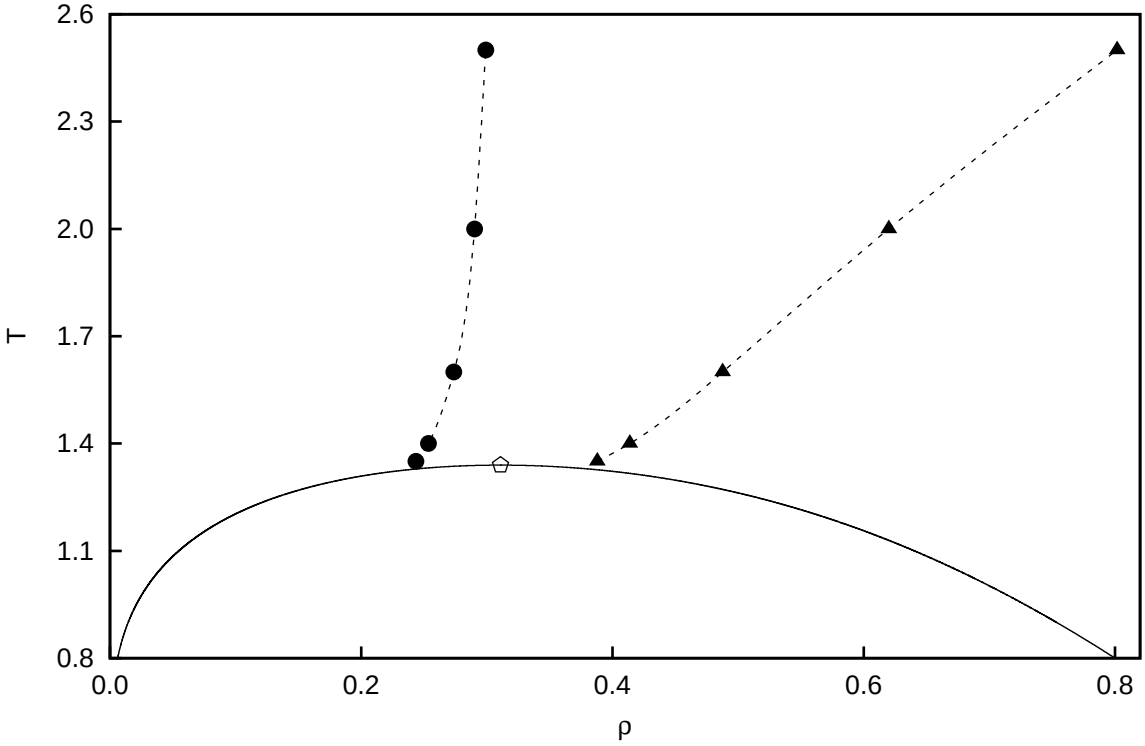

Figure 3: Percolation line for the Lennard-Jones fluid represented by full symbols (dashed lines serve as a guide for eye), where circles and triangles correspond to configurational and Hill clusters, respectively. The vapor-liquid coexistence line (thick solid line) including critical point (open pentagon) is given by the Kolafa-Nezbeda equation of state [11].

also determined this line for the LJ fluid and our results coincide with theirs away from the critical point. On the basis of their results they claim that the percolation line ends in the critical point within the simulation errors in this region. Nonetheless, although with respect to the discussed features of the percolation lines, the one corresponding to the Hill clusters could/should be given preference and be considered "more physical", it is however hard to draw any definite conclusion from the available results.

Conclusions

The thesis is based on two original papers already published in international journals [P1,P2] and one submitted for publication [P3], and on presentations at international conferences. The main goal has been to develop method for the percolation threshold determination and consequently: (i) to examine validity of the concept of universality, and (ii) to locate the percolation line with respect to different definitions of cluster. Extensive Monte Carlo simulations have been used to obtain presented results.

As a first step we have examined the effect of various definitions of a percolating cluster in a finite system on the percolation threshold determination. Comparing the crossing and wrapping probabilities, R_{cr} and R_w, respectively, we have found that the former ones are not convenient for the localization of the percolation threshold in three-dimensional continuous systems because of large finite size corrections to scaling. The wrapping rule, especially the one identifying a percolating cluster as wrapping in any dimension, $R_w^{(e)}$, (whose finite-size corrections at the percolation threshold have been found to be negligible), is recommended to be used. The crossing point of the wrapping probabilities $R_w^{(e)}(\rho)$ for different (sufficiently) large system sizes provides a very good first estimate of ρ_c. To obtain its more accurate estimate and consequently the percolation exponent ν, the numerical procedure that we have specified in [P3] and that is based on a finite-size scaling analysis may be conveniently used.

Secondly we have tested the hypothesis of universality, i.e., that the correlation length exponent ν and the wrapping probability at the percolation threshold $R_{w,c}^{(e)}$ are universal constants for the given dimensionality independent of the particular process of percolation. However, all the obtained results show their strong dependence on the temperature, the nature of the system considered, and the employed definition of the cluster. Thus, the percolation threshold in fluids (i.e., continuum correlated systems) can not be characterized by universal exponents of random percolation and the entire concept of universality does not seem to be supported.

Finally, different percolation lines have been obtained for different supercritical model fluids. However, the question which of them, if any, has a physical relevance and whether they originate from the critical point or not remains open and should be addressed in the future research.

Shrnutí

Předložená dizertační práce je založena na třech původních článcích (dva z nich již byly publikovány a třetí byl zaslán k opublikování a je v recenzním řízení) a dvou konferenčních příspěvcích. Jejím hlavním cílem je vyvinout spolehlivou metodu pro určení perkolačního prahu ve spojitých systémech, na čež navazuje: (i) ověření platnosti konceptu univerzality a (ii) nalezení perkolační křivky s ohledem na různá kritéria vymezující klastr. Všechny prezentované závěry jsou založeny na výsledcích rozsáhlých (Monte Carlo) počítačových simulací.

V prvé řadě jsme vyšetřovali vliv různých způsobů identifikace perkolujícího klastru v konečném systému na určení perkolačního prahu. Srovnávali jsme dva základní způsoby, potažmo dvě různě definované pravděpodobnosti výskytu perkolujícího klastru R, a to konkrétně tzv. „crossing“, R_{cr}, a „wrapping“, R_w, klastru. První z ních se ukázala být nevhodnou pro určení perkolačního prahu v důsledku její silné závislosti na velikosti systému. Naproti tomu druhá z nich, a to konkrétně především $R_w^{(e)}$ (pravděpodobnost, že v systému existuje klastr, který v rámci periodických okrajových podmínek zahrnuje nejméně jeden periodický obraz libovolné své částice) je v perkolačním prahu prakticky nezávislá na velikosti systému. To znamená, že perkolační práh ρ_c (tj. hustotu ρ v perkolačním prahu) lze odhadnout z průsečíku křivek $R_w^{(e)}(\rho)$ získaných pro nejméně dva různě (dostatečně) velké systémy. Numerickou technikou, která je založena na v teorii popsaných škálovacích vlastnostech funkce R, lze získat přesnější odhad ρ_c spolu s odhadem perkolačnícho exponentu ν. V článku [P3] specifikujeme algoritmus, který považujeme za doposud nejvhodnější.

V dalším kroku jsme testovali hypotézu univerzality – konkrétně tvrzení, že perkolační exponent ν a parametr $R_{w,c}^{(e)}$ (pravděpodobnost $R_w^{(e)}$ v perkolačním prahu) jsou konstanty charakteristické pro danou dimenzi systému bez ohledu na jiné vlastnosti systému nebo povaze procesu perkolace. Naše výsledky tuto hypotézu nepotvrzují. Naopak ukazují, že sledované parametry jsou závislé na teplotě systému, charakteru systému (interakční potenciál) a také na vymezení klastru. Tyto parametry, které jsou dostatečně přesně určeny pro mřížkové systémy, tedy nemohou z principu charakterizovat libovolné spojité systémy – tekutiny.

V konečném výsledku jsme ve studovaných nadkritických tekutinách získali

různé tzv. perkolační křivky pro dvě různá vymezení klastru. Ote-vřenou otázkou však zůstává, jaký je jejich fyzikální význam (je-li nějaký) a speciálně pak otázka, zda vycházejí z kritického bodu. Toto by mělo být předmětem dalšího výzkumu.

Papers included in the thesis

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