Perturbed spectra of glasslike chains

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In this paper we calculate the vibrational spectra of classical, disordered, glasslike chains using a perturbation method and examine the effect of various types of disordering on the spectra. The effects of localization are discussed, and the strong influence of this phenomenon on the convergence of the perturbation techniques is discussed. The influence of fluid damping on the lattice is also treated, thereby providing an approximate calculation for the damped oscillatory behavior of coagulated colloidal systems.

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I. INTRODUCTION

This paper seeks to examine the vibrational spectra of one-dimensional classical chains as a function of the extent of disorder. What we compute is the set of eigenfrequencies as a function of the chosen disordering distibution and the density of states implied by this set of states, expanded as a power series in some parameter which expresses the extent of disorder. The problem was motivated by the question of whether a coagulated colloidal structure would exhibit a "useful" response to acoustic excitation, i.e., does the vibrational spectrum of a collection of elastically coupled, near-macroscopic particles of random sizes and coupling forces exhibit features that might be useful in ultrasonic experiments. The existence of emulsion systems with prolonged acoustic resonances [1] indicates that fluid damping is not always overwhelming, and calculations are performed to see whether this is a characteristic feature of coagulated colloids.

The disorder in such colloidal systems is usually "glasslike," i.e., the distribution of particle sizes, their locations, and coupling forces is a continuous function, so the spectra are also continuous funtions [2]. Interesting numerical work has been done on glasslike structures, beginning with Dean [3], but most of the existing analytic work (see, e.g., [4, 5, 2]) is devoted to alloylike problems, where the disorder arises from the random placement of distinct species in a uniform lattice and the spectrum is usually expanded as a power series in the impurity concentration [4, 6]. It is well known that the spectra of such alloylike systems exhibit fine structure, so it seems fruitless to pursue approximation methods of obtaining the spectrum (see in particular [7]), but the smooth, continuous nature of glasslike spectra inspires confidence that an approximation technique might work. In particular, an expansion in the extent of disorder (i.e., some parameter that measures the spread of particle sizes and/or interparticle forces) is now an appropriate entity to seek since it must converge to the well-known spectra of ordered systems as the disordering vanishes.

As would be expected, Anderson localization [8] is strongly manifest for short-wavelength modes, and this creates convergence problems in the spectrum series at high frequencies.

II. FORMALISM OF DYNAMICS OF A LINEAR CHAIN OF OSCILLATORS

Following Dyson [9], we consider a chain of N masses coupled by springs. The jth particle in the chain has mass m_j and the spring coupling the particles j and $j+1$ has elastic modulus K_j.

The equations of motion are

$$m_j \frac{d^2 x_j}{dt^2} = K_j(x_{j+1} - x_j) + K_{j-1}(x_{j-1} - x_j) \qquad (1)$$

and by using the "Dyson" variables

$$\lambda_{2j} = K_j/m_{j+1} \ , \qquad (2)$$

$$\lambda_{2j-1} = K_j/m_j \ , \qquad (3)$$

it can readily be shown that the characteristic frequencies ω_i of the chain are the eigenvalues of the $(2N-1)\times(2N-1)$ matrix Λ whose elements are

$$\Lambda_{k+1,k} = -\Lambda_{k,k+1} = i\lambda_k^{1/2} \ , \qquad (4)$$

all other elements being zero [9]. There is always one zero eigenvalue, and the remaining eigenfrequencies occur in $(N-1)$ pairs, the members of a pair being ω_i and $-\omega_i$.

We will be primarily interested in the "cumulative density of states" function $M(\mu)$, defined as the fraction of eigenvalues ω_i for which $\omega_i^2 < \mu$. As $N \to \infty$, we expect $M(\mu)$ to become a continuous function whose smoothness will depend critically on the set of constants K_j, m_j and their distribution. If it is sufficiently smooth, we can define the density of states function $D(\mu) = dM/d\mu$. A disordered chain can be defined as a chain whose elements are distributed in a random way according to some known probability law. If the distribution is continuous, then we may intuitively expect $M(\mu)$ to be continuous and smooth; this is referred to as "glasslike" disorder. On the other hand, if the distribution is discontinuous (as

in a model of binary alloys), it is well known that $M(\mu)$ will be strongly discontinuous and exhibit fine structure. This type of problem then will not readily succumb to perturbation methods [2].

Furthermore, we may expect the spectral frequencies of a disordered chain to approach those of an ordered system as the extent of the disordering diminishes. A suitable variable to model the extent of disorder is the ratio of the standard deviation to the mean of the distributed variable, which we denote by u. The density of states of a disordered system can then be regarded as a function of the type of disorder, the extent of disorder, and the frequency squared μ. It seems plausible that a power-law expansion for $M(\mu,u)$ of the form

$$M(\mu,u)=\sum_{k=0} u^k M_k(\mu) \tag{5}$$

might exist in some cases, and that a few of the $M_k(\mu)$ might be analytically derivable, a task which occupies much of the remaining discussion. The first correction term in such an expansion has already been derived by Dyson [9] for the only exactly solved model known to date and is readily derived for the low-frequency part of the spectrum starting from some results of Alexander *et al.* [11].

The object $M(\mu,u)$ we call the "average density of states" and must be understood in the sense of the average of an ensemble of density of state functions corresponding to an ensemble of possible chains. It is manifestly different to such hypothetical objects as the "density of states of the average chain."

The first problem is to find the density of states for a given chain; this in turn reduces to the problem of finding the eigenvalues of the matrix Λ. In this task we are facilitated by the introduction of periodic boundary conditions (PBC's), which in effect turns the infinite chain of masses into an infinite ring. As is well known, no bulk effects are introduced by this change in the thermodynamic limit $N\to\infty$.

The imposition of PBC's implies that

$$K_0=K_{N-1}\ , \tag{6}$$

$$m_1=m_N\ , \tag{7}$$

and thus we may write

$$\Lambda=i\begin{bmatrix} 0 & -\lambda_1^{1/2} & 0 & \cdots & \cdots & \lambda_0^{1/2} \\ \lambda_1^{1/2} & 0 & -\lambda_2^{1/2} & \cdots & \cdots & 0 \\ 0 & \lambda_2^{1/2} & 0 & \cdots & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & 0 & -\lambda_{2N-2}^{1/2} \\ -\lambda_0^{1/2} & 0 & 0 & \cdots & \lambda_{2N-2}^{1/2} & 0 \end{bmatrix}. \tag{8}$$

For an ordered crystal, with all $\lambda_k=\overline{\lambda}\equiv K/m$, the eigenvalues of $\Lambda\equiv\Lambda_0$ are well known

$$\omega_k=2\overline{\lambda}^{1/2}\sin q_k\ ,$$

$$k\in\{-N+1,-N+2,...,N-1\} \tag{9}$$

where

$$q_k=\frac{2\pi k}{2N-1}=\frac{2\pi k}{V} \tag{10}$$

and $V\equiv 2N-1$ has been defined for future convenience.

The corresponding orthonormal eigenstates may be written as

$$\{\boldsymbol{u}_k\}_j=\frac{1}{\sqrt{V}}e^{ijq_k}\qquad j\in\{0,1,\ldots,V\} \tag{11}$$

and the density of states can very rapidly be computed to be

$$\begin{aligned} M_0(\mu)&=\frac{1}{V}\sum_{k=-N+1}^{k=N-1}\Theta(\mu-\omega_k^2) \\ &=\begin{cases}\frac{1}{\pi}\cos^{-1}(1-\frac{\mu}{2\overline{\lambda}}), & 0\le\mu\le 4\overline{\lambda} \\ 1, & \mu>4\overline{\lambda}\end{cases}\end{aligned} \tag{12}$$

where $\Theta(x)$ is the usual Heaviside function.

If we now consider a disordered chain and regard $\overline{\lambda}$ in some sense as an "average" value of λ_k, then we may write

$$\Lambda=\Lambda_0+P \tag{13}$$

where

$$P=\frac{i}{2}\begin{bmatrix} 0 & -\beta_1 & 0 & \cdots & \cdots & \beta_0 \\ \beta_1 & 0 & -\beta_2 & \cdots & \cdots & 0 \\ 0 & \beta_2 & 0 & \cdots & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & 0 & -\beta_{V-1} \\ -\beta_0 & 0 & 0 & \cdots & \beta_{V-1} & 0 \end{bmatrix} \tag{14}$$

and

$$\beta_i=2\overline{\lambda}^{1/2}\left[\left(\frac{\lambda_i}{\overline{\lambda}}\right)^{1/2}-1\right]\ , \tag{15}$$

so clearly a weakly disordered chain (i.e. one in which the distribution of masses and/or spring constants is quite narrow; $\lambda_i\approx\overline{\lambda}$) will produce a matrix P whose elements β_k are small compared to those of Λ_0.

A. Perturbation theory

It is now quite a simple matter to apply canonical nondegenerate perturbation theory to Eq. (13) (see, e.g., [10]) in order to compute how the eigenfrequencies are affected by the disorder embodied in the nonzero β_i

$$\omega_l'=\omega_l+\sum_{j=1}\Delta\omega_l^{(j)} \tag{16}$$

where $\Delta\omega_l^{(j)}$ is the jth-order perturbation to the lth eigenfrequency ω_l. The first three perturbation terms are

$$\Delta\omega_l^{(1)}=\boldsymbol{u}_l^\dagger P\boldsymbol{u}_l, \tag{17}$$

$$\Delta\omega_l^{(2)}=\sum_{j\ (\neq l)}\frac{\boldsymbol{u}_j^\dagger P\boldsymbol{u}_l\ \boldsymbol{u}_l^\dagger P\boldsymbol{u}_j}{\omega_l-\omega_j}\ , \tag{18}$$

$$\Delta\omega_l^{(3)} = \sum_{n(\neq l)} \boldsymbol{u}_l^\dagger P \boldsymbol{u}_n \sum_{k(\neq l)} \left\{ \frac{\boldsymbol{u}_n^\dagger P \boldsymbol{u}_k \, \boldsymbol{u}_k^\dagger P \boldsymbol{u}_l}{(\omega_l - \omega_n)(\omega_l - \omega_k)} - \frac{\boldsymbol{u}_n^\dagger P \boldsymbol{u}_l \, \boldsymbol{u}_l^\dagger P \boldsymbol{u}_l}{(\omega_l - \omega_n)^2} \right\} . \quad (19)$$

The question of the convergence of this series has to be considered in the light of the nature of P. If, on the average, each β_i is genuinely "small," then we may assume rapid convergence, at least in the asymptotic sense; but there may very well be "bad" points or regions in which the series does not converge even asymptotically. From the existing eigenstates (9 and 11) we can then calculate explicitly

$$\Delta\omega_l^{(1)} = \frac{\sin q_l}{V} \sum_j \beta_j , \quad (20)$$

$$\Delta\omega_l^{(2)} = \frac{-1}{8\bar{\lambda}^{1/2} V^2} \sum_{(j\neq l)} \frac{(e^{-iq_l} - e^{iq_j})(e^{-iq_j} - e^{iq_l})}{\sin q_l - \sin q_j} \times \sum_{m,k} \beta_m \beta_k e^{i(q_j - q_l)(m-k)} , \quad (21)$$

$$\Delta\omega_l^{(3)} = \Delta\omega_l^{(3,1)} + \Delta\omega_l^{(3,2)} , \quad (22)$$

where

$$\Delta\omega_l^{(3,1)} = \frac{-i}{32\bar{\lambda} V^3} \sum_{n,k\ (\neq l)} \frac{(e^{-iq_l} - e^{iq_n})(e^{-iq_n} - e^{iq_k})(e^{-iq_k} - e^{iq_l})}{(\sin q_l - \sin q_k)(\sin q_l - \sin q_n)} \sum_{m,j,p} \beta_m \beta_j \beta_p e^{i[p(q_n - q_l) + j(q_k - q_n) + m(q_l - q_k)]}, \quad (23)$$

$$\Delta\omega_l^{(3,2)} = \frac{1}{16\bar{\lambda} V^3} \sum_{n\ (\neq l)} \frac{(\sin q_l)(e^{-iq_l} - e^{iq_n})(e^{-iq_n} - e^{iq_l})}{(\sin q_l - \sin q_n)^2} \sum_{s,t,p} \beta_s \beta_t \beta_p e^{i(q_n - q_l)(p-s)} , \quad (24)$$

all of which are clearly of successively higher powers of the small numbers β_i. It turns out that for a symmetric distribution of particle parameters, the power series for $M(\mu, u)$ is even, and consequently we need to know the average value of $\Delta\omega_l^{(j)}$ for all $j \leq 2k$ in order to obtain an $O(u^{2k})$ correction to the density of states. Thus the first correction term requires explicit evaluation of the first- and second-order perturbations.

B. General formalism for obtaining the average density of states

Given a particular disordered chain, the set of eigenvalues of Λ is

$$\{\omega_l'\} = \left\{ \omega_l + \sum_j \Delta\omega_l^{(j)}; \quad l = -N+1, -N+2, \ldots, N-1 \right\} . \quad (25)$$

Now it can readily be shown (see Appendix A) that these eigenvalues "central limit" in some sense in thermodynamic limit $N \to \infty$. The associated average density of states is

$$M(\mu, u) = \left\langle \frac{1}{V} \sum_l \Theta\left(\mu - \left(\omega_l + \sum_j \Delta\omega_l^{(j)}(u) \right)^2 \right) \right\rangle , \quad (26)$$

where the "width" u of the disorder will clearly enter into the perturbations $\Delta\omega_l^{(j)}$ and the average is taken over the entire ensemble of chains. Since a power series in u is sought and the Heaviside step function is not smooth, it is necessary to take the Laplace transform of $M(\mu, u)$ with respect to μ

$$\tilde{M}(s, u) = \left\langle \int_0^\infty M(\mu, u) e^{-s\mu} d\mu \right\rangle = \frac{1}{sV} \left\langle \sum_l \exp\left[-s \left(\omega_l + \sum_j \Delta\omega_l^{(j)}(u) \right)^2 \right] \right\rangle , \quad (27)$$

which is a smooth differentiable function. The ensemble averages can be moved directly onto the eigenvalues because of the central limiting, yielding

$$\tilde{M}(s, u) = \frac{1}{sV} \sum_l \exp\left[-s \left(\omega_l + \sum_j \langle \Delta\omega_l^{(j)}(u) \rangle \right)^2 \right] . \quad (28)$$

Little further can be done without assuming further specifics of the disordering, and for the purposes of the remainder of this discussion we assume that the distribution of the relevant parameter is normal (and therefore glasslike), i.e.,

$$G(\xi_j) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\xi_j - \bar{\xi})^2/(2\sigma^2)} , \quad (29)$$

where the mean is $\bar{\xi}$ and the standard deviation σ. In a

physically realistic model, ξ_j will be the mass m_j or the spring constant K_j or perhaps some likely combination of these. An appropriate width measurement i then $u = \sigma/\overline{\xi}$, and it is fruitful to renormalize the distribution by introducing the coordinates x_j defined by

$$\xi_j = \sqrt{2}\,\overline{\xi} u x_j + \overline{\xi} \tag{30}$$

so then

$$\langle \Delta\omega_l^{(j)}(u)\rangle = \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\prod_k \frac{dx_k e^{-x_k^2}}{\sqrt{\pi}} \times \Delta\omega_l^{(j)}(\sqrt{2}\,\overline{\xi} u x_n + \overline{\xi}) \,. \tag{31}$$

An immediate observation on the structure of $\tilde{M}(s,u)$ is that it is an even function of u; the substitutions $u \to -u$ and $x_k \to -x_k$ leave the perturbation averages invariant. Furthermore, in the limit $u \to 0$, all the perturbations $\Delta\omega_l^{(k)}(\sqrt{2}\,\overline{\xi} u x_n + \overline{\xi})$ vanish and thus

$$\tilde{M}(s,0) = \frac{1}{sV}\sum_l e^{-s\omega_l^2} \tag{32}$$

so

$$M(\mu,0) = M_0(\mu) \,, \tag{33}$$

which is the ordered result. The power series for $\tilde{M}(s,u)$ is even, so the first correction term is $O(u^2)$ and will clearly involve (at most) the second derivatives

$$\left.\frac{\partial^2\langle\Delta\omega_l^{(j)}\rangle}{\partial u^2}\right|_{u=0} = \sum_k \frac{\partial^2\langle\Delta\omega_l^{(j)}\rangle}{\partial\beta_k^2}\frac{\partial^2\beta_k}{\partial u^2}\bigg|_{u=0,\beta_k=0} \,. \tag{34}$$

Now the parameters β_k always vanish in the limit $u \to 0$; for example, if the masses m_j are distributed normally and the spring constants are fixed, we have explicitly

$$\beta_{2j-1} = 2(\overline{\lambda})^{1/2}\left[\left(\frac{\overline{m}}{m_j}\right)^{1/2} - 1\right] \,, \tag{35}$$

$$\beta_{2j} = 2(\overline{\lambda})^{1/2}\left[\left(\frac{\overline{m}}{m_{j+1}}\right)^{1/2} - 1\right] \,, \tag{36}$$

where $\overline{\lambda} = K/\overline{m}$ naturally. Under the renormalization to coordinates x_i this becomes

$$\beta_{2j-1}(u) = 2(\overline{\lambda})^{1/2}[(\sqrt{2}\,u x_j + 1)^{-1/2} - 1] \,, \tag{37}$$

$$\beta_{2j}(u) = 2(\overline{\lambda})^{1/2}[(\sqrt{2}\,u x_{j+1} + 1)^{-1/2} - 1] \,, \tag{38}$$

which shows explicitly that $\lim_{u\to 0}\beta_k = 0$.

Since the perturbation $\Delta\omega_l^{(j)}$ involves the product of j β parameters, it is clear that $\frac{\partial^2}{\partial\beta_k^2}\langle\Delta\omega_l^{(j)}\rangle\big|_{\beta_k=0} = 0$ for all $j \geq 3$. In other words, contributions to the second-order correction in u come entirely from the first- and second-order perturbations.

Proceeding from Eq. (31), if we define

$$Q(u) = \exp\left[s\left(\omega_l + \sum_j \left\langle \Delta\omega_l^{(j)}(\sqrt{2}\,\overline{\xi} u x_i + \overline{\xi})\right\rangle\right)^2\right] \,, \tag{39}$$

then $Q(u)$ has a power series

$$Q(u) = e^{-s\omega_l^2} + u^2\left\{(2s^2\omega_l^2 - s)\left[\left(\frac{\partial}{\partial u}\sum_j\langle\Delta\omega_l^{(j)}\rangle\right)\bigg|_{u=0}\right]^2 - s\omega_l\left(\frac{\partial^2}{\partial u^2}\sum_{j=1,2}\langle\Delta\omega_l^{(j)}\rangle\right)\bigg|_{u=0}\right\} \times e^{-s\omega_l^2} + O(u^4) \,. \tag{40}$$

Evidently the term involving $\frac{\partial}{\partial u}\langle\Delta\omega_l^{(j)}\rangle\big|_{u=0}$ vanishes for all except the first-order perturbation, for the same reasons as advanced previously in the case of the second derivative. Thus we need consider only

$$\left.\frac{\partial}{\partial u}\langle\Delta\omega_l^{(1)}\rangle\right|_{u=0} = \left.\frac{\partial}{\partial u}\frac{\sin q_l}{V}\sum_k\langle\beta_k\rangle\right|_{u=0} = \frac{\sin q_l}{V} \times \sum_k\sum_j \sqrt{2}\,\overline{\xi}\left\langle x_j\frac{\partial\beta_k}{\partial\xi_j}\right\rangle\bigg|_{u=0\Leftrightarrow\xi_j=\overline{\xi}} \,. \tag{41}$$

Now since each β_k vanishes for $u = 0$ (or equivalently $\xi_j = \overline{\xi}$), we can write

$$\beta_k = \sum_l \alpha_l(\xi_l - \overline{\xi}) + O((\xi_l - \overline{\xi})^2) \,, \tag{42}$$

thus

$$\left.\frac{\partial}{\partial u}\langle\Delta\omega_l^{(1)}\rangle\right|_{u=0} = \frac{\sqrt{2}\,\overline{\xi}\sin q_l}{V}\sum_{k,l}\alpha_l\langle x_l\rangle = 0. \tag{43}$$

Hence this term does not contribute to the final result, and so we have from Eqs. (31) and (40)

$$\tilde{M}(s,u) = \tilde{M}(s,0) - \frac{u^2}{V}\sum_l \omega_l\frac{\partial^2}{\partial u^2}\sum_{j=1}^{j=2}\left(\left\langle\Delta\omega_l^{(j)}\right\rangle_{\{x_i\}}\right)\bigg|_{u=0} e^{-s\omega_l^2} + O(u^4) \,. \tag{44}$$

Thus the method to obtain $M_2(\mu)$ simply involves computing the average of the first two perturbations $\Delta\omega_l^{(j)}$ and backtransforming Eq. (44).

III. SPECIFIC MODELS OF DISORDER

We proceed to consider four different types of disordering.

(i) The parameters λ_j defined previously are independent random variables, distributed normally. This coincides with Dyson's "type 1" case [9], where the parameter n is large in his chosen distribution

$$G_n(\lambda) = \frac{n^n}{(n-1)!}\lambda^{n-1}e^{-n\lambda} , \tag{45}$$

thus approximating a Gaussian function with mean 1 and variance $1/n$. The equivalences $u^2 \leftrightarrow 1/n$ and $\overline{\lambda} \leftrightarrow 1$ then enable a comparison of the results of this paper and Dyson's original results.

(ii) The masses of each particle m_j are distributed normally, the spring values being held constant.

(iii) The spring constants K_j are distributed normally, all masses being the same.

(iv) The particles interact via typical colloidal-type interactions, the elastic constant K_j coupling the jth to the $(j+1)$th particles varying as

$$K_j \sim \frac{r_j r_{j+1}}{r_j + r_{j+1}} , \tag{46}$$

where r_j is the radius of the jth particle (assumed spherical). This introduces an r^3 dependence to the mass of the particles if the density is assumed constant, and the radii r_j are distributed normally with mean $\overline{r}$ and variance σ^2.

This interaction arises from modeling a coagulated colloid by a set of spherical particles of uniform molecular number density n, where the potential energy of two adjacent spheres S_a, S_b of radii a and b with surface separation d is

$$U(d) = n^2 \int_{\boldsymbol{r}_1 \in S_a} d^3 r_1 \int_{\boldsymbol{r}_2 \in S_b} d^3 r_2 V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|) . \tag{47}$$

Here $V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)$ is the intermolecular potential energy of the molecules comprising the colloidal particles. If one uses a standard law for $V(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)$ such as the Lennard-Jones potential, then a deep primary minimum is found for $U(d)$ at a spacing d_0 of a few angstroms, typically much less than generic colloidal particle sizes. Explicit evaluation of this integral [Eq. (47)] leads to a "generalized" Hamaker law for the effective spring constant of the particle pair

$$K_{ab} \equiv \left.\frac{\partial^2 U}{\partial d^2}\right|_{d_0} \approx \frac{5ab}{a+b}\frac{A}{d_0^3} , \tag{48}$$

where A is the usual Hamaker constant. Given that values of A in SI are typically around 10^{-20}–10^{-19} (see, e.g., [13]), this yields a very stiff effective spring constant, typically requiring several eV of energy to displace the particles 1 Å. If the mass of a particle is taken to be $m = 4\pi\rho a^3/3$ and typical values of a and ρ are used, the characteristic frequencies of the system ($\sqrt{K/m}$) are very high, certainly in the GHz region.

A. Summary of results

Tables I and II show the first- and second-order shifts in the lth eigenfrequency and the second-order shift in the density of states for each of the four cases itemized above. The methods used to obtain all of these results are virtually identical, so details will be shown only for the distributed mass case, particular details of the other cases being given as necessary. The divergence of these expressions near the band edge ($\mu \approx 4\overline{\lambda}$) is clearly a consequence of localization effects (see [3],[8]) and will be more fully discussed in Sec. IV C.

B. Case of distributed masses

Here we have

$$G(m_j) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(m_j - \overline{m})^2/(2\sigma^2)} \tag{49}$$

and

$$\beta_{2j-1} = 2(\overline{\lambda})^{1/2}[(\overline{m}/m_j)^{1/2} - 1] , \tag{50}$$

$$\beta_{2j} = 2(\overline{\lambda})^{1/2}[(\overline{m}/m_{j+1})^{1/2} - 1] , \tag{51}$$

where $\overline{\lambda}$ is naturally defined as $\overline{\lambda} = K/\overline{m}$. Hence

$$\begin{aligned}\langle \Delta\omega_l^{(1)} \rangle &= \frac{\sin q_l}{V}\sum \langle \beta_j \rangle \\ &= \frac{\omega_l}{V}\left\langle \sum_{j=1}^{N-1}[(1+\sqrt{2}ux_{j+1})^{-1/2} - 1] \right. \\ &\qquad \left. + \sum_{j=1}^{N}[(1+\sqrt{2}ux_j)^{-1/2} - 1] \right\rangle \\ &= \frac{3}{8}u^2\omega_l + O(u^4)\end{aligned} \tag{52}$$

and

TABLE I. First- and second-order perturbations to ω_l.

Disordering type	$\langle \Delta\omega_l^{(1)} \rangle$	$\langle \Delta\omega_l^{(2)} \rangle$
λ	$-u^2\omega_l/8$	$-u^2\omega_l/8$
m	$3u^2\omega_l/8$	$-3u^2\omega_l/8$
K	$-u^2\omega_l/8$	$-3u^2\omega_l/8$
Colloidal	$19u^2\omega_l/16$	$-u^2\omega_l(-25 + 6\omega_l^2/\overline{\lambda} - \omega_l^4/\overline{\lambda}^2)/16$

TABLE II. Second-order shift in density of states $M_2(\mu)$.

Disordering type	$M_2(\mu)$	Range of μ
λ	$\frac{u^2}{2\pi}(4\overline{\lambda}/\mu - 1)^{-1/2}$	$0 \le \mu \le 4\overline{\lambda}$
	0	$\mu > 4\overline{\lambda}$
m	0	$\forall\mu$
K	$\frac{u^2}{\pi}(4\overline{\lambda}/\mu - 1)^{-1/2}$	$0 \le \mu \le 4\overline{\lambda}$
	0	$\mu > 4\overline{\lambda}$
Colloidal	$\frac{u^2}{4\pi}(4\overline{\lambda}/\mu - 1)^{-1/2}[3 - 12\mu/4\overline{\lambda} - 8(\mu/4\overline{\lambda})^2]$	$0 \le \mu \le 4\overline{\lambda}$
	0	$\mu > 4\overline{\lambda}$

$$\langle \Delta\omega_l^{(2)} \rangle = \frac{-1}{8\overline{\lambda}^{1/2}V^2} \sum_{j(\neq l)} \frac{(e^{-iq_l} - e^{iq_j})(e^{-iq_j} - e^{iq_l})}{\sin q_l - \sin q_j} \times \sum_{m,k} \langle \beta_m \beta_k \rangle e^{i(q_j - q_l)(m-k)} . \tag{53}$$

The final summation over m and k is split into four sums corresponding to the possibilities of m and k being even or odd, and if the m_i are normalized to x_i as before and the resulting radicals are written as a power series in u, then this final summation may be written as

$$4\overline{\lambda}\left\{ \sum_{n,k=1}^{N-1} e^{i2q_l - j(n-k)} \frac{u^2}{2} \langle x_{n+1} x_{k+1} \rangle + \sum_{n,k=1}^{N} e^{i2q_l - j(n-k)} \frac{u^2}{2} \langle x_n x_k \rangle + \sum_{n,k=1}^{N-1,N} e^{iq_l - j[2(n-k)+1]} \frac{u^2}{2} \langle x_{n+1} x_k \rangle + \sum_{n,k=1}^{N,N-1} e^{iq_l - j[2(n-k)-1]} \frac{u^2}{2} \langle x_n x_{k+1} \rangle \right\} + O(u^4) . \tag{54}$$

Clearly only the "diagonal" terms in these sums will contribute, giving the expression

$$\langle \Delta\omega_l^{(2)} \rangle = \frac{-u^2\overline{\lambda}^{1/2}}{8V^2} \sum_{j(\neq l)} \frac{(e^{-iq_l} - e^{iq_j})(e^{-iq_j} - e^{iq_l})}{\sin q_l - \sin q_j} \times [V + 2(N-1)\cos(q_l - q_j)] . \tag{55}$$

These sums can be done exactly using the result derived in Appendix B to give the result

$$\langle \Delta\omega_l^{(2)} \rangle = -\frac{3}{8}u^2\omega_l + \frac{u^2\overline{\lambda}^{1/2}\sin^3 q_l}{2V\cos^2 q_l} + O(1/V) . \tag{56}$$

Although the last term superficially looks like it is $O(1/V)$, there are values of l near the band edge ($q_l \approx \pi/2$) where it diverges, so it is retained for completeness. This phenomenon will be discussed more fully in a later section.

The density of states can now be derived from Eq. (44) using these results. It is of interest that the first- and second-order perturbations cancel nearly exactly away from the band edge. We have, using Eqs. (44), (52), and (56),

$$\tilde{M}_2(s) = -\frac{\overline{\lambda}^{1/2}}{V^2} \sum_l \omega_l \frac{\sin^3 q_l}{\cos^2 q_l} e^{-s\omega_l^2} = O(1/V) , \tag{57}$$

so there is no contribution from the second-order term.

That the spectrum exhibits no change to order u^4 is highly interesting; this implies that a spread of mass values corresponding to, say, $\sigma \approx 0.3\overline{m}$ (a very broad distribution) will not affect the spectrum by more than a few percent (for long-wavelength modes, where the series will converge well), assuming that the correction functions $M_j(\mu)$ for $j \ge 4$ are not wildly divergent for small μ values.

C. The Dyson case: Distribution of the λ_j

In this case we have

$$G(\lambda_j) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(\lambda_j - \overline{\lambda})^2/(2\sigma^2)} \tag{58}$$

and

$$\beta_j(u) = 2(\overline{\lambda})^{1/2}[(\lambda_j/\overline{\lambda})^{1/2} - 1] = 2(\overline{\lambda})^{1/2}[(\sqrt{2}ux_j + 1)^{1/2} - 1] . \tag{59}$$

The average first- and second-order perturbations are found by very similar means to those used in the random mass case, except that the second-order term is simpler. These are presented in Table I. Equation (44) now yields

$$\tilde{M}_2(s) = \frac{1}{2V}\sum_l \omega_l^2 e^{-s\omega_l^2}. \tag{60}$$

Inverting the transform, we arrive at

$$M_2(\mu) = \frac{1}{2V}\sum_l \omega_l^2 \delta(\mu - \omega_l^2)\ . \tag{61}$$

This Riemann sum can be done as an integral in the usual way, obtaining

$$M_2(\mu) = \frac{1}{4\pi}\int_{-\pi}^{\pi} 4\overline{\lambda}\ (\sin^2 q)\,\delta(\mu - 4\overline{\lambda}\sin^2 q)\,dq$$

$$= \begin{cases} \frac{1}{2\pi}\frac{1}{\sqrt{4\overline{\lambda}/\mu - 1}}, & 0 \le \mu \le 4\overline{\lambda} \\ 0, & \mu > 4\overline{\lambda}\ . \end{cases} \tag{62}$$

Comparison with Dyson's large n asymptotic results (see [9])

$$M_n(\mu) = \begin{cases} \frac{1}{\pi}\cos^{-1}(1 - \frac{\mu}{2}) + \frac{1}{2\pi n}\frac{1}{\sqrt{4/\mu - 1}} + O(n^{-2}), & 0 \le \mu \le 4 \\ 1 - \frac{\alpha}{\pi}\exp[-\alpha - 2n(\sinh\alpha - \alpha)], & \mu > 4 \end{cases} \tag{63}$$

where

$$\alpha = \cosh^{-1}(\mu/2 - 1) \tag{64}$$

shows that the two expressions are identical for $0 \le \mu \le 4$, but very different for $\mu > 4$ under the equivalences $u^2 \leftrightarrow 1/n$ and $\overline{\lambda} \leftrightarrow 1$. This is due to the fact that there is no power series for expressions of the form $e^{-f(\mu)/u^2}$ about the point $u = 0$, hence attempting to force such a series simply returns a null result. This phenomenon is clearly closely related to the relatively new field of "asymptotics beyond all orders."

D. Case of distributed springs

This is very similar to the distributed mass case, except that the first two average perturbations add rather than cancel. The inversion of $M_2(s,u)$ is done exactly as in the Dyson case.

E. Colloidal distribution

Since the distributed variable here is r_j, the mass m_j and the elastic constant K_j may be written as

$$m_j = \overline{m}r_j^3/\overline{r}^3\ , \tag{65}$$

$$K_j = 2\overline{K}r_j r_{j+1}/[\overline{r}(r_j + r_{j+1})]\ , \tag{66}$$

and defining $\overline{\lambda}$ as $\overline{K}/\overline{m}$, we have

$$\beta_{2j-1} = 2\overline{\lambda}^{1/2}\left[\left(\frac{2\overline{r}^2 r_{j+1}}{r_j^2(r_j + r_{j+1})}\right)^{1/2} - 1\right]\ , \tag{67}$$

$$\beta_{2j} = 2\overline{\lambda}^{1/2}\left[\left(\frac{2\overline{r}^2 r_j}{r_{j+1}^2(r_j + r_{j+1})}\right)^{1/2} - 1\right]\ . \tag{68}$$

Once again the r_j are normalized to r_j in the usual way and the expressions in the perturbation sums are written as power series in u (best done on a program like *Mathematica*). The rest of the details follow as before, giving the results presented in Tables I and II.

IV. SUNDRY MATTERS OF INTEREST

A. Alternative approach to high-frequency limits

These results can be checked against work done by Alexander *et al.* [11]. In their treatment, the distributed mass and spring problems are virtually identical and lead to the integral equation

$$f_\omega(x) = \int_0^\infty dx'\, f_\omega(x') \times \int_0^\infty dy\,\rho(y)\delta\left(x - \left(\frac{1}{y} + \frac{1}{\omega + x'}\right)^{-1}\right), \tag{69}$$

where $\rho(y)$ is the distribution of K or m^{-1} and is naturally usually only nonzero for positive y. If the masses are distributed as $G(m)$, then $\rho(m^{-1}) = m^2 G(m)$. Once a solution $f_\omega(x)$ of (69) is found, the spectrum can be readily computed via the following formulas:

$$D(\mu) = \frac{-1}{\pi}\mathrm{Im}\left\langle \tilde{P}_0(-\mu + i0^+)\right\rangle \tag{70}$$

where for random spring constants

$$\left\langle \tilde{P}_0(\omega)\right\rangle = \int_0^\infty dg'\, f_\omega(g')\int_0^\infty dg''\, f_\omega(g'')\frac{1}{\omega + g' + g''} \tag{71}$$

and for random masses

$$\left\langle \tilde{P}_0(\omega)\right\rangle = \int_0^\infty dc\, G(c)c\int_0^\infty dg'\, f_\omega(g')\int_0^\infty dg''\, f_\omega(g'')\frac{1}{\omega c + \omega/(\omega + g') + \omega/(\omega + g'')}\ . \tag{72}$$

If

$$\hat{g}(z) = \int_0^\infty g(x)(x+z)^{-1}dx \tag{73}$$

denotes the Stieltjes transform of $g(x)$, then it can be shown (see [11]) that the inequality

$$\hat{\rho}(z) \leq \hat{f}_\omega(z) \leq \hat{\rho}(z) + 1/\omega \tag{74}$$

defines $f_\omega(x)$ to order $O(1/\omega)$ for large ω. In fact, for large ω, $\hat{f}_\omega(x)$ can be written as

$$f_\omega(x) = \rho(x) + \sum_{k=1}^{N} \frac{\phi_k(x)}{\omega^k} + R_x^{(N)}(x) \tag{75}$$

if the first $N+1$ moments of the given probability distribution exist and one has the patience to determine the $\phi_k(x)$ recursively.

1. Case of distributed springs

Putting $\omega = -\mu + i\epsilon$ in Eq. (71) produces a pole below the negative real axis in, say, the g' plane at a point $g_0 - iO(\epsilon)$ where $g_0 = O(\mu)$. The contour is indented above this point, and the imaginary part of $D(\mu)$ comes entirely from this indentation, giving the result

$$D(\mu, u) = \frac{1}{2u\overline{\lambda}\sqrt{\pi}} \exp\left[-\frac{1}{u^2}\left(\frac{\mu}{2\overline{\lambda}} - 1\right)^2\right] \tag{76}$$

to leading order, and thus

$$M(\mu, u) = 1 - \frac{u\overline{\lambda}}{\mu\sqrt{\pi}} \exp\left[-\frac{1}{u^2}\left(\frac{\mu}{2\overline{\lambda}} - 1\right)^2\right] . \tag{77}$$

2. Case of distributed masses

The technique illustrated above cannot be applied to random-mass problems where the distribution $G(m)$ is nonzero at the origin (like the Gaussian distribution), since the distribution $\rho(m)$ will then have no finite moments and therefore Eq. (75) is inapplicable. If only a finite number of moments exist, say $\lim_{m\to 0} m^{-k}G(m) = 0$ only for $k < n$, then it is easy to show that

$$D(\mu) \sim \mu^{-2} G\left(\frac{2K}{\mu - K/m}\right) = O(\mu^{-(n+2)}) . \tag{78}$$

3. Implications of the moment-trace method

This technique, described in Chap. 7.4 of Hori's work [2], proceeds from the observation that the pth moment of the density of states $m_p = \int_0^\infty \mu^p D(\mu)d\mu$ is equal to the trace of the $(2p)$th power of the dynamical matrix Λ divided by V, i.e., $\frac{1}{V}\mathrm{tr}(\Lambda^{2p})$. This is true for all finite p, even in the limit $V \to \infty$. The implication of this is that $D(\mu) \to 0$ faster than any power of μ and thus the expansions just outlined in the distributed mass case must be strictly divergent.

B. Low-frequency results

The low end of the spectrum is of interest for both low-temperature thermodynamic results and also for the damped lattice problem discussed later. The expansion converges well in this region, since the low-frequency modes are not strongly localized and consequently the sums in the perturbation cannot "smother" any local effects. Graphs of the perturbed spectrum in this region are similar in nature to those displayed by Dean (p. 734 of [3]) for a glasslike chain with rectangular distribution of spring values. From Table II we compute the low-frequency expansions for both the distributed mass and spring cases, giving

$$D(\mu) = \begin{cases} \frac{1}{2\pi\overline{\lambda}^{1/2}}\mu^{-1/2} & \text{(distributed masses)} \\ \frac{1}{2\pi\overline{\lambda}^{1/2}}(1 + u^2/2)\mu^{-1/2} & \text{(distributed springs)} . \end{cases} \tag{79}$$

A general method to obtain these is given in [11] and gives the result $D(\mu) \approx \frac{1}{2\pi} t_{-1}^{-1/2}\mu^{1/2}$ up to a trivial dimensional correction. Here $t_{-1} = \int_0^\infty x^{-1}\rho(x)dx$ and ρ is the distribution of K or m^{-1}. A simple calculation shows that these results agree to the order given in u, hence confirming the well-known fact that systems with a finite average mass $M_{\mathrm{av}} = \langle m \rangle$ behaves as an ordered system of masses M_{av} as $\omega \to 0$ (see, e.g., [12]).

C. Singularities at the band edge: Effects of localization

Given that the spectrum $M(\mu)$ of an ordered system is not smooth at the band edge $\mu = 4\overline{\lambda}$, it is to be expected that the perturbation method will fail at this point, as can be seen from the function $M_2(\mu)$. Previous results (Chap. 8 of [4] and [3]) lead to the expectation that some of the large eigenvalues will "spill" over the band edge as disordering is introduced. These modes are strongly localized and involve only finite numbers of particles, so it is to be expected that the sums in the perturbation terms swamp these effects in the manner of a "law of large numbers," and consequently the series diverges.

It is interesting, nonetheless, that for $q_l \approx \pi/2$, Eq. (56) shows that

$$\Delta\omega_l^{(2)} \sim \frac{u^2}{Vq_{\Delta l}^2} \sim \frac{u^2 V}{(\Delta l)^2} \tag{80}$$

where $q_{\Delta l} \equiv \pi/2 - q_l$, hence a finite number of (divergent) modes appear above the band edge. (This is comparable to the treatment in Sec. 8.8 of [4] where the insertion of a light atom m_s in a uniform chain of masses m is shown to give rise to a mode of frequency

$$\omega = \omega_{\mathrm{BE}}/(1 - \epsilon^2)^{1/2}, \quad \epsilon \equiv 1 - m_s/m \tag{81}$$

above the band edge ω_{BE}.) By manipulation of Eq. (56), it is readily shown that the fraction of these high-frequency modes goes like $V^{-1/2}$, so no contribution to

the density of states in the $V \to \infty$ limit can be found by this approach.

It is also possible to "invert" the high-frequency spectra given in Sec. IV A in order to obtain an approximate form for $\omega_l'(q_l)$ for $q_l \approx \pi/2$. This is achieved by manipulating the definition

$$D(\mu) = \frac{1}{2\pi}\int_{\pi}^{\pi} \delta(\mu - \omega_l'^2(q_l))dq_l \tag{82}$$

and using the symmetries

$$\Delta\omega_l^{(j)}(-q) = -\Delta\omega_l^{(j)}(q) \ , \tag{83}$$

$$\Delta\omega_l^{(j)}(\pi - q) = \Delta\omega_l^{(j)}(q) \tag{84}$$

together with the requirement that $\Delta\omega_l^{(j)}(q)$ be real. For the distributed spring case at large frequencies, the asymptotic result

$$\frac{d\omega_l'^2}{dq_l} \sim \frac{4\bar{\lambda}u}{\sqrt{\pi}} e^{[\omega_l'^2/(2\bar{\lambda})-1]^2/u^2} \tag{85}$$

can readily be obtained and integrated to give the strictly asymptotic (and therefore nondifferentiable) result

$$\omega_l'^2 \sim 2\bar{\lambda}u(-\ln\epsilon)^{1/2}(1 + O(\ln(-\ln\epsilon)/\ln\epsilon) + \cdots) \tag{86}$$

where

$$\epsilon \equiv \frac{4}{\sqrt{\pi}}(\pi/2 - q_l) \tag{87}$$

and $q_l < \pi/2$.

V. EFFECTS OF DAMPING IN COAGULATED COLLOIDS

One possible way to examine the damping of oscillations in coagulated colloidal systems is to model the system as a lattice of harmonically coupled particles immersed in a fluid. The resistive force acting on particle j moving with velocity $\boldsymbol{v}_j$ may be modelled in two ways: (i) Stokesian damping, i.e. $\boldsymbol{F}_j = -6\pi\eta R_j \boldsymbol{v} \equiv -\gamma_j \boldsymbol{v}$, where R_j is the radius of particle j; and (ii) "Reynolds" damping, a situation in which the resistance to motion is dominated by the force required to "flush" fluid in or out of the volume between two closely packed spheres. This force thus depends on the relative velocity of the neighboring spheres and a geometrical factor which describes the growth of fluid volume away from the point of nearest approach. If we take the dependence on relative velocity as linear, then the Reynolds force on particle j in the chain may be written as

$$F_j = \gamma_j^{(R)}(v_{j+1} - v_j) + \gamma_{j+1}^{(R)}(v_{j-1} - v_j) \ , \tag{88}$$

where $\gamma_j^{(R)} \sim (r_j^{-1} + r_{j+1}^{-1})$ is a consequence of the spherical geometry.

A. Stokesian damping

The equation of motion incorporating Stokesian damping is

$$m_j \frac{d^2x_j}{dt^2} = K_j(x_{j+1} - x_j) + K_{j-1}(x_{j-1} - x_j) - \gamma_j \frac{dx_j}{dt} \ . \tag{89}$$

If the system is ordered ($m_j = m$, $K_j = K$, $\gamma_j = \gamma \ \forall j$), then the ansatz $x_j = \exp[i(jq_k - \omega t)]$ yields the eigenmodes

$$\omega_k^{(S)} = -i\tau_S^{-1} + \sqrt{\omega_k^2 - \tau_S^{-2}} \ , \tag{90}$$

where periodic boundary conditions apply, the notation of Sect. II is used, and $\tau_S = 2m/\gamma \approx$10–100 ns for typical colloids. This indicates that the low-wave-number modes (small q_k) are overdamped, but there is a possibility of ringing modes at high wave numbers, where $\omega_k > \tau_S^{-1}$. Unfortunately, the equation of motion (89) is unlikely to be valid at frequencies much above 1 MHz, so Eq. (90) is an unreliable guide except for systems comprising very heavy or large colloidal particles where $\tau_S \sim O(\rho a^2/\eta)$ might be in the microsecond regime.

B. Reynolds damping

A similar treatment of the equation of motion with the Reynolds force (88) used instead of the Stokes expression yields the eigenmodes

$$\omega_k^{(R)} = \omega_k(-i\tau_R\omega_k + \sqrt{1 - \tau_R^2\omega_k^2}) \ , \tag{91}$$

where $\tau_R = \gamma^{(R)}/2\lambda m$. Clearly the low-wave-number modes are only lightly damped (since the relative velocities of the particles are small), so one would expect Stokesian damping to dominate the long-wavelength modes. The dominance of the Reynolds flushing effect implies that $\tau_R < \tau_S$, but it is still likely that $\tau_R\omega_k < 1$ for all or some of the modes, so high-frequency ($\omega > \tau_S^{-1}$) ringing modes might still be observed.

The combined effect of Reynolds and Stokes damping indicates that ringing modes are only likely to appear at frequencies in the megahertz to gigahertz region, where the mode lifetimes are comparable to the period of the oscillation.

VI. CONCLUSIONS

The method derived in this paper has been found to work well in the low-frequency end of the spectrum of a glasslike disordered structure, where localization effects are not strong, but diverge in the upper part of the spectrum. It seems likely that the method will be unable to elucidate any but gross features of the spectrum, and that the sort of structures to which it is most applicable may not have any spectral features of great interest anyway. In damped colloidal systems, the mode lifetimes

are unlikely to be longer than 100 ns, so any measurable oscillations must have frequency of order 10 MHz or higher.

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APPENDIX A: CENTRAL LIMITING OF THE EIGENVALUES OF THE DISORDERED CHAIN

It is well known that all extensive properties of disordered systems "central limit" in some sense in the thermodynamic limit [8]. The density of states is extensive, so in the limit $N \to \infty$ where the q_k defined by Eq. (10) becomes continuous, we may write

$$D(\mu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \delta(\mu - \omega'(q, \{\beta_k\})^2) dq \ . \tag{A1}$$

Here $\{\beta_k\}$ is the infinite set of distributed constants, and q is now interpreted as a label for the eigenvalues. Since glasslike disorder always leads to a smoothly continuous density-of-states function [as can be deduced from the smoothly continuous integral equations leading to $D(\mu)$ derived by Dyson and others: see [9, 5, 8]], it is clear that the eigenvalues densely fill the acoustic band, so $\omega'(q, \{\beta_k\})$ is continuous in q. But since $D(\mu)$ is scatter free in the thermodynamic limit, we may also write it as

$$D(\mu) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \delta(\mu - [\Omega(q)]^2) dq, \tag{A2}$$

where $\Omega(q)$ is some continuous function in q. Subtracting Eqs. (A1) and (A2) and integrating the result multiplied by any integrable, piecewise-smooth $f(\mu)$ over the positive reals gives

$$\int_{-\infty}^{\infty} (f([\omega'(q, \{\beta_k\})]^2) - f([\Omega(q)]^2)) dq = 0 \ . \tag{A3}$$

Suppose $[\omega'(q, \{\beta_k\})]^2 > \Omega(q)^2$ at some point q'. Then by continuity, $\omega'(q, \{\beta_k\})^2 > \Omega(q)^2$ for all points q in some interval (q_1, q_2) around q'. Hence we can choose

$$f(x) = \begin{cases} x & q \in (q_1, q_2) \\ 0 & \text{otherwise} \ , \end{cases} \tag{A4}$$

so the left-hand side of Eq. (A3) becomes

$$\int_{q_1}^{q_2} ([\omega'(q, \{\beta_k\})]^2 - [\Omega(q)]^2) dq \ , \tag{A5}$$

which is clearly positive, resulting in a contradiction. The rest of the proof is obvious, leading to the conclusion

$$[\omega'(q, \{\beta_k\})]^2 = [\Omega(q)]^2 \quad \forall q \ , \tag{A6}$$

which amounts to saying that the eigenvalues w' are free from statistical scatter in the thermodynamic limit. It is nevertheless interesting to observe that the statistic $\Delta\omega_l^{(1)}(\{\beta_k\})$ does central limit to its average value, whereas the statistic $\Delta\omega_l^{(2)}(\{\beta_k\})$ does not (as can be confirmed by tedious calculation). Since we know that the eigenvalues central limit as $N \to \infty$, it seems likely that all the $\Delta\omega_l^{(i)}$ for $i > 1$ do not.

APPENDIX B: A USEFUL SUM FOR EVALUATING THE SECOND-ORDER PERTURBATIONS

We seek to evaluate

$$S(N, p, l) = \sum_{j(\neq l)} \frac{e^{ipq_j}}{\sin q_l - \sin q_j} \ , \tag{B1}$$

where $q_l = \frac{2\pi l}{2N-1} = \frac{2\pi l}{V}$ and the sum over j runs from $-N+1$ to $N-1$. By writing the sine functions as complex exponentials, we can write this as

$$S(N, p, l) = 2ie^{-iq_l} \sum_{j(\neq l)} \frac{e^{ipq_j}}{(1 + e^{-i(q_j+q_l)})(1 - e^{-i(q_j-q_l)})} \tag{B2}$$

and if we define

$$f(\epsilon) = \sum_{j(\neq l)} \frac{e^{ipq_j}}{(1 + \epsilon e^{-i(q_j+q_l)})(1 - \epsilon e^{-i(q_j-q_l)})} \ , \tag{B3}$$

then

$$S(N, p, l) = \lim_{\epsilon \to 1^-} 2ie^{-iq_l} f(\epsilon) \ . \tag{B4}$$

These sums can now be done exactly if the denominators in $f(\epsilon)$ are rewritten as geometric series:

$$\begin{aligned} f(\epsilon) &= \sum_{m,n=0}^{\infty} (-\epsilon e^{-iq_l})^m (\epsilon e^{-iq_l})^n \sum_{j(\neq l)} e^{i(p-m+n)q_j} \\ &= \sum_{m,n=0}^{\infty} (-\epsilon e^{-iq_l})^m (\epsilon e^{-iq_l})^n \begin{cases} -e^{iq_l(p-m+n)}, & q_{p-m+n} \neq 0 (\mathrm{mod} 2\pi) \\ V - 1, & q_{p-m+n} = 0 (\mathrm{mod} 2\pi) \end{cases} \\ &\equiv \sum_{m=0}^{\infty} (-\epsilon e^{-iq_l})^m Q_{mp} \ . \end{aligned} \tag{B5}$$

Doing the sum over n requires that we pick out the values of n such that $q_{p-m+n} = 0 (\mathrm{mod} 2\pi)$, which can be written

as

$$n = Vk + m - p, \quad k \in J \ , \tag{B6}$$

where the requirement $n \geq 0$ implies that $k \geq (p-m)/V$. Hence

$$\begin{aligned} Q_{mp} &= \sum_{k=[\frac{p-m}{V}]^+}^{\infty} (\epsilon e^{-iq_l})^{Vk+m-p} V - \sum_{n=0}^{\infty} e^{-iq_l(p-m+n)} (\epsilon e^{-iq_l})^n \\ &= e^{iq_l(p-m)} \left(V\epsilon^{m-p} \frac{\epsilon^{V[\frac{p-m}{V}]^+}}{1-\epsilon^V} - \frac{1}{1-\epsilon} \right) . \end{aligned} \tag{B7}$$

Now the sum over m has to be broken up into intervals in which $[(p-m)/V]^+$ is a constant integer, say j. For each j, this interval is $[p-jV, p-1+V(1-j)]$ and the constraint $m \geq 0$ means that j can run from $-\infty$ to $[p/V]^-$. Hence

$$\begin{aligned} f(\epsilon) &= \sum_{m=0}^{\infty} (-\epsilon e^{-iq_l})^m e^{iq_l(p-m)} \left(V\epsilon^{m-p} \frac{\epsilon^{V[\frac{p-m}{V}]^+}}{1-\epsilon^V} - \frac{1}{1-\epsilon} \right) \\ &= \frac{V\epsilon^{-p} e^{ipq_l}}{1-\epsilon^V} \left\{ \sum_{j=-\infty}^{[p/V]^-} \epsilon^{jV} \sum_{m=p-jV}^{p-1+V(1-j)} (-\epsilon^2 e^{-i2q_l})^m \right. \\ &\quad \left. + \epsilon^{V([p/V]^-+1)} \sum_{m=0}^{p-1-V[p/V]^-} (-\epsilon^2 e^{-i2q_l})^m \right\} - \frac{e^{ipq_l}}{1-\epsilon} \sum_{m=0}^{\infty} (-\epsilon e^{-i2q_l})^m \\ &= \left\{ (1+\epsilon^V)^{-1} (-\epsilon^2)^p (-\epsilon^V)^{-[p/V]^-} (1+\epsilon^{2V}) e^{-i2pq_l} + \epsilon^{V([p/V]^-+1)} (1 - (-\epsilon^2)^{p-V[p/V]^-} e^{-i2pq_l}) \right\} \\ &\quad \times \frac{V\epsilon^{-p} e^{ipq_l}}{(1-\epsilon^V)(1+\epsilon^2 e^{-i2q_l})} - \frac{e^{ipq_l}}{(1-\epsilon)(1+\epsilon e^{-i2q_l})} . \end{aligned} \tag{B8}$$

The limit $\epsilon \to 1^-$ is best taken by writing $\epsilon = 1 - \eta$ and expanding $f(\epsilon)$ as a power series in η. This yields the result

$$S(N,p,l) = \frac{i}{\cos q_l} \left(\frac{V}{2} e^{-ipq_l} (-1)^{p+[p/V]^-} + \left\{ p - V \left(\left[\frac{p}{V} \right]^- + \frac{1}{2} \right) - \frac{i}{2} \tan q_l \right\} e^{ipq_l} \right) . \tag{B9}$$

In principle it is possible to obtain analytic expressions for the perturbation sums of every order by extending this method, but the algebra rapidly becomes prohibitive, even for the third-order perturbation sums.

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