

Analytic Computation of the Instantaneous Normal Modes Spectrum in Low-Density Liquids

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We analytically compute the spectrum of the Hessian of the Hamiltonian for a system of N particles interacting via a purely repulsive potential in one dimension. Our approach is valid in the low-density regime, where we compute the exact spectrum also in the localized sector. We finally perform a numerical analysis of the localization properties of the eigenfunctions.

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Great efforts have recently been made to find a comprehensive microscopic theory able to describe the behavior of supercooled liquids [1]. Among others, a key point is to understand the mechanism of the glass transition, and to find a description suitable both for the supercooled liquid and for the amorphous solid which forms at low temperatures.

The general frame, where a great number of recent analyses have been performed, is the instantaneous normal modes (INM) approach [2]. The main idea of this approach is that liquids are “solidlike” at short times $t < \tau$, where the typical diffusion time τ increases strongly when lowering the temperature. Liquid dynamics would correspond in this picture to vibrations about some equilibrium positions with periodic jumps into new local minima [3]. In order to describe in a quantitative way this behavior, it is important to study the properties of the Hessian matrix of the Hamiltonian, averaged over the equilibrium Boltzmann distribution. The crucial quantity is the typical *spectrum* of the Hessian, whose eigenvectors are the so-called instantaneous normal modes. The determination of the spectrum therefore represents a vital task for any theoretical study of liquids.

The aim of this Letter is to outline an analytic approach for the computation of the INM spectrum. Some important steps in this direction have recently been done in [4] and [5], where a remarkably good agreement with numerical simulations on liquids has been achieved and where more realistic models than the one we study here were considered. However, these former analytic computations of the INM spectrum assumed a *Gaussian* probability distribution for the auxiliary degrees of freedom of the liquid [5] (this technical point will be clarified later) and we think that a Gaussian approach is likely to be too simple for a study of nontrivial spectral properties, such as localization. This is a crucial difference with the computation we present here, which, going beyond the Gaussian approximation, allows us to better investigate the spectrum in the localized sector.

Let us consider a system of N interacting particles with Hamiltonian $H = \sum_{k>l}^N V(r_{kl})$, where $V(r)$ is a

two-body potential. The Hessian matrix \mathbf{A} is defined by $A_{kl}^{\mu\nu} = \partial_k^\mu \partial_l^\nu H$, with $\mu, \nu = 1, \dots, d$, d being the dimension of the space. In the present Letter we shall consider the one dimensional case $d = 1$, in order to keep the algebra as simple as possible. The form of \mathbf{A} is $A_{kl} = -J_{kl} + \delta_{kl} \sum_i^N J_{ki}$, where $J_{kl} = V''(r_{kl})$. The diagonal term of \mathbf{A} is a consequence of the translational invariance of the system, which requires $\sum_k^N A_{kl} = 0$.

As a first step in our analysis, we must find out what is the probability distribution of the matrix \mathbf{J} induced by the equilibrium probability over the positions of the particles. We introduce here our first approximation, assuming that the probability distribution $P[\mathbf{J}]$ is factorized into the single probabilities of the particle pairs. In this way the elements of \mathbf{J} (but not of \mathbf{A}) are independently distributed, i.e., $P[\mathbf{J}] \equiv \prod_{k>l}^N p(J_{kl})$. This approximation works well at low densities, where the three-particle correlations are negligible.

Once this factorized form for $P[\mathbf{J}]$ is assumed, we can express the pair probability $p(J)$ as

$$p(J) = \frac{\rho}{N} \int dr g^{(2)}(r) \delta(J - V''(r)), \quad (1)$$

where $g^{(2)}(r)$ is the two-particle correlation function and ρ is the density. In the following we shall consider the soft-sphere potential $V(r) = 1/r^m$. In this case density and temperature scale homogeneously, so that we can simply fix the density $\rho = 1$ and consider the high temperature regime as equivalent to the low-density one. This does not hold for a nonhomogeneous potential and what follows must be interpreted as a low-density calculation.

In the definition of $p(J)$ we must insert the explicit form of $g^{(2)}(r)$, which can be obtained by means of some approximation schemes in liquid theory or by numerical simulations. In the present context we want to show the results of our method in the simplest analytical way, so that we stop at the first order of the virial expansion and assume $g^{(2)}(r) = \exp[-\beta V(r)]$. Thus, from Eq. (1), we have

$$p(J) \sim \frac{1}{N} \frac{e^{-\beta J^b}}{J^{1+c}} \equiv \frac{1}{N} q(J), \quad (2)$$

with $\beta_s = \beta [m(m+1)]^{1/(m+2)}$, $b = m/(m+2)$ and $c = 1/(m+2)$. For realistic values of m (typically $m = 12$) the parameter b is very close to one. Therefore, we will directly set $b = 1$ in $p(J)$ in order to simplify our calculation. We will show in the discussion of our results that the actual spectrum is very weakly dependent on this approximation. As it stands the distribution $p(J)$ is not normalizable, but we can regularize it in the following way. Let us put an infrared cutoff \bar{r} , by setting $V(r) = 0$ for $r > \bar{r}$, and let $\eta = V(\bar{r})$. We obtain in this way a regularized form of the pair probability

$$p_\eta(J) = \delta(J) + \frac{1}{N} \left(q(J)\theta(J - \eta) - \delta(J) \int_\eta^\infty dJ' q(J') \right), \quad (3)$$

where $q(J)$ is defined in Eq. (2). In the following we shall use the notation

$$\langle f(J) \rangle \equiv \int_\eta^\infty dJ q(J) [f(J) - f(0)]. \quad (4)$$

Note the following important point: the distribution $p_\eta(J)$ is *diluted*, since the probability of finding an element of the matrix \mathbf{J} larger than η is of order $1/N$.

In order to compute the spectrum of \mathbf{A} we introduce the resolvent $G_{kl}(\lambda | \mathbf{J}) = [\lambda - \mathbf{A} + i\epsilon]_{kl}^{-1}$. In the following we shall include the small imaginary term $i\epsilon$ in λ . The spectrum (or density of states) $D(\lambda)$ is then given by $D(\lambda) = \lim_{\epsilon \rightarrow 0} \text{Im Tr} \mathbf{G}(\lambda) / \pi N$, where $\mathbf{G}(\lambda)$ is the average over \mathbf{J} of the resolvent. Following the recursive method of [6], we now write a self-consistent equation for \mathbf{G} . Given a system of N particles, we add an extra particle, with label 0, and we write the expression of the (0,0) component of \mathbf{G} in the $(N+1)$ -particle system, isolating the contribution of the 0th particle:

$$iG_{00}^{(N+1)}(\lambda | \mathbf{J}) = \frac{1}{Z} \int d\phi d\psi_1 \dots d\psi_N \phi^2 e^{S(\phi, \psi_1 \dots \psi_N)},$$

where Z is the effective partition function and $\phi \equiv \psi_0$. The action S is given by

$$S = \frac{i}{2} \lambda \phi^2 - \frac{i}{2} \sum_{k=1}^N J_{0k} (\phi - \psi_k)^2 + \frac{i}{2} \sum_{k,l=1}^N \psi_k [G^{(N)}]_{kl}^{-1} \psi_l.$$

In the same spirit as the cavity method [7], we have written a self-consistent equation which relates the element $G_{00}^{(N+1)}$ of the system with $(N+1)$ particles, to the matrix $G_{kl}^{(N)}$ of the system with N particles. We note that $G_{kl}^{(N)}$ is the resolvent of the system in the absence of the 0 particle and therefore it does not depend on the new vector J_{0k} . Besides, it is shown in [6] that only the diagonal elements contribute to the last sum in the action S .

Since we have to perform an average over \mathbf{J} , it is useful to introduce replicas, by writing $Z^{-1} = \lim_{n \rightarrow 0} Z^{n-1}$. After

replication we have

$$iG_{00}^{(N+1)}(\lambda | J_{0k}, G_{kk}^{(N)}) = \lim_{n \rightarrow 0} \frac{1}{n} \int d\vec{\phi} (\vec{\phi})^2 \Omega(\vec{\phi} | J_{0k}, G_{kk}^{(N)}),$$

where $\vec{\phi} \equiv (\phi_1 \dots \phi_n)$ and

$$\begin{aligned} \Omega(\vec{\phi} | J_{0k}, G_{kk}^{(N)}) &= e^{i(\lambda/2) \sum_a \phi_a^2} \\ &\times \int \prod_{k=1}^N d\vec{\psi}_k e^{-(i/2) \sum_{k,a} J_{0k} (\phi_a - \psi_{k,a})^2} \\ &\times e^{(i/2) \sum_{k,a} \psi_{k,a}^2 [G^{(N)}]_{kk}^{-1}}. \end{aligned} \quad (5)$$

The crucial quantity is now the average probability distribution $\Omega(\vec{\phi})$, obtained by averaging expression (5) over \mathbf{J} . Indeed, from Ω we can reconstruct the average resolvent \mathbf{G} by integration over $\vec{\phi}$ and therefore obtain the spectrum. Thus, unlike what has been done in [6], we shift our attention to the pursuit of a self-consistent equation for Ω and not for the resolvent \mathbf{G} itself. Let us note that, it is this very distribution, $\Omega(\vec{\phi})$, as mentioned in the introduction, that is assumed to be Gaussian in the calculations of [4] and [5] [the distribution $s(X)$ in Section III.B of [5] is exactly the same object as our $\Omega(\vec{\phi})$].

The dependence on the matrix \mathbf{J} of Ω is divided into two independent parts: the vector J_{0k} and the matrix $\mathbf{G}^{(N)}$. We can therefore compute separately the two averages and, after some algebra, we have

$$\begin{aligned} \Omega(\vec{\phi}) &= e^{i(\lambda/2) \sum_a \phi_a^2} \\ &\times \exp \left(\int d\vec{\psi} \Omega(\vec{\psi}) \langle e^{-(i/2)J \sum_a (\phi_a - \psi_a)^2} \rangle \right). \end{aligned}$$

We can now obtain a more tractable integral equation by defining the following function g :

$$g(\vec{\phi}) \equiv \int d\vec{\psi} \Omega(\vec{\psi}) \langle e^{-(i/2)J \sum_a (\phi_a - \psi_a)^2} \rangle.$$

Note that g measures the deviation from the Gaussianity of Ω , so that obtaining a nonquadratic form of g means going beyond the Gaussian approximation of [4] and [5]. The integral self-consistent equation for g is

$$g(\vec{\phi}) = \int d\vec{\psi} e^{i(\lambda/2) \sum_a \psi_a^2 + g(\vec{\psi})} \langle e^{-(i/2)J \sum_a (\phi_a - \psi_a)^2} \rangle. \quad (6)$$

We now assume that g depends only on the modulus x of the replica vector $\vec{\phi}$, so that we can perform the angular part of the integral, then average over the disorder distribution $p_\eta(J)$, and finally let $\eta \rightarrow 0$, to get

$$\begin{aligned} g(x) &= \frac{\Gamma(2-c)}{c(c-1)} \left[\left(\beta_s + \frac{ix^2}{2} \right)^c - \beta_s^c \right] \\ &- x \int_0^\infty dy K(x, y) e^{i(\lambda/2)y^2 + g(y)} \end{aligned} \quad (7)$$

$$K(x, y) = \frac{\Gamma(2-c)(1+c)xy}{\Gamma(\frac{3-c}{2})\Gamma(\frac{3+c}{2})4} \times \int_0^1 dt \left(\frac{t}{1-t}\right)^{(1-c)/2} \times \left\{ \left[\beta_s + \frac{i}{2}(x^2 + y^2) \right]^2 + tx^2y^2 \right\}^{(c-2)/2}.$$

These two equations are the main result of this letter. It is possible to prove analytically that $g(x) \sim -x^{2c}$ for $x \gg 1$, thus proving that Ω is definitely *not* a Gaussian distribution. Notably, we have been able to numerically solve the equation for $g(x)$ without any further approximation. Indeed, Eq. (7) has the form of a fixed-point equation, so that it is tempting to try to solve it numerically by iteration. This is what we have done: discretized the function g and the kernel K on a lattice. We have found that the convergence is rather fast and very weakly dependent on the small imaginary part ϵ of λ . Indeed, by setting directly $\epsilon = 0$, the results are very satisfactory and we are able to obtain the solution up to arbitrary precision. Once g for a given value of λ was obtained, we computed the spectrum $D(\lambda)$, using the formula

$$D(\lambda) = \text{Re} \left\{ \frac{1}{\pi} \int_0^\infty dx x e^{i(\lambda/2)x^2 + g(x)} \right\},$$

which follows from the definitions of D , \mathbf{G} and g . The results are shown in Fig. 1, where we have plotted the INM spectrum D as a function of λ , for $m = 12$.

The spectrum has positive support because $d = 1$ and it depends on the scaled inverse temperature β_s in the expected way: for low temperatures (high β_s) the collisions among particles are weaker, so that the spectrum is peaked on the lower value of the eigenvalues. On the other hand, the tail for large λ is larger at higher temperature. We have found that $D(\lambda) \sim e^{-\alpha\lambda}$ for $\lambda \gg 1$, but we have not been able to express α as a function of the parameters β and m , even if it is numerically evident that α is a monotonically increasing function of β_s .

A crucial task is now to check whether the result we found is correct. To this end we have done extensive numerical simulations. Once we draw a matrix \mathbf{J} with probability (3), we build \mathbf{A} and diagonalize it numerically. Since the spectrum has huge tails for large eigenvalues, it is convenient to compare simulations with analytic results to consider the probability distribution π of $\mu \equiv \ln \lambda$, that is, $\pi(\mu) = D(e^\mu)e^\mu$. In Fig. 2 we plot $\pi(\mu)$ as obtained from the analytic form of $D(\lambda)$, together with the one obtained from numerical simulations. The two curves are in excellent agreement confirming the validity of our result. Besides, we show in the inset of Fig. 2 the numerical spectrum obtained with the original value of $b = m/(m+2)$. The result justifies the sensibility of the approximation $b \sim 1$.

An equation similar to (6) was derived in [8], with a different method and within a different context. In that case too, the distribution of the disorder was diluted and translationally invariant, but the explicit probability distribution $p(J)$ was bimodal, $p(J) = \delta(J) +$

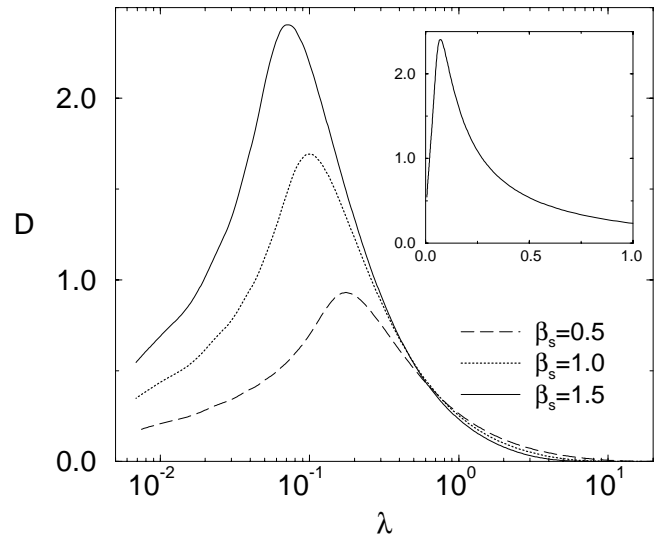


FIG. 1. The INM spectrum D as a function of λ for different values of the scaled temperature β_s ; $m = 12$ and $\epsilon = 0$. The plot is in log-linear scale. Inset: $D(\lambda)$ for $\beta_s = 1.5$ in linear-linear scale. The spectrum vanishes at $\lambda = 0$.

$\frac{p}{N} [\delta(J - 1/p) - \delta(J)]$, where p was the connectivity [8]. Yet, even with this simple bimodal distribution the spectrum had not been worked out explicitly until now. Remarkably, we have been able to compute exactly the spectrum associated with this bimodal distribution, by numerically solving the corresponding self-consistent equation [8]. The spectrum is shown in Fig. 3 and can be compared with the approximated solution of [9]. Note that in the liquid spectrum there is no trace of the small tail oscillations present in the bimodal case [9].

An important issue is the analysis of the localization properties of the eigenfunctions. With respect to this an

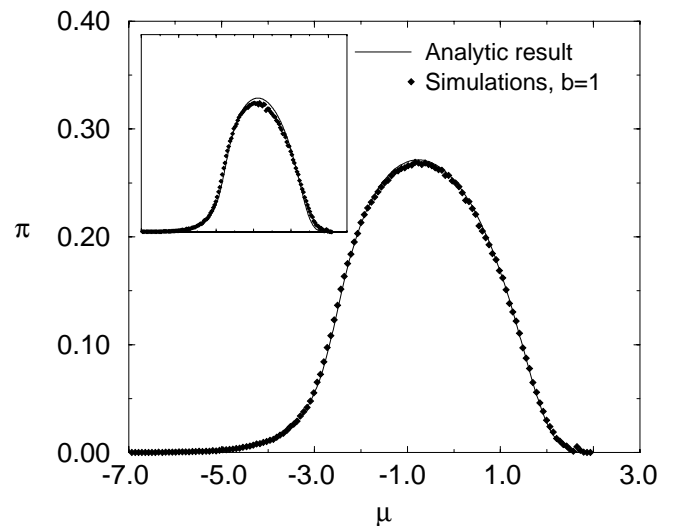


FIG. 2. Numerical simulations versus analytic solution. We plot here for $b = 1$ the probability distribution $\pi(\mu)$, with $\mu = \ln \lambda$; $N = 600$, $\eta = 10^{-4}$, $\beta_s = 1$, and $m = 12$. Inset: On the same scale, analytic result for $b = 1$ versus simulations performed with $b = m/(m+2)$.

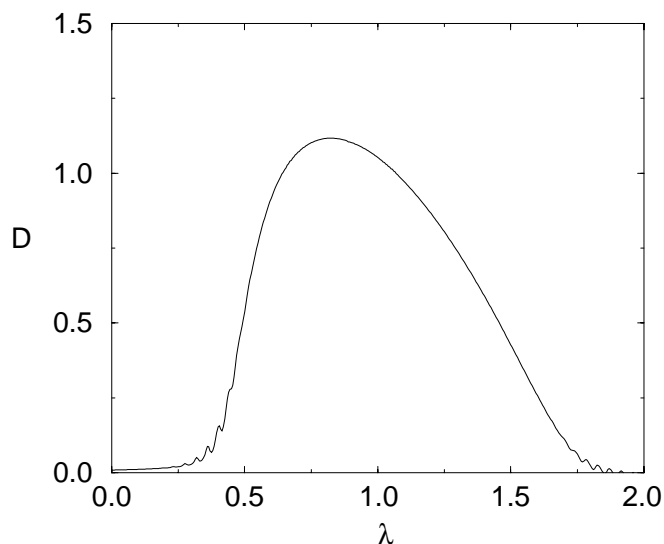


FIG. 3. Analytic solution. The spectrum in the case of the bimodal distribution, with $p = 20$ and $\epsilon = 0.005$. The small nonzero value of D for $\lambda \rightarrow 0$ is due to the nonzero value of ϵ , since the limit $\epsilon \rightarrow 0$ is very delicate in the bimodal case.

important quantity is the average inverse participation ratio (IPR) $Y(\lambda)$, which provides information on the nature of the eigenfunctions and can be easily computed via numerical simulations. The IPR is defined as $Y(\lambda_\alpha) = \sum_{i=1}^N (w_\alpha^i)^2$, where $\alpha = 1, \dots, N$ is the eigenvalue index and $w_\alpha^i = [\langle \lambda_\alpha | i \rangle]^2$ is the weight of site i in the eigenfunction $|\lambda_\alpha\rangle$.

In Fig. 4 we plot Y as a function of λ . It is clear that there are two localization edges, separating a central region of extended eigenvalues from the tails where localized states are present. For $\lambda \rightarrow 0$ the IPR goes to 1 and this corresponds to a single particle nearly decoupled from the rest of the system. Note that the limit $Y \rightarrow 1$ for $\lambda \rightarrow 0$ is smooth, due to the fact that the J distribution we consider is divergent at $J = 0$, so that it never happens that one single element in a row of \mathbf{J} is of order 1, with all others equal to zero. This behavior in the left tail cannot be present in the case of a bimodal distribution. On the other hand, the localized states of the right tail correspond to pairs of very strongly interacting particles and this naturally leads to an IPR equal to $1/2$. A more detailed discussion of localization, following [10], will be presented elsewhere.

In this Letter we have outlined a general method to study analytically the INM spectrum of a liquid at low densities. We have succeeded in an exact computation in the simple $d = 1$ case, but our method is suitable for extending to dimensions larger than 1, where the Hessian is not positively defined and negative eigenvalues exist. The presence of negative modes in three-dimensional systems is particularly relevant in connection with the glass transition [2]. Indeed, it has been argued in the context of the INM approach that the mode coupling transition, marking the crossover from a non-Arrhenius behavior of the viscosity to an Arrhenius one, occurs when the fraction

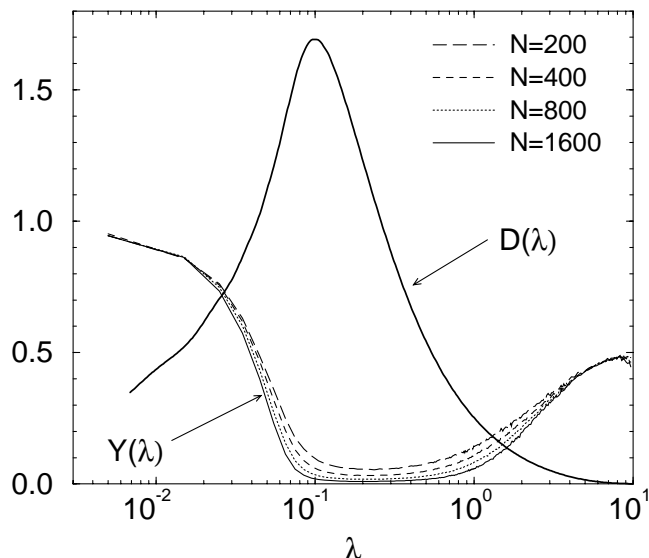


FIG. 4. The IPR Y as a function of the eigenvalue λ at different values of N . $\eta = 10^{-4}$, $\beta_s = 1$, and $m = 12$. The thick curve is the corresponding spectrum $D(\lambda)$.

of negative delocalized modes (the only ones related to collective particle diffusion) drops to zero [11]. In view of this, an approach such as the one presented here, which is able to investigate also the properties of the localized modes, can prove extremely useful. We will address the extension of our method to higher dimensions in a future paper.

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