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M. H. Müser^a

^a Institut für Physik, Johannes Gutenberg-Universität, Mainz, Federal Republic of Germany

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THE PATH-INTEGRAL MONTE CARLO OF RIGID LINEAR MOLECULES IN THREE DIMENSIONS

M. H. MÜSER

*Institut für Physik, Johannes Gutenberg-Universität,
KoMa 331, D-55099 Mainz, Federal Republic of Germany*

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The applicability of the path-integral Monte Carlo (PIMC) method to the description of quantized orientational degrees of freedom of rigid linear molecules in three dimensions is discussed. Special attention is paid to the sign problem. It is shown that the sign problem is severe for anti-symmetric rotational states at low temperatures, while it is completely absent in the case of symmetric and non-symmetric rotational states. The presented PIMC method is applied to a model potential. Using higher order correction terms according to the Takahashi Imada algorithm, even tunneling anomalies in the specific heat could be computed to very high numerical precision.

KEY WORDS: Path-integral Monte Carlo simulation, two-dimensional rotation, correction potential, sign problem, tunneling.

1 INTRODUCTION

The quantum mechanical description of orientational motion becomes important at low temperatures where the intra-molecular bond length of a huge class of molecules are frozen in. A classical description of the orientational degrees of freedom is not appropriate for systems such as H_2 -clusters [1] and H_2 -solids or D_2 -solids [2] and even adsorbed layers of N_2 on graphite show a 10% lowering of the transition temperature T_c where an orientationally disordered state transforms on cooling into a state with long range orientational order [3]. Still more interesting are the low temperature anomalies in the specific heat of orientational glasses [4]. These anomalies are often attributed to the tunneling of orientational degrees of freedom between different (meta-) stable states [5].

Tunneling of isolated molecular impurities in solids is well understood [6,7]. Especially if the average local potential has a well defined symmetry, approximative methods such as numerical solutions of Langevin type equations [8] and memory function formalisms [9] are appropriate methods to describe qualitatively the temperature dependence of rotational tunneling.

However, a detailed microscopic understanding of tunneling phenomena in strongly disordered media does not yet exist beyond mean field approximations. There is a need to fill this gap, *e.g.* by computer simulation. Further, it is desirable to determine the amount of anharmonicity which arises from quantum fluctuations because they strongly influence the thermo-mechanical properties of solids.

Path-integral Monte Carlo (PIMC) techniques for translational degrees of freedom have become standard tools for studying finite-temperature many-body systems, for a recent review see Ref. [10]. This is not the case for orientational degrees of freedom. The reason is the so-called sign problem. Matrix elements of the type $\langle \Phi | \exp(-\tau H) | \Psi \rangle$ can become negative and quantities of interest are sums of negative and positive contributions which may nearly cancel out [11]. It is important to mention that the sign problem depends on the representation.

If the orientational degrees of freedom at Trotter slice i are represented by the angles (ϑ_i, φ_i) and by the degree l of a Legendre polynomial, then a PIMC simulation suffers from an extremely severe sign problem for all temperatures [12].

The sign problem of orientational motion may be avoided by confining the degrees of the Legendre polynomials to even values [2]. The PIMC simulation of molecules such as CO or *ortho*-H₂, however, remains problematic.

Another possibility to avoid the sign problem is to use Cartesian coordinates in order to represent the atoms within a diatomic molecule and to integrate out the stiff bond [1]. But this method requires huge Trotter numbers, and for practical purposes it can not be applied at very low temperatures where tunneling phenomena occur. Furthermore, the sign problem remains severely for the simulation of *ortho*-H₂, *para*-D₂ and related molecules.

The density matrix can be integrated out in a reduced Hilbert space of dimension d_H [13,14] in order to avoid the sign problem. Treating N (directly) interacting molecules would blow up the dimension of the Hilbert space according to d_H^N so that this method does not apply to many-particle systems.

Clearly, it is of interest to have a tool which facilitates the determination of quantum mechanical effects arising from orientational degrees of freedom which avoids the sign problem without the use of huge Trotter numbers and without the use of giant Hilbert space dimensions. In the following, we present a general simulation scheme for including orientational degrees of freedom into the standard PIMC-approach. The algorithm does not suffer from the sign problem in the even l case and in the mixed l case. In the odd l case the sign problem is only severe at low temperatures.

The details of the method are given in section II. Higher order correction terms to the density matrix based on the Takahashi-Imada-algorithm [15,16] are given as well. In section III, the method is applied to a positionally fixed rotator in a static cubic potential. The simulation results are compared to “exact” results. In the last section, we summarize, and the applicability of the presented method to the simulation of many-rotator systems is discussed.

2 PIMC OF ORIENTATIONAL DEGREES OF FREEDOM

2.1 General Remarks

We consider first the partition function $Z(\beta) = \text{Tr}\{\exp(-\beta\hat{H})\}$ which can be expressed as

$$Z(\beta) = \lim_{P \rightarrow \infty} \text{Tr}\{(e^{-\beta\hat{T}/P} e^{-\beta\hat{V}/P})^P\}, \quad (1)$$

where \hat{T} and \hat{V} are the operators of the kinetic energy and the potential energy respectively. P is called the Trotter number. This decomposition of the density operators leads to the PIMC approach in which one quantum mechanical point particle can be represented by a chain of P "classical" beads [17]. Linear molecules would rather have to be visualized by spillikin-sticks than by beads, of course. The statistical weight of one configuration is then given by the product of matrixes

$$\tilde{K}_{ii+1} = \langle \phi_i | e^{-\beta \hat{T}_{\text{rot}}/P} e^{-\beta \hat{T}_{\text{trans}}/P} e^{-\beta \hat{V}/P} | \phi_{i+1} \rangle \quad (2)$$

with $|\phi_i\rangle$ the state of the system at Trotter slice i . Without any loss of generality, we consider a system that consists of only one linear molecule. For details of the PIMC method, see *e.g.* Ref. [18].

If the real space representation is chosen in order to work out the trace in Equation (1), the only Boltzmann factor in Equation (2) that can become negative is the one that is associated with the rotational kinetic energy:

$$K_{ii+1}^{(\text{rot})} = \langle \underline{n}_i | \exp(-\beta \hat{L}^2/2\theta P) | \underline{n}_{i+1} \rangle, \quad (3)$$

where \hat{L} is the operator of the angular momentum, \underline{n}_i a normalized vector indicating the orientation of the molecule at the Trotter slice i , and θ the moment of inertia. $K_{ii+1}^{(\text{rot})}$ can also be expressed as:

$$K_{ii+1}^{(\text{rot})} = \sum_l \sum_{m=-l}^l \langle \underline{n}_i | Y_{lm} \rangle \langle Y_{lm} | \underline{n}_{i+1} \rangle \exp[-\beta l(l+1)B/P], \quad (4)$$

where $|Y_{lm}\rangle$ denotes a state of the standard representation and $B = \hbar^2/2\theta$ is the rotational constant. Using the addition theorem for spherical harmonics, we get the final form for $K_{ii+1}^{(\text{rot})}$:

$$K_{ii+1}^{(\text{rot})} = \sum_l \frac{2l+1}{4\pi} P_l(\cos \gamma_i) \exp[-\beta l(l+1)B/P], \quad (5)$$

with $P_l(\cos \gamma)$ the Legendre polynomial of degree l and $\cos(\gamma_i) = \underline{n}_i \cdot \underline{n}_{i+1}$. For finite temperatures, $\beta > 0$, the sum obviously converges. Note that the sum in Equation (5) corresponds to a Gaussian integral if the orientational degrees of freedom are replaced by translational ones.

The sum over l in Equation (5) can not be carried out analytically. Hence, it seems convenient to introduce a new variable l_i that characterizes the degree of the Legendre polynomial of the molecule at Trotter slice i . Thus, the internal energy U becomes

$$U = \left\langle \frac{1}{P} \sum_{i=1}^P [\Theta l_i(l_i+1) + V(\mathbf{g}_i, \boldsymbol{\varphi}_i)] \right\rangle \quad (6)$$

and the specific heat can be calculated using the standard fluctuation formula [19]. However, a severe sign problem is encountered, and even at high temperatures the average sign is close to zero [12].

Although $K_{ii+1}^{(\text{rot})}$ might not be accessible analytically, it can be computed numerically to very high precision and then be tabulated on a fine grid. Only one function needs to be stored at each effective temperature PT in order to compute the

Boltzmann weight, while in the case where the degree l of the Legendre polynomial is a “Monte Carlo variable”, a large set of Legendre polynomials has to be stored.

In Figure 1, we show $K_{ii+1}^{(\text{rot})}$ as a function of γ for $\beta B/P = 0.1$ in the three different cases: (i) the sum is confined to even l -values (symmetric rotational states) as this would have to be done for the simulation of *para*-H₂. (ii) even and odd values of l are considered (non-symmetrical rotational states). This is necessary in a simulation of heteronuclear molecules such as CN. (iii) the sum is restricted to odd l -values (anti-symmetric rotational states) as in the case of *ortho*-H₂.

For even l -values $K_{ii+1}^{(\text{rot})}$ is symmetric at $\gamma = \pi/2$ and in the odd l -case it is anti-symmetric which leads to the sign problem for a Trotter number $P > 2$. In the even l case and in the mixed l case, the Boltzmann factor, Equation (5), always remains positive, and hence no sign problem exists. These characteristics do not depend on temperature and Trotter number. For $PT \gg B$, the kernel $K_{ii+1}^{(\text{rot})}$ can even be approximated by the expression:

$$K_{ii+1}^{(\text{rot})} \propto \exp(-P\gamma^2/4\beta B) \quad (7)$$

The difference between $K_{ii+1}^{(\text{rot})}$ given in Equation (5) and $K_{ii+1}^{(\text{rot})}$ given in Equation (7) is so small that it could not be visualized in Figure 1. Even on a logarithmic scale they differ so slightly when $K_{ii+1}^{(\text{rot})}$ tends to zero that the difference seems to be of numerical nature. Then even l case and the odd l case can be approximated as well

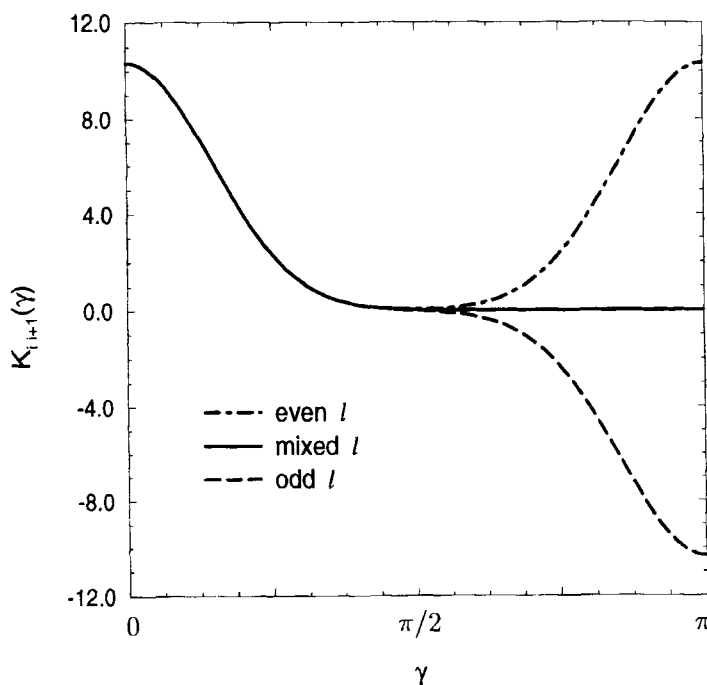


Figure 1 Unnormalized Boltzmann factor $K_{ii+1}^{(\text{rot})}$ for $\beta B = 0.1$ as a function of γ .

by such a formular after implementation of the relevent symmetry operations $K_{ii+1}^{(\text{rot}, \pm)}(\gamma_i) = K_{ii+1}^{(\text{rot})}(\gamma_i) \pm K_{ii+1}^{(\text{rot})}(\pi - \gamma_i)$.

The internal energy can be calculated as the derivative of $-\ln Z(\beta)$ with respect to β :

$$U = \left\langle \frac{1}{P} \sum_{i=1}^P [T_i + V(\vartheta_i, \varphi_i)] \right\rangle$$

with

$$T_i = (K_{ii+1}^{(\text{rot})})^{-1} \sum_l \frac{2l+1}{4\pi} l(l+1) B P_l(\cos \gamma_i) \exp[-\beta l(l+1) B/P]. \quad (8)$$

Other observables can be obtained in analogy to the procedures which are applied for the PIMC treatment of translational degrees of freedom.

2.2 The Odd l -Case

In the odd l case, the Boltzmann weight of the isomorphic classical picture can become negative and therefore one has to separate the average of an observable O_+ when the sign σ of the Boltzman weight is positive from the average of O_- when σ is negative [20,21]. The expectation value $\langle O \rangle$ of the observable is then

$$\langle O \rangle = \frac{O_+ Z_+ - O_- Z_-}{Z_+ - Z_-}, \quad (9)$$

where Z_+ and Z_- are the (positive valued) partition functions of the system with σ constrained to positive and negative values respectively.

In the “Monte Carlo language” this means

$$\langle O \rangle = \lim_{M \rightarrow \infty} \frac{\sum_{i=1}^M \sigma_i O_i}{\sum_{i=1}^M \sigma_i}, \quad (10)$$

where i enumerates the Monte Carlo steps and σ_i denotes the sign of the Boltzmann weight at Monte Carlo step i .

Clearly, the statistical treatment of a free anti-symmetric rotator is trivial. In the context of the PIMC simulation, however, it is important to know the average sign $\langle \sigma \rangle$ of the free anti-symmetric rotator as a function of temperature T and Trotter number P . Of course, $\langle \sigma \rangle = 1$ for $P = 1$ and $P = 2$.

For very high Trotter numbers and very low temperatures, the following procedure seems to be reasonable: the Markov chain which is generated for anti-symmetric rotational states resembles the one generated for non-symmetric rotational states if we disregard inversion operations and if we only take into account configurations with positive Boltzmann weight. Hence,

$$\langle O_+ \rangle_{\text{anti-symmetric}} \approx \langle O \rangle_{\text{non-symmetric}}. \quad (11)$$

Let us take the internal energy as the quantity of interest and let us make the ad-hoc assumption that $\langle O \rangle_{\text{anti-symmetric}} \approx -\langle O \rangle_{\text{non-symmetric}}$. We can find an approximative expression for the average sign:

$$\langle \sigma \rangle_{\text{anti-symmetric}} \approx \frac{U_{\text{non-symmetric}}}{U_{\text{anti-symmetric}}}. \quad (12)$$

In Figure 2 we show σ obtained by simulation of the free rotator in the limit $P \rightarrow \infty$ as a function of temperature. σ as proposed in Equation (12) is inserted as well and we already add some results for the case where a strong symmetric but anisotropic potential is switched on. Equation (12) describes qualitatively the disappearance of the average sign and therefore $\ln\langle\sigma\rangle \approx -B/k_B T$ at low temperatures. The existence of the potential alters the sign-problem considerably, fortunately for the better. This might be due to the effect that in symmetric potentials the level splitting between the (symmetric) groundstate and the (anti-symmetric) first excited state decreases with increasing potential strength [7].

2.3 Higher Order Corrections

It is well known that a faster convergence to the quantum limit is obtained if the Trotter formula, Equation (1) is replaced by higher order approximants for the density matrix [22]. Very easy to implement is the approximant proposed by Imada and Takahashi [15,16]:

$$Z(\beta) = \lim_{P \rightarrow \infty} \text{Tr} \{ (e^{-\beta \hat{T}/P} e^{-\beta(\hat{V} + \hat{V}_c)/P})^P \},$$

$$\hat{V}_c = \frac{\beta^2}{24P^2} [\hat{V}, [\hat{T}, \hat{V}]]. \quad (13)$$

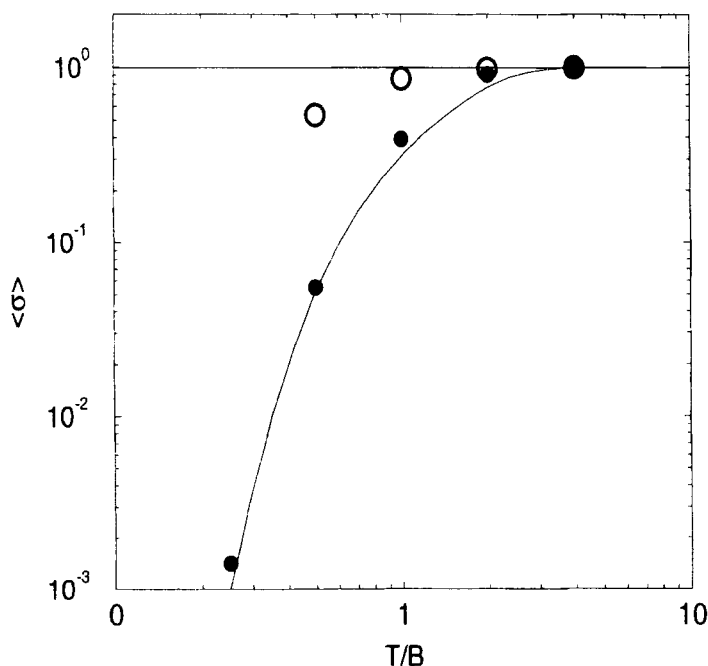


Figure 2 $\langle\sigma\rangle$ as a function of temperature; circles are numerical results for the free rotator, lines correspond to Equation (12).

The convergence of expectation values such as internal energy U to the quantum limit is now proportional to $(\beta/P)^4$ instead of the slow convergence proportional to $(\beta/P)^2$. Apart from terms that do not contribute to the partition function, the correction potential V_c defined in Equation (13) becomes for orientational degrees of freedom

$$\hat{V}_c = \frac{\beta^2 B}{12P^2} \{(\nabla \hat{V})^2 - [\underline{n}(\nabla \hat{V})]^2\}, \quad (14)$$

whith $(x, y, z) = \underline{n}$ and $\nabla = (\partial/\partial x, \partial/\partial y, \partial/\partial z)$.

Again the internal energy can be calculated as the derivative of $-\ln Z(\beta)$ with respect to β , and the same result is obtained as for translational degrees of freedom:

$$U = \left\langle \frac{1}{P} \sum_{i=1}^P [T_i + V(\vartheta_i, \varphi_i) + 3V_c(\vartheta_i, \varphi_i)] \right\rangle \quad (15)$$

The averages of observables O which are diagonal in the real space representation have to be computed according to:

$$\langle O \rangle = \left\langle \frac{1}{P} \sum_{i=1}^P O(\vartheta_i, \varphi_i) \right\rangle + \frac{\beta^2 B}{P^2} \langle (\nabla V - \underline{n} \nabla V)(\nabla O - \underline{n} \nabla O) \rangle. \quad (16)$$

Note that extrapolation from averages obtained with finite Trotter number to the quantum limit further reduces the necessary Trotter number to be taken into account.

3 APPLICATION OF THE METHOD TO A MODEL HAMILTONIAN

3.1 Model Hamiltonian

The algorithm presented above has been applied to a single-particle potential which may be used to model a H_2 or a N_2 impurity in a fcc Ar-crystal [12,23]. For the local potential we therefore chose the Devonshire potential [7]:

$$V = \frac{3}{2} C (1 - x^4 - y^4 - z^4), \quad (17)$$

where C is the minimal barrier height separating the classical stable orientations and $(x, y, z) = \underline{n}$ [23]. The correction potential is then given by

$$V_c = 3B \left(\frac{\beta C}{P} \right)^2 [(x^6 + y^6 + z^6) - (x^4 + y^4 + z^4)^2]. \quad (18)$$

The following parameters were used in the simulations: We chose for the rotational constant $B = 1$ and for the barrier height $C = 40$. This is quite an extreme case as long as small molecules are concerned, but the computational problem is the more challenging the more B and C differ.

The exact partition function and other thermodynamic quantities can easily be calculated for this single-particle problem using Equation (1) and choosing a sufficiently large Hilbert space spanned by the spherical harmonics Y_{lm} with $-l \leq m \leq l$ and $l \leq l_{\max}$. For temperatures $k_B T \leq C$, very good convergence of the specific heat is

obtained with $l_{\max} = 21$. For higher temperatures, larger l -numbers would be needed, but at such high temperatures the rotator resembles a free rotator which is a trivial problem.

3.2 Computational and Exact Results

We concentrate on the observables internal energy U and specific heat c the latter of which is obtained by performing the derivative of U with respect to the temperature T .

The computational results have been obtained with the following procedure. U is computed by performing a Trotter scaling plot. At each temperature at least three different Trotter numbers P are investigated and the quantum limit $U = \lim_{P \rightarrow \infty} U(T, P)$ is obtained from a fit of

$$U(T, P) = U + \alpha(T)P^{-4}, \quad (19)$$

with $U, \alpha(T)$ as fit parameters and $U(T, P)$ the simulation results. Note that because of tunneling phenomena at very low temperatures, U is approached from above with increasing P and not from below as for “simple” anharmonic solids like a fcc-Ne-crystal [24]. The smallest Trotter number P_{\min} in a scaling plot was chosen such that $P_{\min}T \geq 20$ K. The largest Trotter number P_{\max} was chosen $P_{\max} \approx P_{\min}$. The correction potential V_c is already fairly small when the tunneling effects set in with increasing P . Hence, the linearity of $U(T, P)$ with P^{-4} must be waited for before the extrapolation to $P = \infty$ can be carried out.

The specific heat c was calculated indirectly by first computing the internal energy at two different temperatures T_1 and T_2 where the Trotter numbers in the two runs were chosen such that the systematic errors remained nearly constant, namely $P_1T_1 = P_2T_2$. Then c was approximated according to $c[(T_1 + T_2)/2] \approx [U(T_1) - U(T_2)]/(T_1 - T_2)$.

One Monte Carlo (MC) step consists in making one local move of each spillikin stick and one global move of the whole chain. 192 rotators are set up in parallel in order to obtain good vectorization. In this way, $10^8/P$ MC steps of the total system can be performed within 10 hours of CPU time on a Cray YMP. It turned out that only at thermal energies well below the rotational constant B this numerical effort was necessary. At $T \approx 4B$, where Trotter numbers $P = 5, 6, 7$ are quite close to the quantum limit, 10^5 MC steps for relaxation and 10^5 MC steps for measurements are already sufficient to reduce the relative statistical error of U to 0.03%.

In Figure 3, U is shown as a function of temperature for the three cases of even l values, odd l values and mixed l values. The numerical results are (nearly) identical with the “exact” results. The differences between the three above mentioned cases are clearly observed in the simulation.

At very low temperatures tunneling occurs if the potential barrier C is large in comparison with the rotational constant B because in this limit the problem is closely related to the one-dimensional Φ^4 potential from a statistical point of view. The tunneling should lead to a level splitting of the three “ground states” being smeared out orientations parallel to the x, y and z axis respectively. The level splitting leads to a peak of c at very low temperatures, while at intermediate temperatures the system appears to be frozen in. This behavior is found in Figure 4.

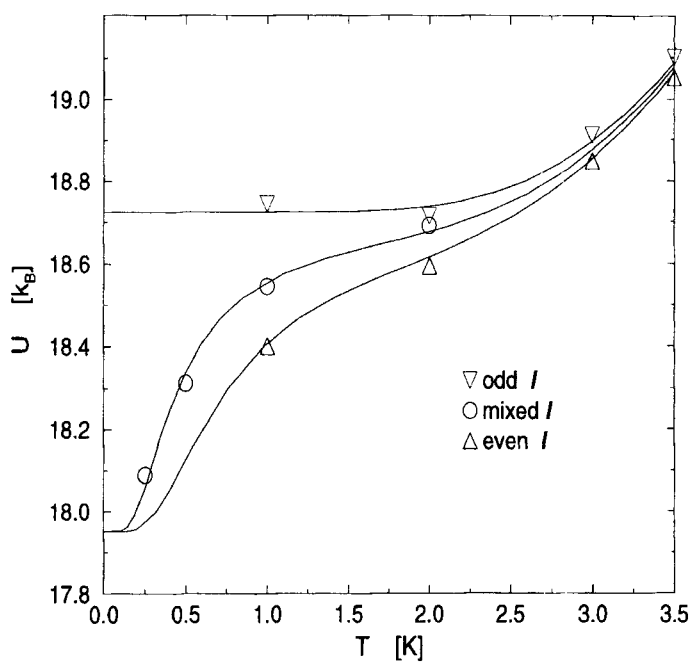


Figure 3 Internal energy U of a rotator in a Heaviside potential for the three cases: (i) odd l , (ii) mixed l and (iii) even l . Lines are exact results, the symbols represent numerical values obtained by PIMC.

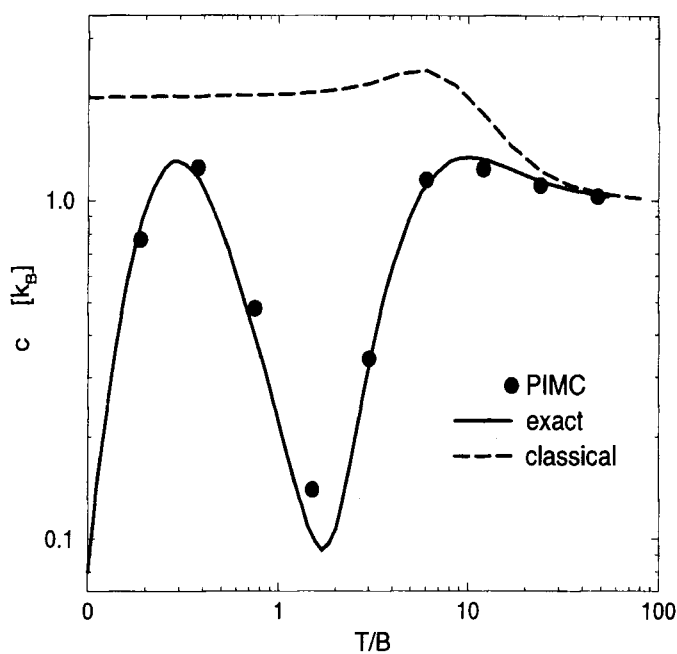


Figure 4 Specific heat c as a function of temperature T for the mixed l case.

Note that the Debye anomaly of the classical simulation at $T \approx 20$ is strongly reduced through quantum effects although $B/C = 40$ should be considered as quite an extreme case. This might be an important result for the interpretation of specific heat data of orientational glasses [4].

4 CONCLUSIONS AND DISCUSSION

A new PIMC method for linear molecules has been presented in detail. It was shown that the problem has been absent for symmetric and non-symmetric rotational states. For anti-symmetric rotational states, evidence has been found that with increasing local potential the average sign gets shifted more and more to unity. Nevertheless, many-particle problems presumably can no more be addressed in the odd l case when the temperature is smaller or in the order of the rotational constant B . Isotope effects can therefore only be quantified by PIMC simulation if they are mass-induced by a changed anharmonicity but not if they are induced by altered exchange characteristics which presumably is only important for H_2 and D_2 solids (differences in the phase diagram of *para*- H_2 and HD as reported in Ref. [25] should nevertheless be accessible by the presented PIMC method). Note that often these anharmonic effects dominate the exchange effects, and even the isotope shift of He melting pressure can only be explained by anharmonicity effects [26,27].

The simulations reproduce very well the exact results for the internal energy as a function of temperature, and even tunneling anomalies in the specific heat are captured for the given choice of B and barrier height C . The application of the method to N_2 -solids, ArN_2 mixtures and $KBrKCN$ type mixtures will be suitable to determine their thermomechanical properties at low temperatures.

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References

- [1] D. Scharf, M. L. Klein and G. J. Martyna, "Path-integral Monte Carlo of orientational ordering in compressed H_2 ", *J. Chem. Phys.*, **97**, 3590 (1992).
- [2] K. J. Runge, M. P. Surh, C. Mailhot and E. L. Pollock, "Path-integral Monte Carlo studies of para-hydrogen clusters", *Phys. Rev. Lett.*, **69**, 3527 (1992).
- [3] D. Marx, O. Opitz, P. Nielaba and K. Binder, "Quantum effects on the herringbone ordering of N_2 on graphite", *Phys. Rev. Lett.*, **70**, 2908 (1993).
- [4] U. T. Höchli, K. Knorr and A. Loidl, "Orientational glasses", *Adv. Phys.*, **39**, 405 (1990).
- [5] K. Binder and J. D. Reger, "Theory of orientational glasses; Models, concepts, simulations", *Adv. Phys.*, **41**, 547 (1992).
- [6] V. Narayanamurti and R. O. Pohl, "Tunneling states of defects in solids", *Rev. Mod. Phys.*, **42**, 201 (1970).
- [7] W. Press, *Single-Particle Rotations in Molecular Crystals* (Springer, Berlin, 1981).

- [8] A. Hüller and L. Baetz, "Rotational tunneling: A computer simulation at finite temperatures", *Z. Phys., B* **72**, 47 (1988).
- [9] A. Würger, "The temperature dependance of rotational tunneling", *Z. Phys., B*, **76**, 65 (1989).
- [10] K. E. Schmidt and D. M. Ceperley, in *Monte Carlo techniques for quantum fluids, solids and droplets*, ed. K. Binder (Springer, Berlin, 1992).
- [11] H. De Raedt and M. Frick, "Stochastic diagonalization", *Phys. Rep.*, **231**, 107 (1993).
- [12] D. Marx, "Rotational motion of linear molecules in three dimensions: A path-integral Monte Carlo approach", *Molecular Simulation*, **12**, 33 (1994).
- [13] P. Nielaba and K. Binder, "Lattice Deformations in a N_2 -Ar mixture model in the dilute limit", *Europhys. Lett.*, **13**, 327 (1990).
- [14] M. H. Müser, W. Helbing, P. Nielaba and K. Binder, "Low-temperature anharmonic lattice deformations near rotator impurities: A quantum Monte Carlo approach", *Phys. Rev., E*, **5**, 3956 (1994).
- [15] M. Takahashi and M. Imada, "Monte Carlo Calculation of Quantum Systems. II. Higher order Corrections", *J. Phys. Soc. Jpn.*, **53**, 3765 (1984).
- [16] X-P Li and J. Q. Broughton, "High-order correction to the Trotter expansion for use in computer simulations", *J. Chem. Phys.*, **86**, 5094 (1987).
- [17] D. Chandler and G. Wolynes, "Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids", *J. Chem. Phys.*, **74**, 4078 (1981).
- [18] H. Kleinert, *Path-Integrals in Quantum Mechanics, Statistics and Polymer Physics* (World Scientific, Singapore, 1990).
- [19] D. Marx, P. Nielaba and K. Binder, "On the calculation of the heat capacity in pathintegral Monte Carlo simulations", *Int. J. Mod. Phys., C*, **3**, 337 (1992).
- [20] S. Sorella, S. Baroni, R. Car and M. Parrinello, "A novel technique for the simulation of interacting fermion systems", *Europhys. Lett.*, **8**, 663 (1989).
- [21] E. Y. Loh, Jr. and J. E. Gubernatis, R. T. Scalettar, S. R. White, D. J. Scalapino and R. L. Sugar, "Sign problem in the simulation of many-electron systems", *Phys. Rev., B*, **41**, 9301 (1990).
- [22] M. Suzuki, in *Quantum Monte Carlo Methods in Equilibrium and Nonequilibrium Systems*, ed. M. Suzuki, (Springer, Berlin, 1987).
- [23] M. H. Müser and G. Ciccotti, "Two-dimensional orientational motion as a multichannel reaction by computer simulation", *J. Chem. Phys.*, **103**, 4273 (1995).
- [24] M. H. Müser, P. Nielaba and K. Binder, "Path-integral Monte Carlo study of crystalline Lennard-Jones systems", *Phys. Rev., B*, **51**, 2723 (1995).
- [25] F. Moshary, N. H. Chen and I. F. Silvera, "Remarkable high pressure phase line of orientational order in solid hydrogen deuteride", *Phys. Rev. Lett.*, **71**, 3814 (1993).
- [26] J. L. Barrat, P. Loubeyre and M. L. Klein, "Isotopic shift in the melting curve of helium: A path-integral Monte Carlo study", *J. Chem. Phys.*, **90**, 5644 (1989).
- [27] M. Boninsegni, C. Pierloni and D. M. Ceperley, "Isotopic Shift of Helium Melting Pressure: Path-integral Monte Carlo Study", *Phys. Rev. Lett.*, **72**, 1854 (1994).